METHOD 8270C

SEMIVOLATILE ORGANIC COMPOUNDS
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d_{10} (IS)		X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS(43)	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS(62)	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d_{12} (IS)		X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS(68)	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (cis or trans)	2303-16-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4-Diaminotoluene	95-80-7	DC,0E(42)	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
1,4-Dichlorobenzene-d_4 (IS)		X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW,0S(67)	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dihydrosaffrole	56312-13-1	ND	ND	ND	ND	ND
Dimethoate	60-51-5	HE,HS(31)	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP(45)	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE(14)	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Dioxathion	78-34-2	ND	ND	ND	ND	ND
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW,CP(62)	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE,OS(0)	ND	ND	ND	LR

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE,HS(68)	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene-d_8 (IS)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS(44)	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
Nitrobenzene-d_5 (surr)		X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-n-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d_{12} (IS)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d_{10} (IS)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d_6 (surr)		DC(28)	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS(65)	ND	ND	ND	X
Phosmet	732-11-6	HS(15)	ND	ND	ND	X
Phosphamidon	13171-21-6	HE(63)	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP,HE(1)	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,OE(10)	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW,0S(55)	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d_{14}(surr)	1718-51-0	X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr)	118-79-6	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,O,O-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

IS = This compound may be used as an internal standard.
surr = This compound may be used as a surrogate.
AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
HS = Hydrolysis during storage (number in parenthesis is percent stability).
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
OS = Oxidation during storage (number in parenthesis is percent stability).
X = Greater than 70 percent recovery by this technique.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (Table 11 contains surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (Table 12 contains performance data), and Method 3561 describes a supercritical fluid extraction of solids for PAHs (see Tables 13, 14, and 15 for performance data).

1.3 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, Method 8270 is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. Refer to Sec. 7.0 of Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.

1.4.6 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.7 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4.8 Toluene diisocyanate rapidly hydrolyses in water (half-life of less then 30 min.). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.9 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1 µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer

4.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 3 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria in Table 3 when 5 or 50 ng are introduced.

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.1.6 Guard column (optional) - (J&W Deactivated Fused Silica, 0.25 mm ID x 6 m, or equivalent) between the injection port and the analytical column joined with column joiners (Hewlett-Packard Catalog No. 5062-3556, or equivalent).

4.2 Syringe - 10-µL.

4.3 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

4.4 Balance - Analytical, capable of weighing 0.0001 g.

4.5 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

5.3.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.3.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

5.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the requirements given in Sec. 7.3.2 are met.

5.4.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1 mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store at -10°C or less when not in use. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.4.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at -10°C or less when not in use. If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method.

5.6.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.6.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored at -10°C or less, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification standard should be prepared weekly and stored at 4°C. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7 Surrogate standards - The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

5.7.1 Surrogate Standard Check: Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

5.7.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute surrogate solution may be necessary.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS).

5.8.1 Matrix Spike Check: Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.8.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, a more dilute matrix and LCS spiking solution may be necessary.

5.8.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking

standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Store the sample extracts at -10°C, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air	3542
Water	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3550, 3560, 3561, 3580

7.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected.

7.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of interest	Methods
Aniline & aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3610, 3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620

Analytes of interest	Methods
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-270°C at 10°C/min
Final temperature:	270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

7.3.1.2 Use the DFTPP mass intensity criteria in Table 3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD

should not exceed 20%. (See Sec. 8.0 of Method 8081 for the percent breakdown calculation). Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

7.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column. The use of a guard column (Sec. 4.1.6) between the injection port and the analytical column may help prolong analytical column performance.

7.3.2 The internal standards selected in Sec. 5.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation).

7.3.3 Analyze 1-2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 5.6 and Method 8000). The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

Calculate response factors (RFs) for each target analyte relative to one of the internal standards as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

17

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC (see Table 4) must be less than or equal to 30%.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 7.3.

7.3.5.4 If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

7.3.7 Linearity of target analytes - If the RSD of any target analytes is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.6.2).

7.3.7.1 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 in Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 designates a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8270 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

18

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000B for method blank performance criteria.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Table 4 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference for each CCC is less than or equal to 20%, then the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project,

and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1-mL concentrated sample extract obtained from sample preparation.

7.5.3 Inject a 1-2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 7.3). The volume to be injected should contain 100 ng of base/neutral and 200 ng of acid surrogates (assuming 100% recovery), unless a more sensitive GC/MS system is being used and the surrogate solution is less concentrated then that listed in Sec. 5.7. The injection volume must be the same volume used for the calibration standards.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/µL, unless a more sensitive GC/MS system is being used).

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. However, SIM

analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 7.3.5). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, by Methods 8081 or 8082. However, Method 8270 may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be identified, quantitated and reported as the sum of both compounds by the GC.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the

7.7.6 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are quantitated as isomeric pairs. Diastereomeric pairs (e.g., Aramite and Isosafrol) that may be separable by the GC should be summed and reported as the sum of both compounds.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Sec. 7.0 of Method 8000 and include calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8270:

8.2.1 The GC/MS system must be tuned to meet the DFTPP criteria listed in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the calibration verification acceptance criteria in Sec. 7.4, each 12 hours.

8.2.4 The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 7.6.1.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed, a septum is changed), see the guidance in Sec 8.2 of Method 8000 regarding whether recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 (the packed column version of Method 8270) was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations ranging from 5 to 1,300 µg/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7. These values are presented as guidance only and are not intended as absolute acceptance criteria. Laboratories should generate their own acceptance criteria for capillary column method performance. (See Method 8000.)

9.2 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 8.

9.3 Method performance data (using Method 3541 Automated Soxhlet extraction) are presented in Table 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three determinations were performed and each extract was analyzed by gas chromatography/ mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in Table 10 and were taken from Reference 7.

9.4 Surrogate precision and accuracy data are presented in Table 11 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by Method 8270.

9.5 Single laboratory precision and bias data (using Method 3545 Accelerated Solvent Extraction) for semivolatile organic compounds are presented in Table 12. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by Perstorp Environmental Soxtec™ (automated Soxhlet). The data presented in Table 12 represents seven replicate extractions and analyses for each individual sample and were taken from reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low-101.2%, mid-97.2% and high-99.2%.

9.6 Single laboratory precision and bias data (using Method 3561 SFE Extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (one, EC-1, a lake sediment from Environment Canada and the other, HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 13 and 14 and were taken from Reference 10.

9.7 Single laboratory precision and accuracy data (using Method 3561 SFE Extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in Table 15 and were taken from Reference 11.

10.0 REFERENCES

1. Eichelberger, J.W., Harris, L.E., and Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems", Analytical Chemistry, 47, 995-1000, 1975.

2. "Method Detection Limit for Methods 624 and 625", Olynyk, P., Budde, W.L., and Eichelberger, J.W., unpublished report, October 1980.

3. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides", Final Report for EPA Contract 68-03-3102.

4. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects", Journal of the Association of Official Analytical Chemists (AOAC), 48, 1037, 1965.

5. Lucas, S.V., Kornfeld, R.A., "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes ", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

6. Engel, T.M., Kornfeld, R.A., Warner, J.S., and Andrews, K.D., "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

7. Lopez-Avila, V. (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV, October 1991; EPA 600/X-91/140.

8. Bursey, J., Merrill, R., McAllister, R., and McGaughey, J., "Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List", Vol. 1 and 2, U.S. Environmental Protection Agency, EPA 600/R-93/123a and b, (NTIS PB 93-227163 and 93-27171), Research Triangle Park, NC, July 1993.

9. Richter, B., Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report: Extraction of Target Compound List/Priority Pollutant List BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD", Document 101124, Dionex Corporation, Salt Lake City, UT, June 16, 1994.

10. Lee, H.B., Peart, T.E., Hong-You, R.L., and Gere, D.R., "Supercritical Carbon Dioxide Extraction of Polycyclic Aromatic Hydrocarbons from Sediments", J. Chromatography, A 653 83-91 (1993).

11. Personal communication from Sue Warner, EPA Region 3, Central Regional Laboratory, 839 Bestgate Road, Annapolis, MD 21401.

TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75[a]	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	44,45,74
Thiophenol (Benzenethiol)	7.42	110	66,109,84
Methyl methanesulfonate	7.48	80	79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodiethylamine	8.70	102	42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	79,95,109,140
Ethyl methanesulfonate	9.62	79	109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d_8 (IS)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	155,127,81,109
Diethyl sulfate	11.37	139	45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	108,77,79,90
Hexachloropropene	12.45	213	211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	41,42,68,69
Acetophenone	12.67	105	71,51,120
4-Methylphenol	12.82	107	108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	107,77,51,79
3-Methylphenol	12.93	107	108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,55,56,41
1,4-Phenylenediamine	13.62	108	80,53,54,52
1-Chloronaphthalene	13.65[a]	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	76,50,148
o-Anisidine	15.00	108	80,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d_{10} (IS)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	164,126,98,63
4-Chloroaniline	15.50	127	129,65,92
Isosafrole	15.60	162	131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00[a]	143	115,116
1,4-Naphthoquinone	16.23	158	104,102,76,50,130
p-Cresidine	16.45	122	94,137,77,93
Dichlorovos	16.48	109	185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	135,134,91,77
N-Nitrosodi-n-butylamine	16.73	84	57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	104,77,103,135

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	17.50	92	127,129,65,39
Diphenylamine	17.54[a]	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	214,179,108,143,218
1-Naphthylamine	18.20	143	115,89,63
1-Acetyl-2-thiourea	18.22	118	43,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,79,106,94
Thionazine	19.35	107	96,97,143,79,68
4-Nitroaniline	19.37	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	75,50,76,92,122
Mevinphos	19.90	127	192,109,67,164
Naled	20.03	109	145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	76,50,75,92,122
Diallate (cis or trans)	20.57	86	234,43,70
1,2-Dinitrobenzene	20.58	168	50,63,74
Diallate (trans or cis)	20.78	86	234,43,70
Pentachlorobenzene	21.35	250	252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	79,52,138,153,77
Pentachloronitrobenzene	21.72	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	131,230,166,234,168
Dihydrosaffrole	22.42	135	64,77
Demeton-O	22.72	88	89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	74,213,120,91,63
Dicrotophos	23.82	127	67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	43,264,41,290
Bromoxynil	23.90	277	279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	192,67,97,109
Phorate	24.10	75	121,97,93,260

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Sulfallate	24.23	188	88,72,60,44
Demeton-S	24.30	88	60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	93,125,143,229
Phenobarbital	24.70	204	117,232,146,161
Carbofuran	24.90	164	149,131,122
Octamethyl pyrophosphoramide	24.95	135	44,199,286,153,243
4-Aminobiphenyl	25.08	169	168,170,115
Dioxathion	25.25	97	125,270,153
Terbufos	25.35	231	57,97,153,103
α,α-Dimethylphenylamine	25.43	58	91,65,134,42
Pronamide	25.48	173	175,145,109,147
Aminoazobenzene	25.72	197	92,120,65,77
Dichlone	25.77	191	163,226,228,135,193
Dinoseb	25.83	211	163,147,117,240
Disulfoton	25.83	88	97,89,142,186
Fluchloralin	25.88	306	63,326,328,264,65
Mexacarbate	26.02	165	150,134,164,222
4,4'-Oxydianiline	26.08	200	108,171,80,65
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	152,141,169,151
Phosphamidon	26.85	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	185,41,193,266
Methyl parathion	27.03	109	125,263,79,93
Carbaryl	27.17	144	115,116,201
Dimethylaminoazobenzene	27.50	225	120,77,105,148,42
Propylthiouracil	27.68	170	142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d_{12} (IS)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	125,127,93,158
Kepone	28.18	272	274,237,178,143,270
Fenthion	28.37	278	125,109,169,153
Parathion	28.40	109	97,291,139,155
Anilazine	28.47	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	106,196,180
Carbophenothion	28.58	157	97,121,342,159,199
5-Nitroacenaphthene	28.73	199	152,169,141,115
Methapyrilene	28.77	97	50,191,71
Isodrin	28.95	193	66,195,263,265,147

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Captan	29.47	79	149,77,119,117
Chlorfenvinphos	29.53	267	269,323,325,295
Crotoxyphos	29.73	127	105,193,166
Phosmet	30.03	160	77,93,317,76
EPN	30.11	157	169,185,141,323
Tetrachlorvinphos	30.27	329	109,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	167,195
Barban	30.83	222	51,87,224,257,153
Aramite	30.92	185	191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	139,253,111,141
Fensulfothion	31.87	293	97,308,125,292
Ethion	32.08	231	97,153,125,121
Diethylstilbestrol	32.15	268	145,107,239,121,159
Famphur	32.67	218	125,93,109,217
Tri-p-tolyl phosphate[b]	32.75	368	367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d_{12} (IS)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	241,239,120
5,5-Diphenylhydantoin	33.40	180	104,252,223,209
Captafol	33.47	79	77,80,107
Dinocap	33.47	69	41,39
Methoxychlor	33.55	227	228,152,114,274,212
2-Acetylaminofluorene	33.58	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	201,229
3-Methylcholanthrene	35.07	268	252,253,126,134,113
Phosalone	35.23	182	184,367,121,379
Azinphos-methyl	35.25	160	132,93,104,105
Leptophos	35.28	171	377,375,77,155,379
Mirex	35.43	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,119,217,219,199
Dibenz(a,j)acridine	36.40	279	280,277,250
Mestranol	36.48	277	310,174,147,242
Coumaphos	37.08	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2:4,5-Dibenzopyrene	41.60	302	151,150,300

TABLE 1
(continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	135,105,77
Hexachlorophene	47.98	196	198,209,211,406,408
Aldrin	--	66	263,220
Aroclor 1016	--	222	260,292
Aroclor 1221	--	190	224,260
Aroclor 1232	--	190	224,260
Aroclor 1242	--	222	256,292
Aroclor 1248	--	292	362,326
Aroclor 1254	--	292	362,326
Aroclor 1260	--	360	362,394
α-BHC	--	183	181,109
β-BHC	--	181	183,109
δ-BHC	--	183	181,109
γ-BHC (Lindane)	--	183	181,109
4,4'-DDD	--	235	237,165
4,4'-DDE	--	246	248,176
4,4'-DDT	--	235	237,165
Dieldrin	--	79	263,279
1,2-Diphenylhydrazine	--	77	105,182
Endosulfan I	--	195	339,341
Endosulfan II	--	337	339,341
Endosulfan sulfate	--	272	387,422
Endrin	--	263	82,81
Endrin aldehyde	--	67	345,250
Endrin ketone	--	317	67,319
2-Fluorobiphenyl (surr)	--	172	171
2-Fluorophenol (surr)	--	112	64
Heptachlor	--	100	272,274
Heptachlor epoxide	--	353	355,351
Nitrobenzene-d_5 (surr)	--	82	128,54
N-Nitrosodimethylamine	--	42	74,44
Phenol-d_6 (surr)	--	99	42,71
Terphenyl-d_{14} (surr)	--	244	122,212
2,4,6-Tribromophenol (surr)	--	330	332,141
Toxaphene	--	159	231,233

IS = internal standard
surr = surrogate
[a]Estimated retention times
[b]Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
a,a-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenebis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND

TABLE 2 (cont.)

Compound	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND
O,O,O-Triethyl phosphorothioate	NT	ND

[a] Sample EQLs are highly matrix-dependent. The EQLs listed here are provided for guidance and may not always be achievable.

[b] EQLs listed for soil/sediment are based on wet weight. Normally, data are reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. These EQLs are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined
NA = Not Applicable
NT = Not Tested

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]EQL = (EQL for Low Soil/Sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 3.
[b] Alternate tuning criteria may be used, (e.g., CLP, Method 525, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 4

CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr)	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluor-anthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluor-anthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)-perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl-phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	
Pentachlorophenol	7,12-Dimethylbenz-(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd) pyrene	
Phenanthrene	3-Methylchol-anthrene	
Pronamide		

(surr) = surrogate

TABLE 6

MULTILABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl) ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192

TABLE 6
(continued)

Compound	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range p, p_s (%)
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Aroclor 1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L

p, p_s = Measured percent recovery

D = Detected; result must be greater than zero

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{x}$-0.12	0.21$\bar{x}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{x}$-1.06	0.26$\bar{x}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{x}$-1.28	0.43$\bar{x}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{x}$-0.32	0.27$\bar{x}$-0.64
Benz(a)anthracene	0.88C-0.60	0.15$\bar{x}$+0.93	0.26$\bar{x}$-0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{x}$+0.43	0.29$\bar{x}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{x}$+1.03	0.35$\bar{x}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{x}$+0.48	0.32$\bar{x}$+1.35
Benzo(g,h,i)perylene	0.98C-0.86	0.29$\bar{x}$+2.40	0.51$\bar{x}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{x}$+0.94	0.53$\bar{x}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{x}$-0.58	0.30$\bar{x}$+1.94
δ-BHC	0.29C-1.09	0.34$\bar{x}$+0.86	0.93$\bar{x}$-0.17
Bis(2-chloroethyl) ether	0.86C-1.54	0.35$\bar{x}$-0.99	0.35$\bar{x}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{x}$+1.34	0.26$\bar{x}$+2.01
Bis(2-chloroisopropyl) ether	1.03C-2.31	0.24$\bar{x}$+0.28	0.25$\bar{x}$+1.04
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26$\bar{x}$+0.73	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{x}$+0.66	0.16$\bar{x}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{x}$+0.52	0.13$\bar{x}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{x}$-0.94	0.30$\bar{x}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{x}$+0.13	0.33$\bar{x}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{x}$-0.32	0.66$\bar{x}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{x}$-1.17	0.39$\bar{x}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{x}$+0.19	0.65$\bar{x}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{x}$+8.51	0.59$\bar{x}$+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{x}$+1.16	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{x}$+0.47	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{x}$+0.68	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{x}$+0.23	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{x}$+7.33	0.47$\bar{x}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{x}$-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{x}$+1.44	0.52$\bar{x}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{x}$+0.19	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{x}$+1.06	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{x}$+1.26	0.19$\bar{x}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{x}$+1.19	0.37$\bar{x}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{x}$+2.47	0.63$\bar{x}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{x}$+3.91	0.73$\bar{x}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{x}$-0.73	0.28$\bar{x}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{x}$+0.26	0.13$\bar{x}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{x}$-0.56	0.50$\bar{x}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{x}$-0.46	0.28$\bar{x}$+0.64

TABLE 7
(continued)

Compound	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Hexachlorobenzene	0.74C+0.66	0.18$\bar{x}$-0.10	0.43$\bar{x}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{x}$+0.92	0.26$\bar{x}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{x}$+0.67	0.17$\bar{x}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{x}$+1.46	0.50$\bar{x}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{x}$+0.77	0.33$\bar{x}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{x}$-0.41	0.30$\bar{x}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{x}$+0.92	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{x}$+0.68	0.44$\bar{x}$+0.47
Aroclor 1260	0.81C-10.86	0.35$\bar{x}$+3.61	0.43$\bar{x}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{x}$+0.57	0.15$\bar{x}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{x}$+0.06	0.15$\bar{x}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{x}$+0.85	0.21$\bar{x}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{x}$+0.75	0.29$\bar{x}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{x}$+1.46	0.28$\bar{x}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{x}$+1.25	0.21$\bar{x}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{x}$+1.21	0.22$\bar{x}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{x}$+2.36	0.42$\bar{x}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{x}$+42.29	0.26$\bar{x}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{x}$+1.94	0.27$\bar{x}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{x}$+2.57	0.44$\bar{x}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{x}$+3.03	0.30$\bar{x}$+4.33
Phenol	0.43C+1.26	0.26$\bar{x}$+0.73	0.35$\bar{x}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{x}$+2.22	0.22$\bar{x}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{x}$, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

[a] Criteria from 40 CFR Part 136 for Method 625, using a packed GC column. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7. These values are for guidance only. Appropriate derivation of acceptance criteria for capillary columns should result in much narrower ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 8

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

Compound	Percent Recovery on Day 0		Percent Recovery on Day 7	
	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 9

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANICS FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

Compound	Clay Soil		Topsoil	
	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 10

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9

TABLE 10
(continued)

Compound	Mean Recovery	RSD
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 11

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 11 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 12

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	**102.0**
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	**101.9**
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	**101.6**
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	**120.6**
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	**119.2**
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	**112.5**
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	**104.7**
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	**100.2**
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	**110.3**
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	**98.1**
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	**118.6**
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	**100.2**
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	**101.7**
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	**109.8**
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	**96.3**
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	**97.2**
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	**98.6**
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	**104.2**
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	**106.1**
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	**108.1**
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	**104.7**
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	**99.7**
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	**102.1**
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	**75.8**
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	**95.9**
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	**94.1**
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	**96.2**
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	**92.6**
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	**90.3**
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	**101.7**
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	**92.9**
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	**98.4**
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	**75.6**
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	**90.7**

TABLE 12 (cont.)

ACCELERATED SOLVENT EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

COMPOUND	CLAY			LOAM			SAND			AVE
	LOW	MID	HIGH	LOW	MID	HIGH	LOW	MID	HIGH	
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	**98.8**
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	**94.4**
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	**95.4**
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	**99.1**
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	**96.8**
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	**95.8**
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	**93.7**
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	**81.2**
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	**100.6**
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	**101.2**
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	**99.1**
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	**102.7**
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	**105.2**
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	**116.5**
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	**101.5**
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	**102.9**
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	**99.0**
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	**103.1**
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	**99.9**
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	**102.7**
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	**98.6**
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	**66.4**
Average	**95.1**	**94.3**	**101.0**	**95.5**	**96.5**	**104.1**	**113.0**	**100.9**	**92.5**	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 15

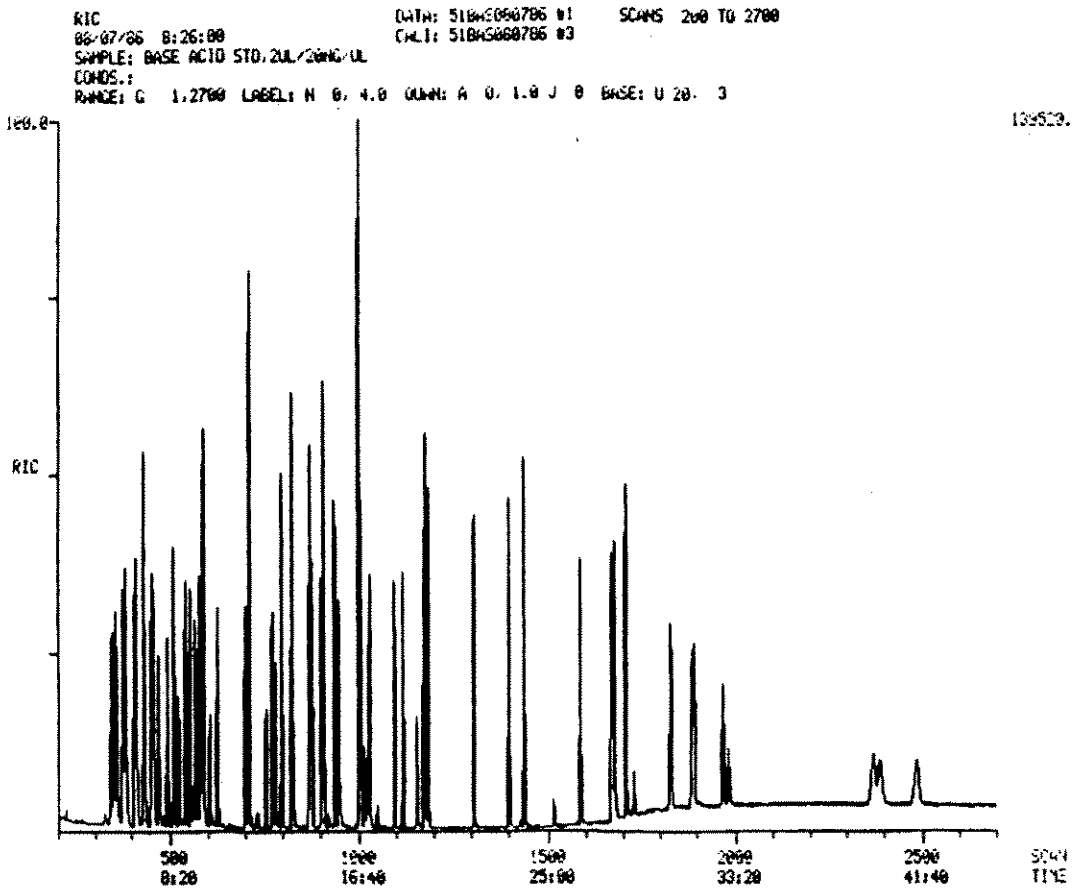
SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)			SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4	±	8.2	29.55	91	10.5
2-Methylnaphthalene	62.1	±	11.5	76.13	122	2.0
Acenaphthene	632	±	105	577.28	91	2.9
Dibenzofuran	307	±	49	302.25	98	4.1
Fluorene	492	±	78	427.15	87	3.0
Phenanthrene	1618	±	340	1278.03	79	3.4
Anthracene	422	±	49	400.80	95	2.6
Fluoranthene	1280	±	220	1019.13	80	4.5
Pyrene	1033	±	285	911.82	88	3.1
Benz(a)anthracene	252	±	38	225.50	89	4.8
Chrysene	297	±	26	283.00	95	3.8
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153	±	22	130.88	86	10.7
Benzo(a)pyrene	97.2	±	17.1	58.28	60	6.5

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

FIGURE 1
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



55

METHOD 8000B

DETERMINATIVE CHROMATOGRAPHIC SEPARATIONS

1.0 SCOPE AND APPLICATION

1.1 Method 8000 is not a determinative method but instead provides guidance on analytical chromatography and describes calibration and quality control requirements that are common to all SW-846 chromatographic methods. Apply Method 8000 in conjunction with all SW-846 determinative chromatographic methods. The methods include, but are not limited to, the following:

Method Number	Analytes	Chromatographic Technique (see Sec. 1.5)	Detector
7580	White phosphorus (P_4)	GC, capillary column	NPD
8011	EDB, DBCP	GC, capillary column	ECD
8015	Nonhalogenated volatiles	GC, packed & capillary column	FID
8021	Volatiles	GC, capillary column	PID, ELCD
8031	Acrylonitrile	GC, packed column	NPD
8032	Acrylamide	GC, packed column	ECD
8033	Acetonitrile	GC, capillary column	NPD
8041	Phenols	Underivatized or derivatized, GC, capillary column	FID, ECD
8061	Phthalates	GC, capillary column	ECD
8070	Nitrosamines	GC, packed column	NPD, ELCD, TED
8081	Organochlorine pesticides	GC, capillary column	ECD, ELCD
8082	Polychlorinated biphenyls	GC, capillary column	ECD, ELCD
8091	Nitroaromatics and cyclic ketones	GC, capillary column	ECD
8100	PAHs	GC, packed & capillary column	FID
8111	Haloethers	GC, capillary column	ECD
8121	Chlorinated hydrocarbons	GC, capillary column	ECD

Method Number	Analytes	Chromatographic Technique (see Sec. 1.5)	Detector
8131	Aniline and selected derivatives	GC, capillary column	NPD
8141	Organophosphorus pesticides	GC, capillary column	FPD, NPD, ELCD
8151	Acid herbicides	Derivatize; GC, capillary column	ECD
8260	Volatiles	GC, capillary column	MS
8270	Semivolatiles	GC, capillary column	MS
8275	Semivolatiles	Thermal extraction/GC	MS
8280	Dioxins and Dibenzofurans	GC, capillary column	Low resolution MS
8290	Dioxins and Dibenzofurans	GC, capillary column	High resolution MS
8310	PAHs	HPLC, reverse phase	UV, Fluorescence
8315	Carbonyl compounds	Derivatize; HPLC	Fluorescence
8316	Acrylamide, acrylonitrile, acrolein	HPLC, reverse phase	UV
8318	N-Methyl carbamates	Derivatize; HPLC	Fluorescence
8321	Extractable nonvolatiles	HPLC, reverse phase	TS/MS, UV
8325	Extractable nonvolatiles	HPLC, reverse phase	PB/MS, UV
8330	Nitroaromatics and nitramines	HPLC, reverse phase	UV
8331	Tetrazene	HPLC, ion pair, reverse phase	UV
8332	Nitroglycerine	HPLC, reverse phase	UV
8410	Semivolatiles	GC, capillary column	FT-IR
8430	Bis(2-chloroethyl) ether hydrolysis products	GC, capillary column	FT-IR

DBCP = Dibromochloropropane
ECD = Electron capture detector
EDB = Ethylene dibromide
ELCD = Electrolytic conductivity detector
FID = Flame ionization detector
FPD = Flame photometric detector
FT-IR = Fourier transform-infrared
GC = Gas chromatography
HPLC = High performance liquid chromatography
MS = Mass spectrometry
NPD = Nitrogen/phosphorous detector
PAHs = Polynuclear aromatic hydrocarbons
PB/MS = Particle beam mass spectrometry
PID = Photoionization detector
TED = Thermionic emission detector
TS/MS = Thermospray mass spectrometry
UV = Ultraviolet

58

1.2 Analytical chromatography is used to separate target analytes from co-extracted interferences in samples. Chromatographic methods can be divided into two major categories: gas chromatography (GC) and high performance liquid chromatography (HPLC).

1.2.1 Gas chromatography (more properly called gas-liquid chromatography) is the separation technique of choice for organic compounds which can be volatilized without being decomposed or chemically rearranged.

1.2.2 High performance liquid chromatography (HPLC) is a separation technique useful for semivolatile and nonvolatile chemicals or for analytes that decompose upon heating. Successful liquid chromatographic separation requires that the analyte(s) of interest be soluble in the solvent(s) selected for use as the mobile phase. Because the solvents are delivered under pressure, the technique was originally designated as high pressure liquid chromatography, but now is commonly referred to as high performance liquid chromatography.

1.3 All chromatographic processes achieve separation by passing a mobile phase over a stationary phase. Constituents in a mixture are separated because they partition differently between the mobile and stationary phases and thus have different retention times. Compounds that interact strongly with the stationary phase elute slowly (i.e., long retention time), while compounds that remain in the mobile phase elute quickly (i.e., short retention time).

1.3.1 The mobile phase for GC is an inert gas, usually helium, and the stationary phase is generally a silicone oil or similar material.

1.3.2 In "normal phase" HPLC, the mobile phase is less polar than the stationary phase. In "reverse phase" HPLC, the converse is true. Reverse phase HPLC is the technique of choice for environmental and waste analyses of non-volatile organic target analytes.

1.4 A number of specific GC and LC techniques are used for environmental and waste analyses. The specific techniques are distinguished by the chromatographic hardware or by the chemical mechanisms used to achieve separations.

1.4.1 GC methods, including those in SW-846, can be categorized on the basis of the chromatographic columns employed.

1.4.1.1 Packed columns are typically made from glass or stainless steel tubing and generally are 1.5 - 3 m long with a 2 - 4 mm ID, and filled with small particles (60-100 mesh diatomaceous earth or carbon) coated with a liquid phase.

1.4.1.2 Capillary columns are typically made from open tubular glass capillary columns that are 15 - 100 m long with a 0.2 - 0.75 mm ID, and coated with a liquid phase. Most capillary columns are now made of fused silica, although glass columns are still sold for the analysis of volatiles. Capillary columns are inherently more efficient than packed columns and have replaced packed columns for most SW-846 applications.

1.4.2 SW-846 HPLC methods are categorized on the basis of the mechanism of separation.

1.4.2.1 Partition chromatography is the basis of reverse phase HPLC separations. Analytes are separated on a hydrophobic column using a polar mobile phase pumped at high pressure (800 - 4000 psi) through a stainless steel column 10 -

25 cm long with a 2 - 4 mm ID and packed with 3 - 10 µm silica or divinyl benzene-styrene particles.

1.4.2.2 Ion exchange chromatography is used to separate ionic species.

1.5 SW-846 methods describe columns and conditions that have been demonstrated to provide optimum separation of all or most target analytes listed in that specific procedure. Most often, those columns were the ones used by EPA during method development and testing. Analysts may change those columns and conditions, provided that they demonstrate performance for the analytes of interest that is appropriate for the intended application. This is especially true when limited groups of analytes are to be monitored (i.e., if only a subset of the list of target analytes in a method are required, then the chromatographic conditions and columns may be optimized for those analytes).

1.5.1 Chromatographic performance is demonstrated by the resolution of standards and the ability to model the response of the detector during calibration, and by the sensitivity, accuracy, precision, frequency of false positives, and frequency of false negatives during analysis. The laboratory must demonstrate that an alternate chromatographic procedure provides performance that satisfies the analytical requirements of the specific application for which it is being used. Such demonstrations should be performed using the procedures outlined in Secs. 8.2 to 8.5 of this method and those in Chapter One.

1.5.2 In addition, laboratories must be cautious whenever the use of two dissimilar columns is included in a method for confirmation of identification. For instance, a DB-5 column generally cannot be used for confirmation of results obtained using an SPB-5 column because the stationary phases are not sufficiently dissimilar and the changes in elution order (if any) will not provide adequate confirmation.

1.6 When gas chromatographic conditions are changed, retention times and analytical separations are often affected. For example, increasing the GC oven temperature changes the partitioning between the mobile and stationary phases, leading to shorter retention times. GC retention times can also be changed by selecting a column with a different length, stationary-phase loading (i.e., capillary film thickness or percent loading for packed columns), or alternate liquid phase. As a result, two critical aspects of any SW-846 chromatographic method are the determination and/or verification of retention times and analyte separation.

1.7 HPLC retention times and analytical separations are also affected by changes in the mobile and stationary phases. The HPLC mobile phase is easily changed by adjusting the composition of the solvent mixture being pumped through the column. In reverse phase HPLC, increasing the ratio of methanol (or acetonitrile) to water shortens retention times. HPLC retention times can also be changed by selecting a column with (1) a different length, (2) an alternate bonded phase, or (3) a different particle size (e.g., smaller particles generally increase column resolution). SW-846 methods provide conditions that have been demonstrated to provide good HPLC separations using specific instruments to analyze a limited number of samples. Analysts (particularly those using HPLC/MS) may need to tailor the chromatographic conditions listed in the method for their specific application and/or instrument. HPLC methods are particularly sensitive to small changes in chromatographic conditions, including temperature. HPLC column temperature control ovens should be used to maintain constant retention times since ambient laboratory temperatures often fluctuate throughout the course of a day.

1.8 Chromatographic methods can be used to produce data of appropriate quality for the analysis of environmental and waste samples. However, data quality can be greatly enhanced when

the analyst understands both the intended use of the results and the limitations of the specific analytical procedures being employed. Therefore, these methods are recommended for use only by, or under the close supervision of, experienced analysts. Many difficulties observed in the performance of SW-846 methods for the analysis of RCRA wastes can be attributed to the lack of skill and training of the analyst.

1.8.1 Methods using selective (e.g., PID, NPD, ELCD) or non-selective (e.g., FID) detectors may present serious difficulties when used for site investigations, including co-elution of target analytes, false negatives due to retention time shifts, and false positives and quantitation errors due to co-eluting non-target sample components.

1.8.2 In contrast, GC methods employing selective or non-selective detectors may be appropriate for remediation activities where the analytes of concern are known, of limited number, and of significantly greater concentration than potentially interfering materials.

1.8.3 If the site is not well characterized, and especially if large numbers of target analytes are of concern, analysis by GC/MS or HPLC/MS may be more appropriate.

1.9 Each of the chromatographic methods includes a list of the compounds that it may be used to determine. The lists in some methods are lengthy and it may not be practical or appropriate to attempt to determine all the analytes simultaneously. Such analyte lists do not imply a regulatory requirement for the analysis of any or all of the compounds, but rather, indicate the method(s) which may be applicable to those analytes.

1.10 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

Method 8000 describes general considerations in achieving chromatographic separations and performing calibrations. Method 8000 is to be used in conjunction with all SW-846 determinative chromatographic methods, including, but not limited to, each method listed in Sec. 1.1. Each of these chromatographic methods recommends appropriate procedures for sample preparation, extraction, cleanup, and/or derivatization. Consult the specific procedures for additional information on these crucial steps in the analytical process.

2.1 Sec. 3.1 of this method provides general guidance on minimizing contamination, including cross-contamination between samples. Sample screening procedures are strongly recommended, and discussed in Sec. 3.2.

2.2 Before any sample or blank is introduced into a chromatographic system, the appropriate resolution criteria and calibration procedure(s) described in Method 8000 must be satisfied (see Secs. 3.3 and 8.3).

2.3 Secs. 3.4 and 3.5 provide information on the effects of chromatographic interferences.

2.4 Sec 4.0 of this method contains generalized specifications for the components of both GC and HPLC systems used in SW-846 analyses.

2.5 Calibration of the analytical system is another critical step in the generation of quality data. Sec. 7.5 discusses specific procedures and calculations for both linear and non-linear calibration relationships. The continued use of any chromatographic procedure requires a verification of the calibration relationship, and procedures for such verifications are described in this method as well (see Sec. 7.7).

2.6 The identification of target compounds by any chromatographic procedure is based, at least in part, on retention times. Sec. 7.6 provides procedures for the determination of retention times and retention time windows to be used with the specific methods listed in Sec. 1.1.

2.7 The calculations necessary to derive sample-specific concentration results from the instrument responses are common to most of the analytical methods listed in Sec. 1.1. Therefore, Sec. 7.10 of Method 8000 contains a summary of the commonly used calculations.

2.8 Preventive maintenance and corrective actions are essential to the generation of quality data in a routine laboratory setting. Suggestions for such procedures are found in Sec. 7.11.

2.9 Most of the methods listed in Sec. 1.1 employ a common approach to quality control (QC). While some of the overall procedures are described in Chapter One, Sec. 8.0 describes routinely used procedures for calibration verification, instrument performance checks, demonstrating acceptable performance, etc.

2.10 Before performing analyses of specific samples, analysts should determine acceptable recovery ranges for all target analytes of interest in the type of matrices to be tested. These procedures are described in Secs. 8.4, 8.5, and 8.7. Analysts must also be able to demonstrate that the sensitivity of the procedure employed is appropriate for the intended application. One approach to such a demonstration is to estimate the method detection limits for the analytes of interest using the procedures in Chapter One.

3.0 INTERFERENCES/CHROMATOGRAPHIC PERFORMANCE

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples. Where practical, samples with unusually high concentrations of analytes should be followed by a solvent blank or by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of a solvent blank or organic-free reagent water is not necessary.

Purging vessels may be cleaned by rinsing with methanol, followed by a distilled water rinse and drying in a 105°C oven between analyses. Detergent solutions may also be used, but care must be taken to remove the detergent residue from the purging vessel. Other approaches to cleaning purging vessels may also be employed, provided that the laboratory can demonstrate that they are effective in removing contaminants.

3.2 In addition to carryover of compounds from one sample to the next, the analysis of high-concentration samples can lead to contamination of the analytical instrument itself. This is particularly true for GC/MS. Eliminating this contamination can require significant time and effort in cleaning the instruments, time that cannot be spent analyzing samples. The most reliable procedure for ensuring minimum down time during the GC/MS analysis of samples is to screen samples by some other technique. Samples to be analyzed for volatiles can be screened using an automated headspace sampler (Method 5021) connected to a GC/PID/ELCD detector (Method 8021). Samples to be analyzed for semivolatiles can be screened using GC/FID. Other screening methods are also acceptable. The analyst should use the screening results to choose an appropriate dilution factor for the GC/MS analysis that will prevent system contamination yet still provide adequate sensitivity for the major constituents of the sample.

3.3 One of the most important measures of chromatographic performance is resolution, the separation of chromatographic peaks (peak separation/average peak width). Peak separations are facilitated by good column efficiency (i.e., narrow peak widths) and good column selectivity (i.e., analytes partition differently between the mobile and stationary phases).

3.3.1 The goal of analytical chromatography is to separate sample constituents within a reasonable time. Baseline resolution of each target analyte from co-extracted materials provides the best quantitative results, but is not always possible to achieve.

3.3.2 In general, capillary columns contain a greater number of theoretical plates than packed columns. (A theoretical plate is a surface at which an interaction between the sample components and the stationary phase may occur). As a result, capillary columns generally provide more complete separation of the analytes of interest. However, packed columns can provide adequate resolution of some analytes and are most appropriately employed when the list of analytes to be determined is relatively short.

3.3.3 The ability to resolve individual compounds is generally the limiting factor for the number of analytes that can be measured using a single procedure. Some procedures, particularly Method 8081 (Organochlorine Pesticides), Method 8082 (PCBs), and Method 8141 (Organophosphorus Pesticides), list analytes that may not all be resolved from one another. Therefore, while each of these methods is suitable for the listed compounds, they may not be suitable to measure the entire list in a single analysis. In addition, some methods include analytes that are isomers or closely related compounds which are well-known as co-eluting or are not completely separable. In these instances, the results should be reported as the sum of the two (or more) analytes. Laboratories should demonstrate that target analytes are resolved during calibration and satisfy the requirements in Sec. 8.3, or should report the results as "totals" or "sums" (e.g., m+p-xylene). Methods that utilize mass spectrometry for detection are less affected by resolution problems, because overlapping peaks may often be mass-resolved. However, even mass spectrometry will not be able to mass resolve positional isomers such as m-xylene and p-xylene if the compounds co-elute.

3.4 Elevated chromatographic baselines should be minimized or eliminated during these analyses. Baseline humps can usually be reduced or eliminated by the application of appropriate sample clean-up (see Method 3600), extract dilution, the use of pre-columns and/or inserts, or use of a selective detector. Integration of "hump-o-grams" can result in significant quantitative errors. When elevated baselines are observed during the analysis of blanks and standards, the chromatographic system should be considered contaminated. This contamination may be the result of impure carrier gas, inadequate gas conditioning, septum bleed, column oxidation, and/or pyrolysis products in the injector or column. Such contamination is unacceptable and should be addressed through a program of preventive maintenance and corrective action.

3.5 GC preventive maintenance and corrective action

Poor GC performance may be expected whenever a chromatographic system is contaminated with high-boiling materials, particularly in the injector. Analysts should perform routine maintenance, including replacement of septa, cleaning and deactivating injector liners, and removing as much as 0.5 - 1 m from the injector side of a capillary column.

If chromatographic performance or ghost peaks are still a problem, cleaning of the metallic surfaces of the injection port itself may be necessary. Capillary columns are reliable and easy to use, but several specific actions are necessary to ensure good performance.

3.5.1 Contact between the capillary column and the wall of the GC oven can affect both chromatographic performance and column life. Care should be taken to prevent the column from touching the oven walls.

3.5.2 Care should be taken to keep oxygen out of capillary columns.

3.5.3 Septa should only be changed after the oven has cooled.

3.5.4 Columns should be flushed with carrier gas for 10 minutes before reheating the oven.

3.5.5 Carrier gas should be scrubbed to remove traces of oxygen and scrubbers should be changed regularly.

3.5.6 Carrier gas should always be passed through the column whenever the oven is heated.

3.6 HPLC preventive maintenance and corrective action

HPLC band broadening results from improper instrument setup or maintenance. Band broadening results whenever there is a dead volume between the injector and the detector. Therefore, plumbing connections should be of minimum length and diameter, and ferrules should be properly positioned on the tubing to minimize dead volume.

3.6.1 Columns should not be subjected to sudden physical stress (e.g., dropping) or solvent shocks (e.g., changing solvents without a gradient).

3.6.2 Columns can become contaminated with particulates or insoluble materials. Guard columns should be used when dirty samples are analyzed.

3.6.3 High quality columns are packed uniformly with small uniform diameter particles with a minimum number of free silol groups. Use of such columns will result in optimum chromatographic performance.

3.6.4 Columns should be replaced when performance degrades (e.g., significant band broadening, peak splitting, or loss of chromatographic resolution occurs).

3.6.5 Pumping systems should deliver reproducible gradients at a uniform flow rate. Rates can be checked by collecting solvent into a graduated cylinder.

64

3.6.6 Column temperatures should be regulated by the use of column temperature control ovens to ensure reproducibility of retention times.

3.6.7 Small changes in the composition or pH of the mobile phase can have a significant effect on retention times.

4.0 APPARATUS AND MATERIALS

4.1 GC inlet systems

4.1.1 Volatile organics

Volatile organic analytes are introduced into a GC through a purge-and-trap system, by direct injection, or by other devices. The purge-and-trap apparatus is described in Method 5030 for water samples and in Method 5035 for soil and other solid samples. See Method 5000 for guidance on all forms of sample introduction of volatiles into the GC and GC/MS system.

4.1.2 Semivolatile organics

Sample extracts containing semivolatile organic compounds are introduced into a GC with a syringe that passes through a septum into an injection port. The injection port allows the sample extract to be vaporized prior to being flushed onto the GC column, hence the term "gas" chromatography. Correct set up and maintenance of the injector port is necessary to achieve acceptable performance with GC methods. Septa should be changed frequently enough to prevent retention time shifts of target analytes and peak tailing. The schedule for such septa changes is dependent on the quality of the septa, the sharpness of the needle, and the operation of the injection system. Appropriate injector liners should be installed, and liners should be cleaned and deactivated (with dichlorodimethylsilane) regularly.

4.1.3 Injector difficulties include the destruction of labile analytes and discrimination against high boiling compounds in capillary injectors.

4.1.3.1 Packed columns and wide-bore capillary columns (> 0.50 mm ID) should be mounted in 1/4-inch injectors. An injector liner is needed for capillary columns.

4.1.3.2 Narrow-bore capillary columns (≤ 0.32 mm ID) should be mounted in split/splitless (Grob-type) injectors. Split/splitless injectors require automated valve closures that direct most of the flow (and sample) onto the head of the analytical column. After 30 - 45 seconds, the split valve is opened, so that most of the flow is vented during analysis, thus eliminating the solvent tail, and maintaining proper flow through the column. The initial oven temperature should be below the boiling point of the injection solvent if the solvent front interferes with early eluting analytes or if the solvent effect is needed to resolve difficult-to-separate analytes.

4.1.3.3 Cool on-column injection allows the analysis of labile compounds that degrade on packed columns and in split/splitless injectors.

4.2 GC flow control

Precise control of the gas mobile phase is necessary to achieve reproducible GC retention times. Flow controllers within any GC used for SW-846 analyses must deliver a precisely metered gas flow at a rate appropriate for the GC column mounted in the instrument.

4.2.1 Most GCs have restrictors built into flow controllers. These restrictors are used to provide precise flow at the carrier gas flow rate specified in the method (e.g., use <20 mL/min restrictors for wide-bore capillary methods). Carrier gas flow rates should be checked regularly (with both the injector and the oven heated) using a bubble meter or other appropriate procedure.

4.2.2 Cylinder pressures should also be regulated properly. Manifold pressures must be sufficiently large that a change in the head pressure of an individual instrument does not affect the flow through all instruments. Toggle valves that allow instruments to be isolated are recommended for all multi-instrument gas delivery systems. Analysts should spend time each week conducting preventative maintenance in order to ensure that proper flow control is maintained. One needs to search for leaks using a helium tester or soap solution at each connector in the gas delivery systems. Analysts should routinely conduct preventive maintenance activities, including those designed to ensure proper flow control and to identify potential leaks in the gas delivery system. The search for leaks may be conducted with a helium leak tester, soap solutions, performing static pressure tests, or other appropriate measures.

4.2.3 Carrier gas should be of high purity and should be conditioned between the cylinder and the GC to remove traces of water and oxygen. Scrubbers should be changed according to manufacturers recommendations. Gas regulators should contain stainless steel diaphragms. Neoprene diaphragms are a potential source of gas contamination, and should not be used.

4.3 Gas chromatographic columns

Each determinative method in SW-846 provides a description of a chromatographic column or columns with associated performance data. Other packed or capillary (open-tubular) columns may be substituted in SW-846 methods to improve performance if (1) the requirements of Secs. 8.3 and 8.4 are satisfied, and (2) target analytes are sufficiently resolved from one another and from co-extracted interferences to provide data of the appropriate quality for the intended application.

4.3.1 Narrower columns are more efficient (i.e., can resolve more analytes) but have a lower capacity (i.e., can accept less sample without peak distortion).

4.3.2 Longer columns can resolve more analytes, as resolution increases as a function of the square root of column length.

4.3.3 Increasing column film thickness or column loading increases column capacity and retention times.

4.3.4 Use of capillary columns has become standard practice in environmental and waste analysis. Capillary columns have an inherently greater ability to separate analytes than packed columns. However, packed columns can provide adequate resolution of some analytes and are most appropriately employed when the list of analytes to be determined is relatively short.

66

4.3.5 Columns used for SW-846 analyses should be installed properly. Column ends should be cut square. Contaminated ends should be trimmed off, and columns should be placed through ferrules before they are trimmed. Columns should not touch the walls of the GC oven during analysis, and the manufacturer's column temperature limits should not be exceeded.

4.3.6 Septa should be changed regularly and septum nuts should not be overtightened. Oxygen should not be introduced into a hot column and carrier gas should be passed through a column whenever it is heated. New columns, particularly packed columns, should be conditioned prior to analyzing samples.

4.4 GC detectors

Detectors are the transducers that respond to components that elute from a GC column and produce the electrical signal that is used for quantitative determinations. SW-846 analyses are conducted using selective detectors or mass spectrometers listed in Sec. 1.1. Except where otherwise recommended by the instrument manufacturer, selective non-MS detectors should be maintained at least 20°C above the highest oven temperature employed to prevent condensation and detector contamination. The transfer lines between the GC and an MS detector should be maintained at a temperature above the highest column temperature, or as specified by the instrument manufacturer, to prevent condensation.

4.5 HPLC injectors

Liquids are essentially non-compressible, so a mechanical device is necessary that allows introduction of the sample into a high pressure flow without significant disruption in the flow rate and hydraulic pressure. Normally, a 6-port valve is used for this purpose. A sample loop (generally 10-100 µL) is isolated from the flow of the mobile phase and filled with a sample extract. (Larger sample loops may be used to increase sensitivity, however, they may degrade chromatographic performance). The extract is then injected by turning the valve so that the mobile phase flows through the loop. This procedure virtually eliminates dead volume in the injector and is fully compatible with automated operation.

4.5.1 When the extract is highly viscous, a pressure spike results which can automatically shut off the HPLC pump.

4.5.2 Contamination of subsequent injections may occur when the extract contains material that is not soluble in the mobile phase.

4.5.3 Injection loops are easily changed but analysts must ensure that the compression fittings are properly installed to prevent leaks. Injectors require maintenance, as the surfaces that turn past each other do wear down.

4.6 HPLC pumps

The mobile phase used for HPLC must be accurately pressurized before it enters the injector. HPLC pumps are generally capable of delivering solvent at 5000 psi with excellent precision. The rate of delivery depends on the column that is used for the separation. Most environmental methods recommend flow rates of 0.25-1.0 mL/min. Flow rates should be checked by collecting column effluent in a graduated cylinder.

Most pumping systems are capable of changing solvent concentration during an analysis (i.e., gradient elution). Gradients are generated by either high pressure mixing of two streams between the pump and the injector or by proportional mixing of the solvents before they are pumped. In either case, solvent mixing can cause changes in the solubility of dissolved gases, the formation of bubbles in the mobile phase, or non-reproducible gradients.

4.6.1 Air bubbles result in erratic baseline and, in the case of low pressure mixing, bubbles can cause the pump to cavitate. Therefore, HPLC solvents should be degassed prior to use.

4.6.2 Non-reproducible gradients can result in significant changes in retention times from run to run.

4.6.3 HPLC solvents should be filtered to remove particles that cause pump piston wear. HPLC pump maintenance includes replacing seals regularly. (Use of strong buffers or solvents like tetrahydrofuran can significantly shorten the lifetime of pump seals.) Pumps should deliver solvent with minimal pulsation.

4.7 HPLC Columns

These columns must be constructed with minimum dead volume and a narrow particle size distribution. HPLC columns are generally constructed of stainless steel tubing and are sealed with compression fittings. Manufacturers provide columns that are bonded with different alkyl groups (e.g., C_{18}, cyano, TMS), have different percent carbon loading, are packed with different particle sizes (3-10 µm), and are packed with particles of different pore size (smaller pores mean greater surface area), or are of different dimensions.

4.7.1 Columns with higher percent loading have the capacity to analyze somewhat larger samples, but extremely high loadings may contribute to problems with the particle beam MS interface.

4.7.2 Columns with free silol groups show less tailing of polar materials (e.g., amines).

4.7.3 A smaller particle (and pore) size generally gives better resolution, higher back pressure, and smaller sample capacity. Columns with 3 µm particle size may have short lifetimes when they are used for the analysis of complex waste extracts.

4.7.4 Improvements in column packing have resulted in 10 and 15 cm columns that provide the separating power necessary for most environmental and waste analyses.

4.7.5 Internal diameters of columns used for environmental and waste analysis are generally 2-5 mm. Narrower columns are called microbore columns. While they provide better separations, they become fouled more easily.

4.7.6 The lifetime and performance of HPLC columns can be improved through proper maintenance. Analysts should filter sample extracts, use compatible guard columns, check for clogged frits and for column voids. Columns should not be stored dry or containing strong buffers.

4.8 HPLC column temperature control ovens

HPLC retention times are much more reproducible if the column is held at a constant temperature. Temperature control ovens capable of maintaining the HPLC column at ± 0.1°C should be utilized to maintain consistent retention times throughout the course of an HPLC analysis. Normal oven operating temperature would be 3-5°C above ambient laboratory temperature.

4.9 HPLC detectors

Detectors are the transducers that respond to components that elute from a HPLC column and produce the electrical signal that is used for quantitative determinations. SW-846 analyses are conducted using selective detectors or mass spectrometers listed in Sec. 1.1. HPLC/MS requires the use of a sophisticated interface that separates target analytes from the aqueous mobile phase. Examples include the thermospray (TSP), electrospray (ESP), and the particle beam (PB) interfaces.

4.10 Data systems

Raw chromatographic data have to be reduced in order to provide the quantitative information required by analysts. The use of sophisticated data systems is strongly recommended for SW-846 chromatographic methods. The ability to store and replot chromatographic data is invaluable during data reduction and review. Organizations should establish their priorities and select the system that is most suitable for their applications.

4.11 Supplies

Chromatographers require a variety of supplies. The specific items that should be stocked depend on laboratory instrumentation and the analyses performed. At a minimum, laboratories need PTFE tape, stainless steel regulators, acid-washed copper tubing, and syringes, and replacement parts for instruments.

4.11.1 Laboratories performing GC analyses also require high purity gases, scrubbers for gas conditioning, gas-tight fittings, capillary cutters, magnifying glasses, septa with proper temperature limits, appropriate ferrules, dichlorodimethylsilane (for deactivating surfaces), glass wool, spare columns, and injection port liners.

4.11.2 Laboratories performing HPLC analyses require high purity solvents, column packing material, frits, 1/16-inch tubing, appropriate ferrules, solvent filtration apparatus, and solvent degassing apparatus.

5.0 REAGENTS

See the specific extraction and determinative methods for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to Chapter Four, Organic Analytes, Sec. 4.1, for information on sample collection, preservation and handling procedures. Additional information may be found in some of the individual sample extraction, preparation, and determinative methods.

7.0 PROCEDURE

Extraction and cleanup are critical for the successful analyses of environmental samples and wastes. Analysts should pay particular attention to selection of sample preparation procedures to obtain reliable measurements.

7.1 Extraction

The individual determinative methods for organic analytes in SW-846 often recommend appropriate sample extraction procedures. General guidance on semivolatile extraction procedures can be found in Method 3500. Guidance on volatile procedures can be found in Method 5000.

7.2 Cleanup and separation

The individual determinative methods for organic analytes in SW-846 often recommend appropriate cleanup procedures. General guidance on cleanup procedures can be found in Method 3600. While some relatively clean matrices (such as ground water samples) may not require extensive cleanups, the analyst should carefully balance the time savings gained by skipping cleanups against the potential increases in instrument down time and loss of data quality that can occur as a result.

7.3 Recommended chromatographic columns and instrument conditions are described in each determinative method. As noted earlier, these columns and conditions are typically those used during the development and testing of the method. However, other chromatographic systems may have somewhat different characteristics. In addition, analytical instrumentation continues to evolve. Therefore, SW-846 methods allow analysts some flexibility to change these conditions (with certain exceptions), as long as they demonstrate adequate performance.

Chromatographic performance is demonstrated by the resolution of standards and the ability to model the response of the detector during calibration, and by the sensitivity, accuracy, precision, frequency of false positives, and frequency of false negatives during analysis. If the laboratory employs an alternative chromatographic procedure or alternative conditions, then the laboratory must demonstrate that the performance satisfies the analytical requirements of the specific application for which the alternative chromatographic procedure is being used. Such demonstrations should be performed using the procedures outlined in Secs. 8.2 to 8.5 of this method and those in Chapter One.

7.4 Initial Calibration

Calibration of an analytical instrument involves the delineation of the relationship between the response of the instrument and the amount or concentration of an analyte introduced into the instrument. The graphical depiction of this relationship is often referred to as the calibration curve. In order to perform quantitative measurements, this relationship must be established prior to the analysis of any samples, and thus, is termed initial calibration.

Historically, many analytical methods have relied on linear models of the calibration relationship, where the instrument response is directly proportional to the amount of a target compound. The linear model has many advantages, among them, simplicity and ease of use. Unfortunately, given the advent of new detection techniques and the fact that many techniques cannot be optimized for all of the analytes to which they may be applied, the analyst is increasingly likely to encounter situations where the linear model neither applies nor is appropriate.

The initial calibration for SW-846 chromatographic methods involves the analysis of standards containing the target compounds at a minimum of five different concentrations covering the working range of the instrument. In order to produce acceptable sample results, the response of the instrument must be within the working range established by the initial calibration. The extrapolation of the calibration to concentrations above or below those of the actual calibration standards is not appropriate and may lead to significant quantitative errors regardless of the calibration model chosen. Analysts are advised that it may be necessary to prepare calibration standards that cover concentration ranges that are appropriate for specific projects or type of analyses. For instance, the analyst should not necessarily expect to be able to perform a calibration appropriate for sub-ppb level analyses and also use the same calibration data for high-ppb or ppm level samples.

The specific options for evaluating the initial calibration are described in Sec. 7.5. The remainder of this section describes the preparation of calibration standards, the use of external and internal standard calibrations, and the calculation of both calibration factors and response factors.

7.4.1 Calibration standards are prepared using the procedures indicated in Sec. 5.0 of the determinative method of interest. However, the general procedure is described here.

7.4.1.1 For each analyte and surrogate of interest, prepare calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to volumetric flasks and diluting to volume with an appropriate solvent.

7.4.1.2 The lowest concentration calibration standard that is analyzed during an initial calibration establishes the method quantitation limit based on the final volume of extract (or sample) described in the preparative method or employed by the laboratory.

7.4.1.3 The other concentrations should define the working range of the detector or correspond to the expected range of concentrations found in actual samples that are also within the working range of the detector.

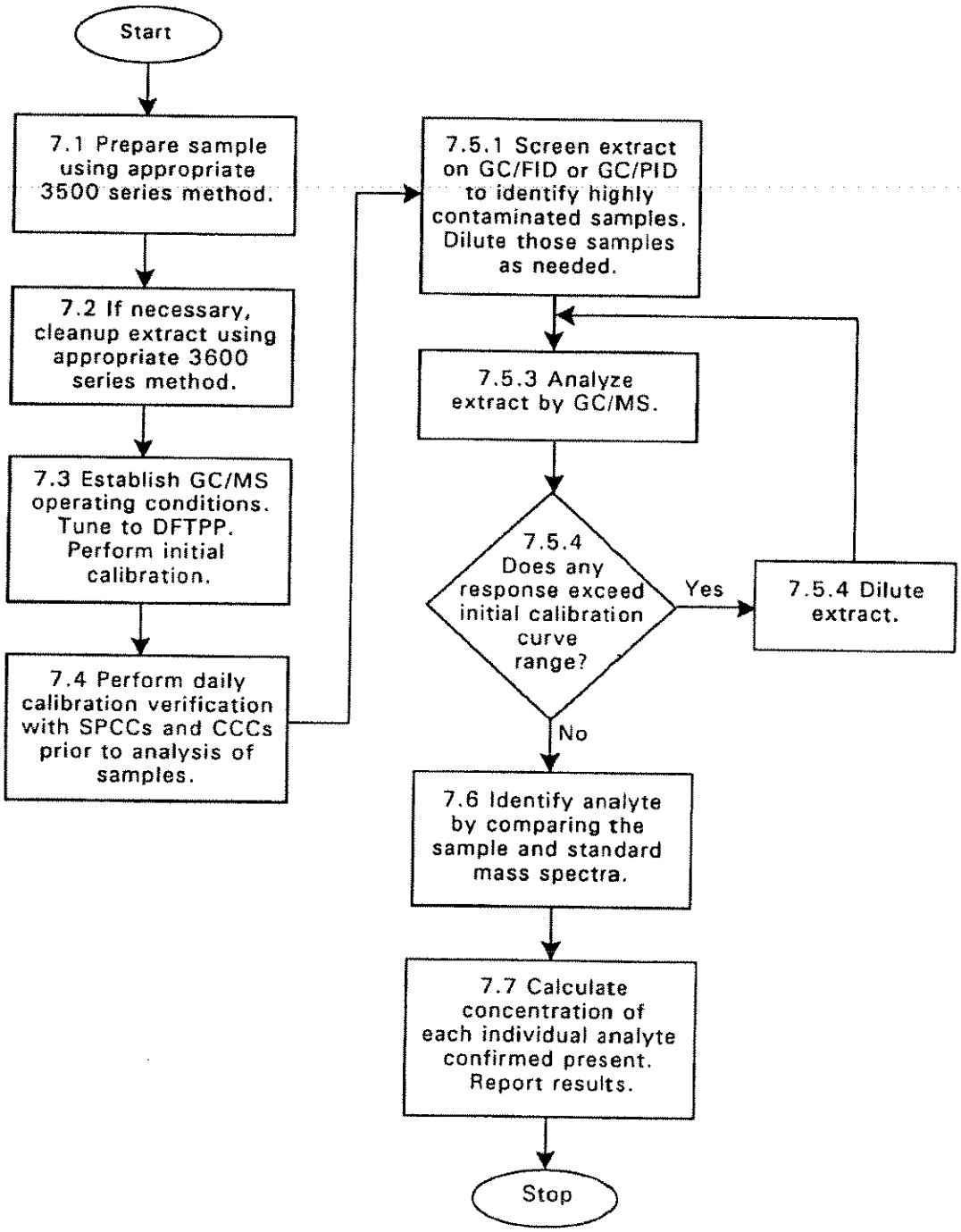
7.4.1.4 For each analyte, at least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project, which may include establishing compliance with a regulatory or action limit.

7.4.1.5 Given the number of target compounds addressed by some of the methods listed in Sec. 1.1, it may be necessary to prepare several sets of calibration standards, each set consisting of five solutions at different concentrations. The initial calibration will then involve the analysis of each of these sets of five standards.

7.4.1.6 Once the standards have been prepared, the initial calibration begins by establishing chromatographic operating parameters that provide instrument performance equivalent to that documented in Sec. 7.0 of the determinative method of interest, or that is appropriate for the data quality objectives of the intended application.

7.4.2 External standard and internal standard calibration techniques

The chromatographic system may be calibrated using either the external standard or the internal standard techniques described below. General calibration criteria are provided in this section for GC and HPLC procedures using non-MS detection. The applicable calibration procedures for GC/MS (e.g., Methods 8260, 8270, 8280, and 8290), HPLC/MS (e.g., Methods 8321 and 8325), and GC/FT-IR (e.g., Method 8410) are described in those methods. Some


Start
7.1 Prepare sample using appropriate 3500 series method.
7.2 If necessary, cleanup extract using appropriate 3600 series method.
7.3 Establish GC/MS operating conditions. Tune to DFTPP. Perform initial calibration.
7.4 Perform daily calibration verification with SPCCs and CCCs prior to analysis of samples.
7.5.1 Screen extract on GC/FID or GC/PID to identify highly contaminated samples. Dilute those samples as needed.
7.5.3 Analyze extract by GC/MS.
7.5.4 Does any response exceed initial calibration curve range?
Yes
7.5.4 Dilute extract.
No
7.6 Identify analyte by comparing the sample and standard mass spectra.
7.7 Calculate concentration of each individual analyte confirmed present. Report results.
Stop

54

determinative methods may provide special guidance on calibration that is specific to that method.

Regardless of whether external standard or internal standard calibration is used, introduce each calibration standard into the instrument using the same technique that is used to introduce the actual samples into the gas chromatograph (e.g., 1-3 µL injections for GC methods, 10-100 µL injections for HPLC methods, purge-and-trap techniques for volatiles, etc.). Tabulate peak area or height responses against the mass or concentration injected, as described below.

7.4.2.1 External standard calibration procedure

External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

For multi-component analytes, see the appropriate determinative method for information on which areas to employ.

The CF can also be calculated using the concentration of the standard rather than the mass in the denominator of the equation above. However, the use of concentrations in CFs will require changes to the equations that are used to calculate sample concentrations (see Sec. 7.10.1.1).

7.4.2.2 Internal standard calibration procedure

Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area (or height) of the target compound in the sample or sample extract to the peak area (or height) of the internal standard in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and may also be known as a relative response factor in other methods.

In many cases, internal standards are recommended in SW-846 methods. These recommended internal standards are often brominated, fluorinated, or stable isotopically labeled analogs of specific target compounds, or are closely related compounds whose presence in environmental samples is highly unlikely. If internal standards are not recommended in the method, then the analyst needs to select one or more internal standards that are similar in analytical behavior to the compounds of interest, and not expected to be found in the samples otherwise.

Whichever internal standards are employed, the analyst needs to demonstrate that the measurement of the internal standard is not affected by method analytes and surrogates or by matrix interferences. In general, internal standard calibration is not as useful for GC and HPLC methods with non-MS detectors because of the inability to chromatographically resolve many internal standards from the target compounds. The

use of MS detectors makes internal standard calibration practical because the masses of the internal standards can be resolved from those of the target compounds even when chromatographic resolution cannot be achieved.

When preparing calibration standards for use with internal standard calibration, add the same amount of the internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The internal standard solution will contain one or more internal standards and the concentration of the individual internal standards may differ within the spiking solution (e.g., not all internal standards need to be at the same concentration in this solution). The mass of each internal standard added to each sample extract immediately prior to injection into the instrument or to each sample prior to purging must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs (e.g., 10 µL of solution added to a 1 mL final extract results in only a negligible 0.1% change in the final extract volume which can be ignored in the calculations).

An ideal internal standard concentration would yield a response factor of 1 for each analyte. However, this is not practical when dealing with more than a few target analytes. Therefore, as a general rule, the amount of internal standard should produce an instrument response (e.g., area counts) that is no more than 100 times that produced by the lowest concentration of the least responsive target analyte associated with the internal standard. This should result in a minimum response factor of approximately 0.01 for the least responsive target compound.

For each of the initial calibration standards, calculate the RF values for each target compound relative to one of the internal standards as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

Note that in the equation above, RF is unitless, i.e., the units from the two area terms and the two concentration terms cancel out. Therefore, units other than µg/L may be used for the concentrations of the analyte, surrogate, and internal standard, provided that both C_s and C_{is} are expressed in the same units. The mass of the analyte and internal standard may also be used in calculating the RF value.

7.5 Calibration linearity

SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data, as described below. Given the limitations in instrument data systems, it is likely that the analyst will have to choose one model for all analytes in a particular method. Both models can be applied to either external or internal standard calibration data.

NOTE: The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Whichever calibration model is employed, a unique analyte or surrogate concentration must fall within the calibration range. Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

NOTE: The following sections describe various options for initial calibration and provide the calibration acceptance criteria used to evaluate each option. The criteria listed in these sections are designed for quantitation of trace level concentrations of the analytes of interest. If data of lesser quality will satisfy project-specific data needs, then less stringent criteria may be employed, provided that they are documented and approved in a project-specific QA project plan.

The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use *a priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of the physics of the detector, or specific manufacturer's recommendations.

7.5.1 Linear calibration using the average calibration or response factor

When calculated as described in Sec. 7.4, both calibration factors and response factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. However, when the variation, measured as the relative standard deviation (RSD), is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstrated by the analysis of the standards

To evaluate the linearity of the initial calibration, calculate the mean CF (external standard calibration) or RF (internal standard calibration), the standard deviation (SD), and the RSD as follows:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n} \qquad \text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100 \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where *n* is the number of calibration standards and RSD is expressed as a percentage (%).

If the RSD of the calibration or response factors is less than or equal to 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations.

7.5.1.1 Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the 20% acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Sec. 7.11 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 20%, the analyst may wish to review the results (area counts, calibration or response factors, and RSD) for those analytes to ensure that the problem is not associated with just one of the five initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Sec. 7.4.1.2, the method quantitation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

7.5.1.2 In those instances where the RSD for one or more analytes exceeds 20%, the initial calibration may still be acceptable if the following conditions are met:

7.5.1.2.1 The mean of the RSD values for all analytes in the calibration is less than or equal to 20%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. If no analyte has an RSD above 20%, then the mean RSD calculation need not be performed.

7.5.1.2.2 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

7.5.1.2.3 The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

NOTE: The analyst and the data user must be aware that the use of the approach listed in Sec. 7.5.1.2.1 (i.e., the average of all RSD values ≤ 20%) will lead to greater uncertainty for those analytes for which the RSD is greater than 20%. The analyst and the data user should review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results (see Sec. 8.0), to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ one of the other calibration approaches (see Secs. 7.5.2 to 7.5.4) or adjust the instrument operating conditions and/or the calibration range until the RSD is ≤ 20%.

7.5.1.3 If all of the conditions in Sec. 7.5.1.2 are met, then the average calibration or response factor may be used to determine sample concentrations, as described in Sec. 7.10.

7.5.2 Linear calibration using a least squares regression

If the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or *a priori* knowledge of the instrument response. Further, at the discretion of the analyst, this approach also may be used for analytes that do meet the RSD limits in Sec. 7.5.1.

This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The analyst may also employ a weighted least squares regression if replicate multi-point calibrations have been performed, e.g., three 5-point curves. For all other instances, an appropriate unweighted least squares method should be used. When using a weighted linear least squares regression, the following weighting factor should be used:

$$\frac{1}{SD^2}$$

76

where SD is the standard deviation of the replicate results at each individual standard concentration.

The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where:

y = Instrument response (peak area or height)
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a sixth calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

In calculating sample concentrations by the external standard method, the regression equation is rearranged to solve for the concentration (x), as shown below.

$$x = \frac{(y - b)}{a}$$

When a weighted linear least squares regression is employed, the regression equation becomes:

$$y = \frac{1}{SD^2}(ax + b)$$

which may be rearranged to solve for x, the concentration. Using internal standard quantitation, the regression equation is rearranged as shown below:

$$\frac{A_s C_{is}}{A_{is}} = aC_s + b$$

where:

A_s = Area (or height) of the peak for the target analyte in the sample
A_{is} = Area (or height) of the peak for the internal standard
C_s = Concentration of the target analyte in the calibration standard
C_{is} = Concentration of the internal standard
a = Slope of the line (also called the coefficient of C_s)
b = The intercept

In calculating sample concentrations by the internal standard method, the regression equation is rearranged to solve for the concentration of the target analyte (C_s), as shown below.

77

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

7.5.3 Non-linear calibration

In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed.

NOTE: It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance. Thus, non-linear calibration should not be employed for methods or instruments previously shown to exhibit linear calibration for the analytes of interest.

When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order, as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

As noted above, the model must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing, and without having breaks in the function (i.e., the pen shall never leave the paper from the minimum to the maximum). The model must also be continuously differentiable, such that all derivatives of the function are continuous functions themselves, and monotonic, such that all tangent lines of the derivative to all of the points on the calibration curve have either only positive or negative slopes.

If the model is not a polynomial, it should not include more than four parameters, i.e.,

$$y = f(a,b,c,d,x)$$

where "f" indicates a function with up to four parameters.

In estimating model parameters for the calibration data, the instrumental response (y) must be treated as the dependent variable, and the calibration of the concentration standard (x) must be the independent variable. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. Model estimates from the regression must be used as calculated, i.e., if the model is a polynomial, the intercept is d and may not be set to 0. Weighting in a calibration model may significantly improve its accuracy.

The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Whereas SW-846 methods employ five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards, and a third order polynomial requires seven standards.

Most curve fitting programs will use some form of least squares minimization to adjust the coefficients of the polynomial (a,b,c, and d, above) to obtain the polynomial that best fits the data. The "goodness of fit" of the polynomial equation is evaluated by calculating the weighted coefficient of the determination (COD).

$$COD = \frac{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right) \sum_{i=1}^{n} (y_{obs} - Y_i)^2}{\sum_{i=1}^{n} (y_{obs} - \bar{y})^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard
$\bar{y}$ = Mean observed response from the initial calibration
Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)
n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)
p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

As noted in Sec. 7.5, whichever of these options is employed, a unique analyte or surrogate concentration must fall within the calibration range. Analysts are advised to check both second and third order calibration models to ensure that this holds true (e.g., no parabolas or repeating functions in the calibration range). Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

7.5.4 Data transformations

An understanding of the fundamental behavior of the detector may be used to choose a data transformation that will then allow for a simple calibration model. For example the response of a flame photometric detector in the sulfur mode is known to be proportional to the square of the sulfur concentration. Therefore, using the data system to take the square root of the instrument response before integration or the square root of the peak height allows for a calibration factor approach rather than a polynomial calibration curve. Instrument response may be transformed prior to any calculations (including integration) subject to the following constraints:

7.5.4.1 Any parameters used in the transformation should be fixed for the calibration and all subsequent analyses and verifications until the next calibration.

7.5.4.2 The transformation model chosen should be consistent with the behavior of the instrument and detector. All data transformations must be clearly defined and documented by the analyst and related back to the fundamental behavior of the detector. In other words, this approach may not be used in the absence of specific knowledge about the behavior of the detector, nor as a "shot in the dark" to describe the calibration.

7.5.4.3 No transformations should be performed on areas or other results (e.g., the transformation must be applied to the instrument response itself).

7.5.4.4 When the transformed data are used to develop calibration factors, those factors must meet the acceptance criteria described in Sec. 7.5.1.

7.6 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC and HPLC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

The following subsections describe <u>one</u> approach that may be used to establish retention time windows for GC and HPLC methods. Other approaches may be employed, provided that the analyst can demonstrate that they provide performance appropriate for the intended application.

<u>NOTE</u>: The criteria listed in Sec. 7.6 are provided for GC and HPLC procedures using non-MS or FTIR detection. Identification procedures are different for GC/MS (e.g., Methods 8260 and 8270), HPLC/MS (e.g., Methods 8321 and 8325), and GC/FT-IR (e.g., Method 8410).

7.6.1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

7.6.2 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate. For multi-component analytes, choose three to five major peaks (see the determinative methods for more details) and calculate the mean and standard deviation of those peaks.

7.6.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).

7.6.4 The width of the retention time window for each analyte, surrogate, and major constituent in multi-component analytes is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in Sec. 7.6.3 is employed, the width of the window will be 0.03 minutes.

7.6.5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration

verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

7.6.6 The laboratory must calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

7.6.7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds. As noted above, other approaches may also be employed, but must be documented by the analyst.

7.6.8 The surrogates are added to each sample, blank, and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

7.7 Calibration verification

The calibration relationship established during the initial calibration (Sec. 7.5) must be verified at periodic intervals. The process of calibration verification applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models.

As a general rule, the initial calibration in an SW-846 method must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. (Some methods may specify more frequent verifications). The 12-hour analytical shift begins with the injection of the calibration verification standard (or the MS tuning standard in MS methods). The shift ends after the completion of the analysis of the last sample or standard that can be injected within 12 hours of the beginning of the shift.

If the response (or calculated concentration) for an analyte is within ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid, and the analyst may continue to use the CF or RF values from the initial calibration to quantitate sample results. The ±15% criterion may be superseded in certain determinative methods.

Except where the determinative method contains alternative calibration verification criteria, if the response (or calculated concentration) for any analyte varies from the mean response obtained during the initial calibration by more than ±15%, then the initial calibration relationship may no longer be valid.

NOTE: The process of calibration verification is fundamentally different from the approach called "continuing calibration" in some methods from other sources. As described in those methods, the calibration factors or response factors calculated during continuing calibration are used to update the calibration factors or response factors used for sample quantitation. This approach, while employed in other EPA programs, amounts to a daily single-point calibration, and is not appropriate nor permitted in SW-846 chromatographic procedures for trace environmental analyses.

In keeping with the approach described for initial calibration in Sec 7.5, if the average of the responses for all analytes is within 15%, then the calibration has been verified. However, the conditions in Sec. 7.5.1.2 also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the 15% limit. The effect of using the average of the response for all analytes for calibration verification will be similar to that for the initial calibration -- namely, that the quantitative results for those analytes where the difference is greater than 15% will include a greater uncertainty. The analyst and the data user should review the note in Sec. 7.5.1.2.

If the calibration does not meet the 15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared.

7.7.1 Verification of linear calibrations

Calibration verification for linear calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the procedure specified in the determinative method.

$$\% \text{ Drift} = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

where the calculated concentration is determined using the mean calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{CF_v - \overline{CF}}{\overline{CF}} \times 100 \qquad \text{or} \qquad = \frac{RF_v - \overline{RF}}{\overline{RF}} \times 100$$

where CF_v and RF_v are the calibration factor and the response factor (whichever applies) from the analysis of the verification standard, and $\overline{CF}$ and $\overline{RF}$ are the mean calibration factor and mean response factor from the initial calibration. Except where superseded in certain determinative methods, the % difference or % drift calculated for the calibration verification standard must be within ±15% for each analyte, or averaged across all analytes (see Sec 7.7), before any sample analyses may take place.

7.7.2 Verification of a non-linear calibration

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Sec. 7.7.1, above. Except where superseded in certain determinative methods, the % drift calculated for the calibration verification standard must be within ±15% for each analyte, or averaged across all analytes (see Sec 7.7), before any sample analyses may take place. It may also be appropriate to employ two standards at different concentrations to verify the calibration. In this instance, one standard should be near the inflection point in the curve. The choice of specific standards and concentrations is generally a method- or project-specific consideration.

7.7.3 Regardless of whether a linear or non-linear calibration model is used, if either the percent drift or percent difference criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications in Sec. 7.5 and those in the determinative method. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance (see Sec. 7.11), and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration must be performed.

7.7.4 All target analytes and surrogates, including those reported as non-detects, must be included in a periodic calibration for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met. The frequency of this periodic calibration is project-, method-, and analyte-specific.

7.7.5 Calibration verification may be performed using both high and low concentration standards from time to time. This is particularly true when the ECD or ELCD is used. These detectors drift and are not as stable as FID or FPD, and periodic use of the high and low concentration standards serves as a further check on the initial calibration. The concentrations of these standards should generally reflect those observed in samples.

7.7.6 Additional analyses of the mid-point calibration verification standard during a 12-hour analytical shift are strongly recommended for methods involving external standard calibration. If the response for any analyte varies from the average initial calibration response by more than 15% in these additional determinations, corrective action (see Sec. 7.11) may be necessary to restore the system or a new calibration curve should be prepared for that compound.

The frequency of verification necessary to ensure accurate measurement is dependent on the detector and the sample matrix. Very sensitive detectors that operate in the sub-nanogram range are generally more susceptible to changes in response caused by column contamination and sample carryover. Therefore, more frequent verification of calibration (i.e., after every 10 samples) may be necessary for the electron capture, electrochemical conductivity, photoionization, and fluorescence detectors.

Sec. 8.2.2 specifies that samples analyzed using external standards must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). Therefore, more frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis. The results from these bracketing standards must meet the calibration verification criteria in Sec. 7.7.1 and 7.7.2 and the retention time criteria in Sec. 7.6. However, if the standard analyzed <u>after</u> a group of samples exhibits a response for an analyte that is <u>above</u> the acceptance limit, i.e., >15%, and the analyte was <u>not</u> detected in any of the previous samples during the analytical shift, then the sample extracts do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present.

7.7.7 Any method blanks specified in the preparative methods (Methods 3500 and 3600) may be run immediately after the calibration verification analyses to confirm that laboratory contamination does not cause false positive results, or at any other time during the analytical shift. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

7.8 Chromatographic analysis of samples

7.8.1 Introduction of sample extracts into the chromatograph varies, depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap techniques (Method 5030, water and Method 5035, soils). However, the use of Method 5021, or another headspace technique, may be advisable for screening volatiles in some sample matrices to prevent overloading and contamination of the purge-and-trap system. Semivolatile and non-volatile analytes are introduced by direct or split/splitless injection.

7.8.1.1 Manual injection (GC)

Inject 1-5 µL of the sample extract. The use of the solvent flush technique is necessary for packed columns. Use 1-2 µL of sample extract for capillary columns.

7.8.1.2 Automated injection (GC)

Using automated injection, smaller volumes (i.e., 1 µL) may be injected, and the solvent flush technique is not necessary. Laboratories should demonstrate that the injection volume is reproducible.

7.8.1.3 Purge-and-trap

Refer to Methods 5000, 5030, or 5035 for details.

7.8.1.4 Manual injection (HPLC)

Inject 10-100 µL. This is generally accomplished by over-filling the injection loop of a zero-dead-volume injector. Larger volumes may be injected if better sensitivity is required, however, chromatographic performance may be affected.

7.8.1.5 Automated injection (HPLC)

Inject 10-100 µL. Laboratories should demonstrate that the injection volume is reproducible. Larger volumes may be injected if greater sensitivity is required, however, chromatographic performance may be adversely affected.

7.8.2 All analyses, including field samples, matrix spike samples, matrix spike duplicates, laboratory control samples, method blanks, and other QC samples, are performed during an analysis sequence. The sequence begins with instrument calibration, which is followed by the analysis of sample extracts. Verification of calibration and retention times is necessary no less than once every 12-hour analytical shift. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. As noted in Secs. 7.7.6 and 8.2.2, when employing external standard calibration, it is necessary that a calibration verification standard be run at the end of the sequence to bracket the sample analyses. Acceptance criteria for the initial calibration and calibration verification are described in Secs. 7.5 - 7.7.

Analysis of calibration verification standards every 10 samples is strongly recommended, especially for the highly sensitive GC and HPLC detectors that detect sub-nanogram concentrations. Frequent analysis of calibration verification standards helps ensure that chromatographic systems are performing acceptably and that false positives, false negatives and poor quantitations are minimized. Samples analyzed using external standard calibration

84

must be bracketed by the analyses of calibration standards that meet the QC limits for verification of calibration and retention times. If criteria are exceeded, corrective action must be taken (see Sec. 7.11) to restore the system and/or a new calibration curve must be prepared for that compound and the samples must be reanalyzed.

Certain methods may also include QC checks on column resolution, analyte degradation, mass calibration, etc., at the beginning of a 12-hour analytical shift.

7.8.3 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Sec. 7.5). If sample response exceeds the limits of the initial calibration range, dilute the extract (or sample) and reanalyze. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, is acceptable, as long as calibration limits are not exceeded. When overlapping peaks cause errors in peak area integration, the use of peak height measurements is recommended.

7.8.4 If chromatographic peaks are masked by the presence of interferences, further sample cleanup is necessary. See Method 3600 for guidance.

7.8.5 When there are a large number of target analytes, it may be difficult to fully resolve these compounds. Examples of chromatograms for the compounds of interest are provided in many determinative methods.

7.9 Compound Identification

Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the composition of samples is not well characterized. Confirmation techniques include analysis on a second column with dissimilar stationary phase, by GC/MS (full scan or SIM) or HPLC/MS (if concentration permits), HPLC/UV data at two different wavelengths, GC or HPLC data from two different detectors, or by other recognized confirmation techniques. For HPLC/UV methods, the ability to generate UV spectra with a diode array detector may provide confirmation data from a single analysis, provided that the laboratory can demonstrate this ability for typical sample extracts (not standards) by comparison to another recognized confirmation technique.

When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc. Confirmation is not required for GC/MS and HPLC/MS methods.

Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses, for instance, when a pesticide known to be produced or used in a facility is found in a sample from that facility.

When using GC/MS for confirmation, ensure that GC/MS analysis is performed on an extract at the appropriate pH for the analyte(s) being confirmed, i.e., do not look for basic analytes in an acidic extract. Certain analytes, especially pesticides, may degrade if extraction conditions were either strongly acidic and/or strongly basic.

Many chromatographic interferences result from co-elution of one or more compounds with the analyte of interest, or may be the result of the presence of a non-analyte peak in the retention time window of an analyte. Such co-elution problems affect quantitation as well as identification, and may

85

result in poor agreement between the quantitative results from two dissimilar columns. Therefore, even when the identification has been confirmed on a dissimilar column, the analyst should evaluate the agreement of the quantitative results on both columns, as described in Sec. 7.10.4.

7.10 Calculations

The calculation of sample results depends on the type of calibration (external or internal standard) and the calibration model employed (linear or non-linear). The following sections describe the calculations used in each instance. Specific determinative methods may contain additional information.

7.10.1 External standard calibration - linear calibration

The concentration of each analyte in the sample is determined by comparing the detector response (peak area or height) to the response for that analyte in the initial calibration. The concentration of an analyte may be calculated as follows, depending on the sample matrix:

7.10.1.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL). For purge-and-trap analysis, V_t is not applicable and therefore is set at 1.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area per ng).

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and therefore is set at 1. If concentration units are used in calculating the calibration factor (see Sec. 7.4.2.1), then V_i is not used in this equation.

V_s = Volume of the aqueous sample extracted or purged in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.10.1.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

96

where A_s, V_t, D, $\overline{CF}$, and V_i are as described in 7.10.1.1, and

W_s = Weight of sample extracted or purged (g). Either the wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

For purge-and-trap analyses where a volume of methanol extract is added to organic-free reagent water and purged, V_t is the total volume of the methanol extract and V_i is the volume of methanol extract that is added to the 5 mL of organic-free reagent water.

7.10.1.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged as shown in Sec. 7.5.2, and the concentration of the analyte is calculated from the area response (y), the slope (a), and the intercept (b). When using this form of linear calibration, it is the laboratory's responsibility to ensure that the calculations take into account the volume or weight of the original sample, the dilution factor (if any), and dry weight (as applicable). One approach to this calculation is to perform the original linear regression using the concentration of the analyte in the final extract volume or the volume purged. The concentration of the analyte in the sample may then be calculated as follows:

$$C_s = \frac{(C_{ex})(V_t)}{(V_s)}$$

where:

C_s = Concentration in the sample
C_{ex} = Concentration in the final extract
V_t = Total volume of the concentrated extract
V_s = Volume of the sample extracted or purged

For solid samples, substitute the weight of the sample, W_s, for V_s.

For purge-and-trap analyses, the concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

7.10.2 Internal standard calibration - linear calibration

The concentration of each analyte in the sample is calculated using the results of the initial calibration, according to one of the following sections, depending on the sample matrix:

7.10.2.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the concentrated sample extract or volume purged in µg/L.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same. For purge-and-trap analysis, V_i is not applicable and is set at 1.

$\overline{RF}$ = Mean response factor from the initial calibration. Unlike calibration factors for external standard calibration, the response factor is dimensionless (see Sec. 7.5).

V_s = Volume of the aqueous sample extracted or purged (mL). If units of liters are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

7.10.2.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s, A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

7.10.2.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged in a fashion similar to that described in Sec. 7.10.1.3.

7.10.3 Calculations for a non-linear calibration curve

When a non-linear curve has been employed, the non-linear model is rearranged to solve for the concentration of the analyte in the extract or purge volume, and the extract concentration is converted to a sample concentration in a fashion similar to that described in Sec. 7.10.1.3.

When non-linear calibrations are employed, it is essential that the laboratory clearly document the calculation of analyte concentrations. Example calculations should be reported that clearly indicate how the instrument response (area) was converted into a sample result.

7.10.4 Comparison between results from different columns or detectors

When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula below.

$$RPD = \frac{| R_1 - R_2 |}{\left(\frac{R_1 + R_2}{2} \right)} \times 100$$

where R_1 and R_2 are the results on the two columns and the vertical bars in the equation above indicate the absolute value of the difference. Therefore, the RPD is always a positive value.

7.10.4.1 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.

7.10.4.2 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. This approach is conservative relative to protection of the environment. The data user should be advised of the disparity between the results on the two columns.

7.11 Suggested chromatographic system maintenance

Corrective measures may involve any one or more of the following remedial actions. This list is by no means comprehensive and analysts should develop expertise in troubleshooting their specific instruments and analytical procedures. The manufacturers of chromatographic instruments, detectors, columns, and accessories generally provide detailed information regarding the proper operation and limiting factors associated with their products. The importance of reading and reviewing this information cannot be over-emphasized.

7.11.1 Capillary GC columns

Routine maintenance may compel the analyst to clean and deactivate the glass injection port insert or replace it with a fresh insert that has been cleaned and deactivated with dichlorodimethylsilane. Cut off 0.5 - 1.0 m of the injector end of the column using a 90° cut. Place ferrule onto the column before cutting.

Exceptional maintenance may compel the analyst to replace gas traps and backflush the column with solvent according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.11.2 Metal (GC) injector body

Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (dichlorodimethylsilane) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.11.3 HPLC columns

Examine the system and check for drips that are indicative of plumbing leaks. Check that tubing connectors are of the shortest possible length to minimize dead volumes and reduce band broadening. Compatible guard columns should be installed to protect analytical columns.

If degradation of resolution or changes in back pressure are observed, the first action should be to replace the guard column if one is installed. Secondly, temporarily reverse the flow through the column to dislodge contamination in the frit with the column disconnected from the detector. If this does not correct the problem, place the analytical column in a vise, remove the inlet compression fitting and examine the column.

Analysts should establish that no void volume has developed, that the column packing has not become contaminated, and that the frit is not clogged. Void volumes can be filled with compatible packing and frits replaced.

Columns must eventually be replaced as the bonding and end-capping groups used to modify the silica are lost with time. Loss of these groups will result in chromatographic tailing and changes in analyte retention times. Retention times may also change because of differences in column temperature or because the composition of the solvent gradient is not completely reproducible.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. The development of in-house QC limits for each method is encouraged, as described in Sec. 8.7. The use of instrument-specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. In general, the following QC requirements pertain to all the determinative methods listed in Sec. 1.1 unless superseded by specific requirements provided in the determinative method.

8.2 Evaluating chromatographic performance

The analyst's expertise in performing chromatography is a critical element in the successful performance of chromatographic methods. Successful generation of data requires selection of suitable preparation and analysis methods and an experienced staff to use these methods.

8.2.1 For each 12-hour period during which analysis is performed, the performance of the entire analytical system should be checked. These checks should be part of a formal quality control program that includes the analysis of blanks, calibration standards, matrix spikes, laboratory control samples and replicate samples, although all of these checks need not be performed during each shift.

8.2.2 Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Therefore, all sample analyses performed using external standard calibration must be bracketed with acceptable calibration verification standards.

8.2.3 In addition to the quantitative measures of comparison described below and in the individual methods, analysts should evaluate chromatograms and instrument operation. Questions that should be asked include:

Do the peaks look normal (Gaussian)?
Is the response obtained comparable to the response from previous calibrations?
Do the column fittings need tightening?
Are non-target peaks present in calibration analyses?
Are contaminants present in the blanks?
Is the injector leaking (e.g., does the GC injector septum need replacing)?
Does the HPLC guard column need replacement?

8.2.4 Significant peak tailing, leaks, changes in detector response and laboratory contamination should be corrected. Tailing problems are generally traceable to active sites on the column, cold spots in a GC, improper choice of HPLC mobile phase, the detector inlet, or leaks in the system.

8.2.5 Recalibration of the instrument must take place when the performance changes to the point that the calibration verification acceptance criteria (Sec. 7.7) cannot be achieved. In addition, significant maintenance activities or hardware changes may also require recalibration. The sections below provide general guidance on the sorts of procedures that may or may not require recalibration.

8.2.5.1 There are various types of instrument maintenance that should <u>not</u> automatically require recalibration of the instrument. Examples include changing: septa; compressed gas cylinders; syringes; moisture, hydrocarbon, or oxygen traps; solvents in an ELCD; purge tubes; PTFE transfer lines; glow plugs; split seals; column fittings; inlets; or filaments. Other procedures include breaking off or changing a guard column or cleaning the inlet. Whenever such procedures are performed, the analyst must demonstrate that the results for a calibration verification standard meet the acceptance criteria in Sec. 7.7. before the analysis of any samples. Otherwise, recalibration is required.

8.2.5.2 In contrast to Sec. 8.2.5.1, some maintenance procedures are so likely to affect the instrument response that recalibration is <u>automatically</u> required, regardless

91

of the ability to meet the calibration verification acceptance criteria. These procedures include: changing, replacing, or reversing the column; recoating the bead in a detector; changing nitrogen tubes in an NPD; changing resins; changing the PID seal or lamp; changing the FID jet; changing the entrance lens, draw out lens, or repeller; cleaning the MS source; changing the electron multiplier, ion source chamber, or injector port. Whenever such procedures are performed, the analyst must perform a new initial calibration that meets the requirement using Sec 7.5. As noted in Sec. 7.6, changing or replacing the column will also require that the retention time windows be redetermined.

8.2.6 The analysis of method blanks is critical to the provision of meaningful sample results. Consult the appropriate 3500 or 5000 series method for the specifics of the preparation of method blanks. The following general guidelines apply to the interpretation of method blank results.

8.2.6.1 Method blanks should be prepared at a frequency of at least 5%, that is, one method blank for each group of up to 20 samples prepared at the same time, by the same procedures. For samples analyzed for volatiles by the purge-and-trap technique, the preparation is equivalent to the analysis. Therefore, one purge-and-trap method blank must be analyzed with each group of up to 20 samples analyzed on the same instrument during the same analytical shift.

8.2.6.2. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments. A solvent blank should be analyzed on all other instruments on which the set of samples were analyzed to demonstrate that the instrument is not contributing contaminants to the samples.

8.2.6.3 Unless otherwise described in a determinative method, the method blank may be analyzed immediately after the calibration verification standard, to ensure that there is no carryover from the standard, or at another point in the analytical shift.

8.2.6.4 When sample extracts are subjected to cleanup procedures, the associated method blank must also be subjected to the same cleanup procedures.

8.2.6.5 As described in Chapter One, the results of the method blank should be:

8.2.6.5.1 Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

8.2.6.5.2 Less than 5% of the regulatory limit associated with an analyte.

8.2.6.5.3 Or less than 5% of the sample result for the same analyte, whichever is greater.

8.2.6.5.4 If the method blank results do not meet the acceptance criteria above, then the laboratory should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

8.2.6.6 The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" is inappropriate for the GC and HPLC methods addressed here, and often leads to negative sample results. If the method blank results do not meet the acceptance criteria in 8.2.6.5 and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

8.2.6.7 Method blanks and/or solvent blanks may also be used to check for contamination by carryover from a high-concentration sample into subsequent samples (see Sec. 3.1). When the analysis of such blanks is not possible, such as when an unattended autosampler is employed, the analyst should review the results for at least the next two samples after the high-concentration sample. If analytes in the high-concentration sample are not present in the subsequent samples, then the lack of carryover has been demonstrated. If there is evidence that carryover may have occurred, then the samples should be reanalyzed.

8.3 Summary of required instrument QC

The following criteria primarily pertain to GC and HPLC methods with non-MS or FTIR detectors, and may be superseded by criteria specified in individual determinative methods (e.g., Methods 8021, 8260, 8270, 8321, 8325, and 8410).

8.3.1 The criteria for linearity of the initial calibration curve is an RSD of $\leq$ 20%.

8.3.2 For non-linear calibration curves, the coefficient of the determination (COD) must be greater than or equal to 0.99 (see Sec. 7.5.2).

8.3.3 Retention time (RT) windows must be established for the identification of target analytes. See Sec. 7.6 for guidance on establishing the absolute RT windows.

8.3.4 The retention times of all analytes in all verification standards must fall within the absolute RT windows. If an analyte falls outside the RT window in a calibration verification standard, new absolute RT windows must be calculated, unless instrument maintenance corrects the problem.

8.3.5 The calibration verification results must be within ± 15% of the response calculated using the initial calibration. If the limit is exceeded, a new standard curve must be prepared unless instrument maintenance corrects the problem.

8.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each combination of sample preparation and determinative methods that it utilizes, by generating data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made.

8.4.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

Preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed in Sec. 8.0 of Methods 3500 and 5000. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or any water miscible solvent) at a concentration such that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.5.1 for information on selecting an appropriate spiking level.

8.4.2 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the aqueous matrix and organic-free sand or soil for the solid matrix.

8.4.3 Preparation of reference samples

8.4.3.1 Volatile organic analytes

Prepare the reference sample by adding 200 µL of the reference sample concentrate (Sec. 8.4.1) to 100 mL of organic-free reagent water. Transfer this solution immediately to a 20- or 25-mL (or four 5-mL) gas-tight syringe(s) when validating water analysis performance by Method 5030. Alternatively, the reference sample concentrate may be injected directly through the barrel of the 5- or 25-mL syringe. See Method 5000 (Sec. 8.0) for guidance on other preparative methods and matrices.

8.4.3.2 Semivolatile and nonvolatile organic analytes

Prepare the reference sample by adding 1.0 mL of the reference sample concentrate (Sec. 8.4.1) to each of four 1-L aliquots of organic-free reagent water. See Method 3500 (Sec. 8.0) for other matrices.

8.4.4 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics or a 5000 series method for volatile organics) and the determinative method (an 8000 series method).

8.4.5 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.4.6 Multiple-laboratory performance data are included in some determinative methods and may be used as guidance in evaluating performance in a single laboratory. Compare s and $\bar{x}$ for each analyte with the corresponding performance data for precision and accuracy given in the performance data table at the end of the determinative method. If s and $\bar{x}$ for all analytes of interest meet the appropriate acceptance criteria, then the system performance is acceptable and analysis of actual samples can begin. If any individual s value exceeds the

precision limit or any individual $\bar{x}$ value falls outside the range for accuracy, then the system performance may be unacceptable for that analyte.

NOTE: The large number of analytes in each of the methods presents a substantial probability that one or more analyte will fail at least one of the performance criteria when all analytes of a given method are determined.

When one or more of the analytes fail at least one of the performance criteria, the analyst should proceed according to Sec. 8.4.6.1 or 8.4.6.2.

8.4.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning at Sec. 8.4.2.

8.4.6.2 Beginning at Sec. 8.4.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning at Sec. 8.4.2.

8.4.7 The performance data in many of the methods are based on single-laboratory performance. As with the multiple-laboratory data, the criteria in those methods may be used as guidance when evaluating laboratory performance. When comparing your laboratory data to performance data developed from single-laboratory data, certain analytes may be outside the limits, however, the majority should be within the acceptance limits.

8.4.8 Even when the determinative method contains performance data (either multiple-laboratory or single-laboratory), the development of in-house acceptance limits is strongly recommended, and may be accomplished using the general considerations described in Sec. 8.7.

8.4.9 In the absence of recommended acceptance criteria for the initial demonstration of proficiency, the laboratory should use recoveries of 70 - 130% as guidance in evaluating the results. Given that the initial demonstration is performed in a clean matrix, the average recoveries of analyte from the four replicates should generally fall within this range. In addition, since the laboratory will repeat the initial demonstration of proficiency whenever new staff are trained or significant changes in instrumentation are made, the resulting data should be used to develop in-house acceptance criteria, as described in Sec. 8.7.

8.5 Matrix spike and laboratory control samples

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this will include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate (MS/MSD) pair with each batch of up to 20 samples of the same matrix processed together (see Chapter One). If samples are expected to contain the target analytes of concern, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample as an alternative to the MS/MSD pair (see Sec. 8.5.3).

In the case of purge-and-trap methods, the MS/MSD, or MS and duplicate samples, should be prepared and analyzed concurrently with the samples. In the case of samples that involve an extraction procedure, the MS/MSD, or MS and duplicate samples, should be extracted with the batch of samples but may be analyzed at any time.

In addition, a Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

The concentration of the matrix spike sample and/or the LCS should be determined as described in Secs. 8.5.1 and 8.5.2.

8.5.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit or action level, the spike should be at or below the limit, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

If historical data are not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.5.2 If the concentration of a specific analyte in a sample is <u>not</u> being checked against a limit specific to that analyte, then the analyst may spike the sample at the same concentration as the reference sample (Sec. 8.4.1), at 20 times the estimated quantitation limit (EQL) in the matrix of interest, or at a concentration near the middle of the calibration range. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.5.3 To develop precision and accuracy data for each of the spiked compounds, the analyst has two choices: analyze the original sample, and an MS/MSD pair; or analyze the original sample, a duplicate sample, and one spiked sample. If samples are not expected to contain the target analytes of concern, then the laboratory may use a matrix spike and matrix spike duplicate pair. If samples are expected to contain the target analytes of concern, then the laboratory may use one matrix spike and a duplicate analysis of an unspiked field sample as an alternative to the MS/MSD pair.

Begin by analyzing one sample aliquot to determine the background concentration of each analyte. Prepare a matrix spike concentrate according to one of the options specified in Sec. 8.5.1 or 8.5.2.

Prepare a matrix spike sample by adding the appropriate volume of the matrix spike concentrate to another aliquot of the sample to yield the desired concentration (see Secs. 8.5.1 and 8.5.2). Prepare a matrix spike duplicate sample from a third aliquot of the sample.

Analyze the MS/MSD samples using the same procedures employed for the original sample, and calculate the concentration of each analyte in the matrix spike and matrix spike duplicate. Likewise, analyze the LCS samples using the same procedures employed for the original sample, and calculate the concentration of each analyte in the LCS.

8.5.3.1 Calculation of recovery

Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of

96

analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate (if performed) and LCS according to the following formula.

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} \times 100$$

where:

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot (use 0 for the LCS)
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS)

8.5.3.2 Calculation of precision

Precision is estimated from the relative percent difference (RPD) of the concentrations (*not* the recoveries) measured for matrix spike/matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. Calculate the RPD according to the formula below.

$$\text{RPD} = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:

C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

8.5.4 Recommended QC acceptance criteria for matrix spike samples and LCS

It is necessary for the laboratory to develop single-laboratory performance data for accuracy and precision in the matrices of interest (see Sec. 8.7). In addition, laboratories should monitor method performance in each matrix, through the use of control charts and other techniques.

Many methods may not contain recommended acceptance criteria for LCS results. The laboratory should use 70 - 130% as interim acceptance criteria for recoveries of spiked analytes, until in-house LCS limits are developed (see Sec. 8.7). Where in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits, as the LCS is prepared in a clean matrix.

Even where the determinative methods provide performance criteria for matrix spikes and LCS, it is necessary for laboratories to develop in-house performance criteria and compare them to those in the methods. The development of in-house performance criteria is discussed in Sec. 8.7.

As a general rule, the recoveries of most compounds spiked into samples should fall within the range of 70 - 130%, and this range should be used as a guide in evaluating in-house performance. However, as described in Sec. 8.5.4.1, matrix spike recoveries and LCS recoveries may be affected by the spike-to-background ratio.

Where methods do contain performance data for the matrix of interest, use Secs. 8.5.4.1 and 8.5.4.2 as guidance in evaluating data generated by the laboratory.

8.5.4.1 When multiple-laboratory performance data for the matrix of interest are provided in the determinative method, compare the percent recovery (%R) for each analyte in a water sample with the performance data. Given that such performance criteria were developed from multi-laboratory data, they should be met in almost all laboratories. See Sec. 8.7.10 for more information on comparisons between limits. The performance data include an allowance for error in measurement of both the background and spike concentrations, and assume a spike-to-background ratio of 5:1. If spiking was performed at a concentration lower than that used for the reference sample (Sec. 8.4), the analyst may use either the performance data presented in the tables, or laboratory-generated QC acceptance criteria calculated for the specific spike concentration, provided that they meet the project-specific data quality objectives.

8.5.4.2 When the sample was spiked at a spike-to-background ratio other than 5:1, the laboratory should calculate acceptance criteria for the recovery of an analyte. Some determinative methods contain a table entitled "Method Accuracy and Precision as a Function of Concentration" which gives equations for calculating accuracy and precision as a function of the spiking concentration. These equations may be used as guidance in establishing the acceptance criteria for matrix spike samples.

The equations are the result of linear regression analyses of the performance data from a multiple-laboratory study. The equations are of the form:

$$\text{Accuracy} = x' = (a)C + b$$

where a is a number less than 1.0, b is a value greater than 0.0, and C is the test concentration (or true value).

Performance criteria for accuracy may be calculated from these equations by substituting the spiking concentration used by the laboratory in place of "C," and using the values of a and b given in the table for each analyte.

Performance criteria for precision are calculated in a similar fashion, using the a and b values for precision given in the table for each analyte. Precision may be calculated as single analyst precision, or overall precision, using the appropriate equations from the table. An acceptable performance range may be calculated for each analyte as:

$$\text{Acceptance range } (\mu g/L) = \text{Accuracy} \pm (2.44)\text{Precision}$$

8.5.5 Also compare the recovery data from the matrix spike with the LCS data (use the average recovery if a matrix spike and matrix spike duplicate were analyzed). If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Sec. 8.6) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems then problems with the recoveries of either matrix spikes or surrogates alone.

98

8.6 Surrogate recoveries

8.6.1 It is necessary that the laboratory evaluate surrogate recovery data from individual samples versus surrogate recovery limits developed in the laboratory. The general considerations for developing in-house acceptance criteria for surrogate recoveries are described in Sec. 8.7.

8.6.2 Surrogate recovery is calculated as:

$$\text{Recovery (\%)} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) added}} \times 100$$

If recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

8.6.2.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

8.6.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

8.6.2.3 Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries can not be measured. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

8.6.2.4 If no instrument problem is found, the sample should be re-extracted and re-analyzed (or re-analyze the sample for volatiles).

8.6.2.5 If, upon re-analysis (in either 8.6.2.2 or 8.6.2.4), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

8.7 Generating performance criteria for matrix spike recoveries, surrogate recoveries, initial demonstration of proficiency, and laboratory control sample recoveries

It is essential that laboratories calculate in-house performance criteria for matrix spike recoveries and surrogate recoveries. It may also be useful to calculate such in-house criteria for laboratory control sample (LCS) recoveries and for the initial demonstration of proficiency when experience indicates that the criteria recommended in specific methods are frequently missed for some analytes or matrices. The development of in-house performance criteria and the use of control charts or similar procedures to track laboratory performance cannot be over-emphasized. Many data systems and commercially-available software packages support the use of control charts.

The procedures for the calculation of in-house performance criteria for matrix spike recovery and surrogate recovery are provided below. These procedures may also be applied to the development of in-house criteria for the initial demonstration of proficiency and for LCS recoveries.

8.7.1 For each matrix spike sample analyzed, calculate the percent recovery of each matrix spike compound added to the sample, in a fashion similar to that described in Sec. 8.5.3.3. For each field sample, calculate the percent recovery of each surrogate as described in Sec. 8.6.

8.7.2 Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after analysis of 15-20 matrix spike samples of the same matrix, using the equations in Sec. 7.5.1, as guidance. Calculate the average percent recovery (p) and the standard deviation (s) for each of the surrogates after analysis of 15-20 field samples of the same matrix, in a similar fashion.

8.7.3 After the analysis of 15-20 matrix spike samples of a particular matrix (or matrix spike limits) or 15-20 field samples (for surrogate limits), calculate upper and lower control limit for each matrix spike or surrogate compound:

Upper control limit = p + 3s
Lower control limit = p - 3s

Calculate warning limits as:

Upper warning limit = p + 2s
Lower warning limit = p - 2s

For laboratories employing statistical software to determine these limits, the control limits approximate a 99% confidence interval around the mean recovery, while the warning limits approximate a 95% confidence interval.

8.7.4 Any matrix spike, surrogate, or LCS results outside of the control limits require evaluation by the laboratory. Such actions should begin with a comparison of the results from the samples or matrix spike samples with the LCS results. If the recoveries of the analytes in the LCS are outside of the control limits, then the problem may lie with the application of the extraction and/or cleanup procedures applied to the sample matrix or with the chromatographic procedures. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots, including new matrix spike samples and LCS.

When the LCS results are within the control limits, the problem may either be related to the specific sample matrix or to an inappropriate choice of extraction, cleanup, and determinative methods. If the results are to be used for regulatory compliance monitoring, then the analyst must take steps to demonstrate that the analytes of concern can be determined in the sample matrix at the levels of interest.

The laboratory may use the warning limits to guide internal evaluations of method performance, track the performance of individual analysts, and monitor the effects of changes to the analytical procedures. Repeated results outside of the warning limits should lead to further evaluation.

8.7.5 Once established, control limits and warning limits for matrix spike compounds should be reviewed after every 10-20 matrix spike samples of the same matrix, and updated at least semi-annually. Control limits and warning limits for surrogates should be reviewed after every 20-30 field samples of the same matrix, and should be updated at least semi-annually. The laboratory should track trends in both performance and in the control limits themselves. The control and warning limits used to evaluate the sample results should be those in place at the time that the sample was analyzed. Once limits are updated, those limits should apply to all subsequent analyses of new samples.

8.7.6 For methods and matrices with very limited data (e.g., unusual matrices not analyzed often), interim limits should be established using available data or by analogy to similar methods or matrices.

8.7.7 Results used to develop acceptance criteria should meet all other QC criteria associated with the determinative method. For instance, matrix spike recoveries from a GC/MS procedure should be generated from samples analyzed after a valid GC/MS tune and a valid initial calibration that includes the matrix spike compounds. Another example is that analytes in GC or HPLC methods must fall within the established retention time windows in order to be used to develop acceptance criteria.

8.7.8 Laboratories are advised to consider the effects of the spiking concentration on matrix spike performance criteria, and to avoid censoring of data. As noted in Sec. 8.5.4, the acceptance criteria for matrix spike recovery and precision are often a function of the spike concentration used. Therefore, use caution when pooling matrix spike/matrix spike duplicate data for use in establishing acceptance criteria. Not only should the results all be from the same (or very similar) matrix, but the spiking levels should also be approximately the same (within a factor of 2).

Similarly, the matrix spike and surrogate results should all be generated using the same set of extraction, cleanup, and analysis techniques. For example, do not mix results from solid samples extracted by ultrasonic extraction with those extracted by Soxhlet.

8.7.9 Another common error in developing acceptance criteria is to discard data that do not meet a preconceived notion of acceptable performance. This results in a censored data set, which, when used to develop acceptance criteria, will lead to unrealistically narrow criteria. Remember that for a 95% confidence interval, 1 out of every 20 observations likely will still fall outside the limits.

While professional judgement is important in evaluating data to be used to develop acceptance criteria, do not discard specific results simply because they do not meet one's expectations. Rather, employ a statistical test for outlier values, or at least calculate the acceptance limits both with and without the results that are considered suspect and observe the effect of deleting suspect data.

8.7.10 In-house QC limits must be examined for reasonableness. It is not EPA's intent to legitimize poor recoveries that are due to the incorrect choice of methods or spiking levels. In-house limits also should be compared with the objectives of specific analyses. For example, recovery limits (for surrogates, MS, MSD, LCS, etc.) that include allowance for a relatively high positive bias (e.g., 70 - 170%) may be appropriate for determining that an analyte is <u>not</u> present in a sample. However, they would be less appropriate for the analysis of samples near but below a regulatory limit, because of the potential high bias.

It may be useful to compare QC limits generated in the laboratory to the performance data that may be listed in specific determinative methods. However, the analyst must be aware that performance data generated from multiple-laboratory data tend to be significantly wider than those generated from single-laboratory data. In addition, comparisons between in-house limits and those from other sources should generally focus more on the accuracy (recovery) limits of single analyses rather than the precision limits. For example, a mean recovery closer to 100% is generally preferred, even if the ±3 standard deviation range is slightly wider, because those limits indicate that the result is likely closer to the "true value." In contrast, the precision range provides an indication of the results that might be expected from repeated analyses of the same sample.

8.8 It is recommended that the laboratory adopt additional quality assurance practices for use with these methods. The specific practices that are most productive depend upon the needs of the laboratory, the nature of the samples, and project-specific requirements. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer (selected ion monitoring or full scan) must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the SW-846 analytical methods generally were obtained using organic-free reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. See Chapter One for more guidance on determination of laboratory-specific MDLs.

9.2 Refer to the determinative methods for method performance information.

10.0 REFERENCES

For further information regarding these methods, review Methods 3500, 3600, 5000, and Chapter One.

102

PART 4

EcoTest Changes and Selected Options

APPENDIX A
MDL WATER

Analyte	MDL ug/L
N-Nitrosodimethylamine	0.26
Pyridine	0.28
Phenol	0.32
aniline	0.91
Bis(2-chloroethyl)ether	0.92
2 Chlorophenol	0.22
1,3 Dichlorobenzene	0.50
1,4 Dichlorobenzene	0.52
benzyl alcohol	0.38
1,2 Dichlorobenzene	0.56
2-Methylphenol	0.46
Bis(2-chloroisopropyl)ether	0.67
4-Methylphenol	0.25
N-nitroso-di-n-propylamine	0.67
Hexachloroethane	0.52
Nitrobenzene	0.69
Isophorone	0.75
2,4 Dimethylphenol	0.31
2 Nitrophenol	0.22
Bis(2-chloroethoxy)methane	0.82
2,4 Dichlorophenol	0.28
1,2,4 Trichlorobenzene	0.63
Naphthalene	0.66
4-Chloroaniline	0.74
Hexachlorobutadiene	0.67
4-chloro-3-methylphenol	0.20
2-Methylnaphthalene	0.72
2-Nitroaniline	0.62
Hexachlorocyclopentadiene	1.70
2,4,6 Trichlorophenol	0.26
2,4,5 Trichlorophenol	0.24
2 Chloronaphthalene	0.77
Dimethylphthalate	0.65
2,6 Dinitrotoluene	0.78
Acenaphthylene	0.76
3-Nitroaniline	0.39
Acenaphthene	0.78
2,4 Dinitrophenol	0.18
4 Nitrophenol	0.18
Dibenzofuran	0.81
2,4 Dinitrotoluene	0.62
Diethylphthalate	0.90
4 Chlorophenylphenyl ether	0.90
Fluorene	0.85
4-Nitroaniline	0.68
4,6 Dinitro-2-methylphenol	0.21
N-Nitrosodiphenylamine	0.94
1,2 Diphenylhydrazine(azo)	0.88
4 Bromophenylphenyl ether	0.95
Hexachlorobenzene	0.97
Pentachlorophenol	0.27
Phenanthrene	0.95
Anthracene	0.96
Carbazole	0.83
Di-n-butylphthalate	0.95
Fluoranthene	0.92
Benzidine	7.91
Pyrene	0.88
Butylbenzylphthalate	0.85
Bis(2-ethylhexyl)phthalate	0.64
Benzo(a)anthracene	0.79
Chrysene	0.77
3,3' Dichlorobenzidine	7.05
Di-n-octyl phthalate	0.86
Benzo(b)fluoranthene	0.93
Benzo(k)fluoranthene	0.92
Benzo(a)pyrene	0.92
Dibenzo(a,h)anthracene	0.73
Indeno(1,2,3-cd)pyrene	0.79
Benzo(g,h,i)perylene	0.76

APPENDIX A
MDL SOIL

Analyte	MDL ug/Kg
N-Nitrosodimethylamine	0.58
Pyridine	0.39
Phenol	0.72
aniline	0.74
Bis(2-chloroethyl)ether	0.58
2 Chlorophenol	0.54
1,3 Dichlorobenzene	0.30
1,4 Dichlorobenzene	0.33
benzyl alcohol	0.76
1,2 Dichlorobenzene	0.46
2-Methylphenol	0.86
Bis(2-chloroisopropyl)ether	0.88
4-Methylphenol	0.69
N-nitroso-di-n-propylamine	0.49
Hexachloroethane	0.42
Nitrobenzene	0.48
Isophorone	0.56
2,4 Dimethylphenol	0.82
2 Nitrophenol	0.73
Bis(2-chloroethoxy)methane	0.87
2,4 Dichlorophenol	0.53
1,2,4 Trichlorobenzene	0.42
Naphthalene	0.45
4-Chloroaniline	0.54
Hexachlorobutadiene	0.84
4-chloro-3-methylphenol	0.32
2-Methylnaphthalene	0.48
2-Nitroaniline	0.33
Hexachlorocyclopentadiene	1.50
2,4,6 Trichlorophenol	0.43
2,4,5 Trichlorophenol	0.29
2 Chloronaphthalene	0.88
Dimethylphthalate	0.27
2,6 Dinitrotoluene	0.41
Acenaphthylene	0.62
3-Nitroaniline	0.27
Acenaphthene	0.72
2,4 Dinitrophenol	1.80
4 Nitrophenol	1.80
Dibenzofuran	0.55
2,4 Dinitrotoluene	0.23
Diethylphthalate	0.24
4 Chlorophenylphenyl ether	0.53
Fluorene	0.45
4-Nitroaniline	0.50
4,6 Dinitro-2-methylphenol	0.42
N-Nitrosodiphenylamine	0.37
1,2 Diphenylhydrazine(azo)	0.30
4 Bromophenylphenyl ether	0.40
Hexachlorobenzene	0.30
Pentachlorophenol	0.20
Phenanthrene	0.28
Anthracene	0.35
Carbazole	0.41
Di-n-butylphthalate	0.21
Fluoranthene	0.30
Benzidine	1.04
Pyrene	0.28
Butylbenzylphthalate	0.20
Bis(2-ethylhexyl)phthalate	0.31
Benzo(a)anthracene	0.21
Chrysene	0.30
3,3' Dichlorobenzidine	1.83
Di-n-octyl phthalate	0.21
Benzo(b)fluoranthene	0.31
Benzo(k)fluoranthene	0.33
Benzo(a)pyrene	0.25
Dibenzo(a,h)anthracene	0.44
Indeno(1,2,3-cd)pyrene	0.28
Benzo(g,h,i)perylene	0.34

APPENDIX B
Laboratory Reporting Limits

Analyte	ug/L water	ug/Kg soil
N-Nitrosodimethylamine	<1	<1
Pyridine	<1	<1
Phenol	<1	<1
aniline	<10	<10
Bis(2-chloroethyl)ether	<1	<1
2 Chlorophenol	<1	<1
1,3 Dichlorobenzene	<1	<1
1,4 Dichlorobenzene	<1	<1
benzyl alcohol	<10	<10
1,2 Dichlorobenzene	<1	<1
2-Methylphenol	<1	<1
Bis(2-chloroisopropyl)ether	<1	<1
4-Methylphenol	<1	<1
N-nitroso-di-n-propylamine	<1	<1
Hexachloroethane	<1	<1
Nitrobenzene	<1	<1
Isophorone	<1	<1
2,4 Dimethylphenol	<1	<1
2 Nitrophenol	<1	<1
benzoic acid	<10	<10
Bis(2-chloroethoxy)methane	<1	<1
2,4 Dichlorophenol	<1	<1
1,2,4 Trichlorobenzene	<1	<1
Naphthalene	<1	<1
4-Chloroaniline	<1	<1
Hexachlorobutadiene	<1	<1
4-chloro-3-methylphenol	<1	<1
2-Methylnaphthalene	<1	<1
2-Nitroaniline	<1	<1
Hexachlorocyclopentadiene	<10	<10
2,4,6 Trichlorophenol	<1	<1
2,4,5 Trichlorophenol	<1	<1
2 Chloronaphthalene	<1	<1
Dimethylphthalate	<1	<1
2,6 Dinitrotoluene	<1	<1
Acenaphthylene	<1	<1
3-Nitroaniline	<1	<1
Acenaphthene	<1	<1
2,4 Dinitrophenol	<10	<10
4 Nitrophenol	<10	<10
Dibenzofuran	<1	<1
2,4 Dinitrotoluene	<1	<1
Diethylphthalate	<1	<1
4 Chlorophenylphenyl ether	<1	<1
Fluorene	<1	<1
4-Nitroaniline	<1	<1
4,6 Dinitro-2-methylphenol	<10	<10
N-Nitrosodiphenylamine	<1	<1
1,2 Diphenylhydrazine(azo)	<1	<1
4 Bromophenylphenyl ether	<1	<1
Hexachlorobenzene	<1	<1
Pentachlorophenol	<10	<10
Phenanthrene	<1	<1
Anthracene	<1	<1
Carbazole	<1	<1
Di-n-butylphthalate	<1	<1
Fluoranthene	<1	<1
Benzidine	<10	<10
Pyrene	<1	<1
Butylbenzylphthalate	<1	<1
Bis(2-ethylhexyl)phthalate	<1	<1
Benzo(a)anthracene	<1	<1
Chrysene	<1	<1
3,3' Dichlorobenzidine	<10	<10
Di-n-octyl phthalate	<1	<1
Benzo(b)fluoranthene	<1	<1
Benzo(k)fluoranthene	<1	<1
Benzo(a)pyrene	<1	<1
Dibenzo(a,h)anthracene	<1	<1
Indeno(1,2,3-cd)pyrene	<1	<1
Benzo(g,h,i)perylene	<1	<1

APPENDIX C
LIST OF ANALYTES

Analyte
N-Nitrosodimethylamine
Pyridine
Phenol
aniline
Bis(2-chloroethyl)ether
2 Chlorophenol
1,3 Dichlorobenzene
1,4 Dichlorobenzene
benzyl alcohol
1,2 Dichlorobenzene
2-Methylphenol
Bis(2-chloroisopropyl)ether
4-Methylphenol
N-nitroso-di-n-propylamine
Hexachloroethane
Nitrobenzene
Isophorone
2,4 Dimethylphenol
2 Nitrophenol
Bis(2-chloroethoxy)methane
2,4 Dichlorophenol
1,2,4 Trichlorobenzene
Naphthalene
4-Chloroaniline
Hexachlorobutadiene
4-chloro-3-methylphenol
2-Methylnaphthalene
2-Nitroaniline
Hexachlorocyclopentadiene
2,4,6 Trichlorophenol
2,4,5 Trichlorophenol
2 Chloronaphthalene
Dimethylphthalate
2,6 Dinitrotoluene
Acenaphthylene
3-Nitroaniline
Acenaphthene
2,4 Dinitrophenol
4 Nitrophenol
Dibenzofuran
2,4 Dinitrotoluene
Diethylphthalate
4 Chlorophenylphenyl ether
Fluorene
4-Nitroaniline
4,6 Dinitro-2-methylphenol
N-Nitrosodiphenylamine
1,2 Diphenylhydrazine(azo)
4 Bromophenylphenyl ether
Hexachlorobenzene
Pentachlorophenol
Phenanthrene
Anthracene
Carbazole
Di-n-butylphthalate
Fluoranthene
Benzidine
Pyrene
Butylbenzylphthalate
Bis(2-ethylhexyl)phthalate
Benzo(a)anthracene
Chrysene
3,3' Dichlorobenzidine
Di-n-octyl phthalate
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Indeno(1,2,3-cd)pyrene
Benzo(g,h,i)perylene

Appendix D

SAFETY :

< Safety glasses are reguired at all times for all lab procedures.
< Wear lab coat when handling corrosives or when heating or distilling.
< Use particular care with flammables to avoid sparks, flames or spills.
< Transport solvents in protective carrying containers.
< Do not allow solvent, acid, ammonium hydroxide, or other chemical vapors to escape from hood into lab air.
< Consult "Chemical Hygene Plan" for general safety measures.

WASTE DISPOSAL :

< Old standards and sample extracts are put into covered containers and stored in the storage room in building one. When a significant amount of old extracts are collected, Tom Powell is notified, and will arrange to have a licensed waste disposal company come and cart the waste away. Consult "Waste Disposal" document for general disposal procedures.

< Extracted SAMPLES are put into a large container (located under hood in building 3). It is than purged with air for an extended period of time to evaporate any residual solvents that may be left in the sample. The sample is then disposed of under hood to sewer. Hood is left on at all times.

Used glass wool and sodium sulfate are emptied into container under hood and left for an extended period of time to allow residual solvents to evaporate. Glass wool and sodium sulfate are than discarded to the dumpster.

Any other miscellaneous things (i.e. empty sample bottles or used glassware) that are used are left under hood for residual solvents to evaporate and than are eithier washed, baked and put away or thrown out into the dumpster.

Whereever mercury is used those extracts end up in store room in bldg. 1 in covered container. When a significant amount of extracts are collected Tom Powell is then notified who will then arrange to have a liscensed waste disposal company come and cart the waste away.

< Consult "Waste Disposal" document for general disposal procedures.

APPENDIX E

EQUIPMENT AND SUPPLIES

Instruments :
Hewlett Packard/Agilent Gas Chromatograph
Hewlett Packard/Agilent Automtatic Sampler (tray and injector tower)
Hewlett Packard/Agilent Series Mass Selective Detector
Edwards Rough Pump
Windows run PC
HP laserkjet Printers

Gases :
Helium

Consumables :
Restek 4mm split liner w/ Wool, p#20783
Restek 11mm thermolite septa, p#20365
Restek column, XTI-5, p#12253
Restek column, RTX-5Sil MS, p#12723
Supelco silicone O-rings, 1/4", p#20407
Agilent filaments, p#05990-60084
Agilent filaments, p#05971-60140
Also use various other Consumable and Supply Catalogs

APPENDIX F
Reagents and Standard Solution Preparation
8270C

This SOP is applicable to the preparation of standard solutions for Semivolatile analysis.

Purchased working stock standards (Supelco) for Base/Neutral and Acid extractable compounds are 2 mg/mL:

A: TCL Base Neutral mix in methylene chloride
B: TCL Hazard Substance mix in methylene chloride
C: TCL Phenols mix in methylene chloride
D: TCL Polynuclear Aromatic Hydrocarbons mix in methylene chloride/benzene(50:50)
E: TCL Benzidines mix in methanol

Purchased working standard (Chem Service) for Pyridine is 99% pure

F: Working Standard for Pyridine
40uL up to 20mL of methylene chloride = 2mg/mL

Purchased Quality Control working stock standards (Cresent Chemicals) for Base/Neutral and Acid extractable compounds are 2 mg/mL:

G: CLP Base Neutral 1 mix in methylene chloride
H: CLP Base Neutral 2 mix in methylene chloride
I:CLP Polynuclear Aromatic Hydrocarbons mix in methylene chloride/benzene(50:50)
J: Semivlatile mix 4 with pyridine in methylene chloride
K: Phenols mix in methylene chloride
L: CLP Toxic Substance mix 1 in methylene chloride
M: Benzidines mix in methanol

Purchased working surrogates and internal standards (Cresent Chemicals) are as follows:

N: Base/Neutral surrogate standard in methylene chloride, 1 mg/mL
2-fluorobiphenyl, nitrobenzene-d5, and 4-terphenyl-d14
O: Acid Extractable surrogate standard in methanol, 2 mg/mL
2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol
P: Semivolatile internal standard in methylene chloride, 4 mg/mL
acenaphthene-d10, chrysene-d12, 1,4dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10

Purchased Instrument Performance check solution (Cresent Chemicals)

Decafluorotripphenylphosphine(DFTPP) in methylene chloride, 25 mg/mL

Preparation of Intermediate and Working Standards for Base/Neutral and Acid Extractables

From each purchased stock standard (2mg/mL) A, B, C, D, working standard (2mg/mL) for F and from purchased surrogate standards N (1mg/mL) and O (2mg/mL) make the following working standards:

Remove same amount that you will be adding

50uL of A, B, C, D, F, 100uL of N and 50uL of O up to 1mL of methylene chloride = 100ppb
30uL of A, B, C, D, F, 100uL of N and 50uL of O up to 1mL of methylene chloride = 60ppb
25uL of A, B, C, D, F, 100uL of N and 50uL of O up to 1mL of methylene chloride = 50ppb
20uL of A, B, C, D, F, 100uL of N and 50uL of O up to 1mL of methylene chloride = 40ppb

From each purchased stock standard(2mg/mL) A, B, C, D, and working standard(2mg/mL) for F make the following intermediate standard:

100uL stock up to 1mL of methylene chloride = 0.2mg/mL

From the intermediate standard (0.2mg/mL) and the purchased surrogate standards N (1mg/mL) and O (2mg/mL) make the following working standards:

Remove same amount that you will be adding

150uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 30ppb
100uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 20ppb
75uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 15ppb
50uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 10ppb
25uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 5ppb
5uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 1ppb

To all final working standards made in 1mL you must add 10 uL of P, (semivolatile internal standard mix, 4mg/mL)

Preparation of Intermediate and Working Reference Standards for Base/Neutral and Acid Extractables.

From each purchased stock(2mg/mL) standard G, H, I, J, K, and L. From purchased surrogate standards N (1mg/mL) and O (2mg/mL) make the following working standards:

Remove same amount that you will be adding

25uL of G, H, I, J, K, F, 100uL of N and 50uL of O up to 1mL of methylene chloride = 50ppb

From each purchased stock standard(2mg/mL) A, B, C, D, E and working standard(2mg/mL) for F make the following intermediate standard:

100uL stock up to 1mL of methylene chloride = 0.2mg/mL

From the intermediate standard (0.2mg/mL) and the purchased surrogate standards N (1mg/mL) and O (2mg/mL) make the following working standards:

Remove same amount that you will be adding

100uL of the intermediate standard, 100uL of N and 50uL of O up to 1mL of methylene chloride = 20ppb

To all final working reference standards made in 1mL you must add 10 uL of P, (semivolatile internal standard mix, 4mg/mL)

Preparation of Intermediate and Working Standards for Benzidines

From purchased stock standard(2mg/mL) E and from purchased surrogate standards N (1mg/mL) make the following working standards:

Remove same amount that you will be adding

50uL of E and 100uL of N up to 1mL of methylene chloride = 100ppb
30uL of E and 100uL of N up to 1mL of methylene chloride = 60ppb
25uL of E and 100uL of N up to 1mL of methylene chloride = 50ppb
20uL of E and 100uL of N up to 1mL of methylene chloride = 40ppb

From purchased stock standard(2mg/mL) E make the following intermediate standard:

100uL stock up to 1mL of methylene chloride = 0.2mg/mL

From the intermediate standard (0.2mg/mL) and the purchased surrogate standards N (1mg/mL) make the following working standards:

Remove same amount that you will be adding

150uL of the intermediate standard and 100uL of N up to 1mL of methylene chloride = 30ppb
100uL of the intermediate standard and 100uL of N up to 1mL of methylene chloride = 15ppb
75uL of the intermediate standard and 100uL of N up to 1mL of methylene chloride = 15ppb
50uL of the intermediate standard and 100uL of N up to 1mL of methylene chloride = 10ppb

To all final Benzidine working standards made in 1mL you must add 10 uL of P, (semivolatile internal standard mix, 4mg/mL)

Preparation of Intermediate and Working Reference Standards for Benzidines

From purchased stock standard(2mg/mL) M and from purchased surrogate standards N (1mg/mL) make the following working standards:

Remove same amount that you will be adding

25uL of M and 100uL of N up to 1mL of methylene chloride = 50ppb

From purchased stock standard(2mg/mL) M make the following intermediate standard:

100uL stock up to 1mL of methylene chloride = 0.2mg/mL

From the intermediate standard (0.2mg/mL) and the purchased surrogate standards N (1mg/mL) make the following working standards:

Remove same amount that you will be adding

150uL of the intermediate standard and 100uL of N up to 1mL of methylene chloride = 30ppb

To all final Benzidine working Reference standards made in 1mL you must add 10 uL of P, (semivolatile internal standard mix, 4mg/mL)

Preparation of DFTPP:

From purchased Instrument Performance check solution (25mg/mL)

8uL up to 10 mL of methylene chloride = 0.02ug/uL
inject 2.5uL = 50ng on column

Reagents:

Methylene Chloride - High Purity

< Stock Standards are purchased as needed.
< Working Standards are prepared monthly or as needed, whichever is sooner.

APPENDIX G

Quality Control :

1. GC/MS system is tuned to meet DFTPP criteria at the start of each sequence and every 12 hour shift thereafter in that sequence.
2. Initial calibration of the GC/MS system
3. Calibration verification of the GC/MS system at the start of each sequence and every 12 hour shift thereafter in that sequence.
4. Method blank matrix is analyzed with each batch
5. Matrix Spike/Matrix Spike Duplicates are analyzed at a rate of 1 per sample matrix, or 1 for every 20 samples of the same matrix, whichever is greater.
6. Laboratory Control Standard is analyzed with each batch

APPENDIX H

Hewlitt Packard/Agilent Gas Chromatograph Mass Spectrometer

GC/MS Procedure

Daily Start Up:

> Cool oven & inlet area to ambient temperature
> Replace old septa with new 11mm thermolite septa
> Replace old inlet liner with cleaned* 4mm split liner with glass wool
> Reheat oven and inlet area to working temperatures

*Inlet cleaning

> Inspect dirty inlet liners, discard any cracked, broken or extremely dirty liners
> Removed used glass wool
> Wipe inside of liners with methanol
> replace small piece of clean glass wool into center of liner
> Rinse once with 5% DMDCS in toluene (Sylon CT)
> Rinse liners twice with toluene
> Rinse liners three times with methanol
> let liners completely air dry before useing
> store cleaned liners in capped vials

Checking system for air and water after changeing inlet liner and septa:

> set oven to 200 degrees C
> open envtop
> click on:
Tune MS
Manual Tune
File Load Tune Values (dfttp.u)
Adj. Param
Edit Acq Params
> change mass 1, 2 and 3
mass 1 - 69
mass 2 - 18 (28)
mass 3 - 28 (32)
> change window to 2.0
> change scan range to 10-75
> click on:
Adj Param
Edit MS Param
Prof (let prof scans scan a bit to stabilize)
File
Generate Report

DO NOT SAVE FILE AT THIS POINT

Repeat above with ions 69, 28, 32

DO NOT SAVE FILE AT THIS POINT

AIR and WATER (18,28,32) should be less than 10% of 69

> After air and water check reload dftpp.u
> click on:
Execute
Repeat Profile (let a few scans scan to stabilize)
File
Generate report

File can be saved at this time

Make sure the Mass Selective detector is operational

Make sure the Gas Chromatography oven is operational.
>Injector B temperature should read 250 celcius.
>Detector B temperaute should read 320 celcius.

Make sure the Auto injector and tray are functional

Computer start up
>Turn on computer and wait for password screen to appear
>Press OK button to enter windows operating system

TuningMass Selective Detector,

>In Envtop make a new sequence starting with a hexane blank and than a DFTPP
>Run sequence
>If tune passes, continue with run.
>If tune fails, use auto-tune and target-tune software until DFTPP tune passes

Procedure

>run hexane blank to start to stabilize system
>Calibration verification - 3 steps that are performed at the beginning of each each 12 hour shift
1.) 50ng of DFTPP must be analyzed and pass criteria given in Part 3, Table 3
2.) SPCC's of a mid-level standard must meet minimum response factor of 0.050 of the initial calibration
3.) CCC's of a mid-level standard less then or equal to 20% of the initial calibration if CCC's are not included in the list of analytes then all analytes must meet the 20% difference
>All Response Factors are automatically calculated by data analysis software.
>System performance check is performed using all target analytes immediately after initial calibration.
>Matrix spikes/Matrix spike duplicates are spike with 50/100ppb spiking solution before extraction.
>Laboratory Control Sample (LCS) or reference sample is run at a mid level concentration with each batch of samples.

Setting up sequence:

> open envtop
> click on:
Sequence
Edit smp log
> put in data file (date+01 thru ?? depending on runs in sequence)
ie: 06210301
06210302
> put in method:
hexane.M for heaxne blank
Dfteval.M for DFTPP
BA8270.M for all standard and data analysis
> put in sample name:
ie: hexane blank
dftpp 50 ng on column
bna std 20 ppb s03-3
bna smp 233123.01
> click on Sequence
save (save as date ie: 062103)

Running Sequence:

> click on sequence
load and run sequence
Edit Data File Directory: c:\hpchem\2\data*month/year**date
*ie:jun03
**ie:062103
> click on sequence
> save
> click on sequence
> Load and Run Sequence
> Run Sequence

For RTX-5Sil MS column - 30m x 0.25mmID x 0.25um DF

> Mass Range: 35-550 amu
> Scan Time: 1 sec/scan
> Initial temperature: 40 degrees C, hold for 2 minutes
> Temperature program: 40-245 degrees C at 25 degrees C/min
245-330 degrees at 6 degrees C/min
> Final temperature: 330 degrees C, hold until benzo(g,h,i)perylene elutes
> Injector temperature: 250 degrees C
> Source Temperature: 320 degrees C
> Injection volumn: 1.5uL
> Carrier gas: 1mL/minutes

For XTI-5 column - 30m x 0.25mmID x 1.0um DF

> Mass Range: 35-550 amu
> Scan Time: 1 sec/scan
> Initial temperature: 40 degrees C, hold for 2 minutes
> Temperature program: 40-320 degrees C at 11 degrees C/min
> Final temperature: 320 degrees C, hold until benzo(g,h,i)perylene elutes
> Injector temperature: 250 degrees C
> Source Temperature: 320 degrees C
> Injection volumn: 1.5uL
> Carrier gas: 1mL/minutes

APPENDIX I

Acceptance Criteria for Quality Control Measures

< Tuning Calibration

Mass Selective Detector must be properly tuned before analysis using auto tune and target tune software in Envtop.

Mass selective detector is properly tuned when 50 ng DFTPP passes all tune criteria. This is run every 12 hours.

< Initial Calibration

A minimum of 5 points of different concentrations rangeing from 1ppb to 100ppb are run for initial start up of machine, when continuing calibration fails, after a new DFTPP tuning, and after any alterations to the system configuration.

All RSD results for 5 point curve must be less than or equal to 15%.

System Performance check Compounds (SPCC's)
(the SPCC is a standard that falls at the mid-level point of the curve)
must be performed (daily and every 12 hours thereafter as needed)
semivolatile SPCC's are N-nitroso-di-n-propylamine; hexachlorocyclopentadiene;
2,4-dinitrophenol; and 4-nitrophenol
the minimum acceptable average RF is 0.050.
corrective actions must be taken if they are not met
possible problems standard degradation, injection port contamination,
front end column contamination
active sites on column or in system

Calibration check compounds (CCC)
(the CCC is a standard that falls at the mid-level point of the curve)
purpose - evaluate the calibration from the integrity of the system
relative std deviation (RSD) for each target analyte should be less than or equal to 15%,
exception being:

base:	acid:
acenaphthe	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
diphenylamine	phenol
di-n-octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

the above cmps must have a RSD <= to 30%

< Continuing Calibration

A mid level continuing calibration standard is run every 12 hours after a DFTPP tune check

System Performance check Compounds (SPCC's)
(the SPCC is a standard that falls at the mid-level point of the curve)
must be performed (daily and every 12 hours thereafter as needed) to ensure
semivolatile SPCC's are N-nitroso-di-n-propylamine; hexachlorocyclopentadiene;
2,4-dinitrophenol; and 4-nitrophenol
the minimum acceptable average RF is 0.050.
corrective actions must be taken if they are not met
possible problems standard degradation, injection port contamination,
front end column contamination
active sites on column or in system

Calibration check compounds (CCC)
(the CCC is a standard that falls at the mid-level point of the curve)
purpose - evaluate the calibration from the integrity of the system
relative std deviation (RSD) for each CCC should be less than or equal to 20%,
CCC compounds are:

base:	acid:
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
diphenylamine	phenol
di-n-octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

< Matrix Duplicates :

"Limits" are established as follows: Upper warning limits are the average of 15-20 readings, plus 1.96 times the Standard Deviation of those 15-20 readings.
Upper control limits are the average of 15-20 readings, plus 2.58 times the Standard Deviation of those 15-20 readings.

< Matrix Spikes :

"Limits" are established as follows: Upper warning limits are the average of 15-20 readings, plus 1.96 times the Standard Deviation of those 15-20 readings.
Lower warning limits are the average of 15-20 readings, minus 1.96 times the Standard Deviation of those 15-20 readings.
Upper control limits are the average of 15-20 readings, plus 2.58 times the Standard Deviation of those 15-20 readings.
Lower control limits are the average of 15-20 readings, minus 2.58 times the Standard Deviation of those 15-20 readings.

LCS

"Limits" are established as follows: Upper warning limits are the average of 15-20 readings, plus 1.96 times the Standard Deviation of those 15-20 readings.
Lower warning limits are the average of 15-20 readings, minus 1.96 times the Standard Deviation of those 15-20 readings.

Upper control limits are the average of 15-20 readings, plus 2.58 times the Standard Deviation of those 15-20 readings.
Lower control limits are the average of 15-20 readings, minus 2.58 times the Standard Deviation of those 15-20 readings.

APPENDIX L

Corrective action for out-of-control data

Initial Calibration

> If any compound has a greater than 15% RSD, the SPCC's do not meet the minimum RF of 0.050 or the CCC's are greater than 30%, plots of compounds are analyzed to expose any errors in standard preparation or instrument error

> If standard preparation is the cause , a new standard will be run. If machine error is the cause, corrective action is taken and a bew 5 point curve is run.

> Immediately run a Initial Verification Standard (ICVS) to verify the 5 point curve is acceptable

Continuing Cakibration

> If the SPCC's do not meet the minimum RF of 0.050 or the CCC's are greater than 20%, to the initial calibration, then a new CC will be analyzed.

> If SPCC's are unable to meet the minimum RF of 0.050 and the CCC's are uanble to pass 20% deviation from initial calibration curve, a new 5 point curve is run

Matrix Spike/Dup Spike

>If any target compounds in the matrix spike are out of linear Initial Calibration range, the LCS will be used to demonstrate the machine is able to accurately operate.

Laboratory Control Sample (reference)

>The LCS may be used to verify correct operation of the maching if matrix spike/ dup spike have compounds out of linear calibration range.

APPENDIX Q

ICVS Fails Acceptance Criteria

If ICVS for an analyte does not pass, no data for that analyte may be reported unless specifically permitted in Section 3.

CCVS OR LCS Fails

If the LCVS fails for an analyte, the analyst may not report any data for that analyte unless specifically permitted in Section 3.

The Laboratory Director may permit data to be reported for an analyte which has not passed the CCVS or LCS criteria if it can be demonstrated to his satisfaction that the cause of the out of control result was due to loss of sample during unattended operation, or due to contamination of the working LCVS solution, or due to some other problem which would not indicate a loss of calibration of the instrument.

Duplicate/Duplicate Spike (Precision) Sample Fail Acceptance Criteria

If the Duplicate/Duplicate Spike samples do not meet acceptance criteria, the analyst may not report any data for t he effected analytes and samples covered by these duplicates.

The Laboratory Director may permit data to be reported for an analyte which as failed the precision acceptance criteria if it can be demonstrated that the failure was due to:

Loss of sample during unattended operation and there is evidence that there is no diminution in the precision of the analytical system.

Loss of internal standard during unattended operation and there is no indication that the loss effected samples for which the data is to be accepted.

If the failed precision data is based on duplicate spikes and the spike added is insignificant compared to the unspiked concentration, and there is no other indication of loss of precision in the analytical system.

If the failed precision data is based on duplicate spikes and the spiked sample must be diluted in order to be within the linear calibration range of the instrument, and there is no other indication of loss precision in the analytical system.

If the failed precision data is traced to a contamination of the sample during preparation
or analysis and it can be demonstrated that the sample data to be accepted was not effected by the contamination.

If the failed precision data is traced to a non-homogeneous sample or samples.

If Spike Sample (Recovery) Data Is Not Within Acceptance Criteria

If the recovery samples do not meet acceptance criteria the analyst may not report any data for the effected analytes and samples covered by this recovery data.

The Laboratory Director may permit data to be reported for an analyte which has failed the recovery acceptance criteria if it can be demonstrated the failure was due to:

Loss of sample during unattended operation and there is evidence that there is no diminution in the recovery of the analytical system.

Loss of internal standard during unattended operation and there is no indication that the loss effected samples for which the data is to be accepted.

If the failed recovery data is based on a spike sample in which one or more analytes had spikes added which were insignificant compared to the unspiked concentration and there is no other indication of loss of recovery in the analytical system.

If the failed recovery data is based on a spiked sample where the sample must be diluted so that the concentration of the analyte in questions is within the linear calibration range of the instrument, and there is no other indication of loss of recovery in the analytical system.

If the failed recovery data is traced to a contamination in the sample during preparation or analysis and it can be demonstrated that the sample data to be accepted was not effected by the contamination.

If the failed recovery data is traced to a non homogeneous sample.

In all of the above cases if the Laboratory Director decides that data should be accepted he should initial and annotate the data sheets with the reason for accepting the data.

He should also enter the reasons for accepting the data in the "Director's Remarks" section of the electronic record.

ECOTEST LABORATORIES INC.

Sheffield Ave.North Babylon, NY 11703
tel. 631-422-5777, fax 631-422-5770, Email ECOTESTLAB@aol.com

STANDARD OPERATING PROCEDURE

METHOD PUBLISHED BY:

US EPA 160.2: *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA 600/R-03/100, Aug. 93

&

SM20 2540C: APHA, *Standard Method for the Examination of Water and Wastewater,* 20th Ed., 1998.

METHOD NUMBERS: EPA 160.2 & SM20 2540C

METHOD TITLE:

RESIDUE, FILTERABLE (GRAVIMETRIC, DRIED at 180°C) aka TOTAL DISSOLVED SOLIDS

ECOTEST VERSION # 3 DATE: 03/21/08

APPROVING AUTHORITY _____

Thomas Powell

TABLE OF CONTENTS:

PART 2:
INDEX OF 23 NELAC REQUIRED SOP ITEMS

1) Identification of the test method; p1
2) Applicable matrix or matrices; Drinking, ground and surface waters, domestic and industrial wastes. (160.1 - Sec 1.0,) Detection limit; 10 mg/L if 100 mL is evaporated.
4) Scope and application, including components to be analyzed; 160.1 -Sec 1.0
5) Summary of the test method; 160.1 - Sec 2.0
6) Definitions; 160.1- Sec 3.0
7) Interferences; 160.1 - Sec 5.0. 2540-Sec 1
8) Safety; Part 4 -Sec F
9) Equipment and supplies; 160.1 -Sec 6.0
10) Reagents and standards; Part 4 -Sec B-c, (reference sample)
11) Sample collection, preservation, shipment and storage; Part 4-Sec E
12) Quality control; Part 4-Sec B
13) Calibration and standardization; Calibrate Balance daily with 2 weights as per normal balance requirements. Calibrate oven thermometers annually (if glass) quarterly if electronic as per normal thermometer requirements.
14) Procedure; 160.1-Sec 7.0 & Part 4,Sec A
15) Calculations; 160.1-Sec 8.0, & Part 4-Sec A-8
17) Pollution prevention: Part 4-Sec G
16) Method performance; 160.1-Sec 9.0
18) Data assessment and acceptance criteria for quality control measures; Part 4- Sec C
19) Corrective actions for out-of-control data; Part 4-Sec D1
20) Contingencies for handling out-of-control or unacceptable data; Part 4-Sec D2
21) Waste management; Part 4-Sec G
22) References; 2540C-Sec 7.
23) Tables, diagrams, flowcharts and validation data; none available

PART 3: METHODS AS PUBLISHED

METHOD #: 160.1	Approved for NPDES (Issued 1971)
TITLE:	Residue, Filterable (Gravimetric, Dried at 180°C)
ANALYTE:	Residue, Filterable
INSTRUMENTATION:	Drying Oven
STORET No.	70300

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
1.2 The practical range of the determination is 10 mg/L to 20,000 mg/L

2.0 Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.

3.0 Definitions

3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

4.0 Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as possible. Refrigeration or icing to 4°C, to minimize micro-biological decomposition of solids, is recommended.

5.0 Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

6.0 Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent
6.2 Filter holder, membrane filter funnel or Gooch crucible adapter
6.3 Suction flask, 500 mL
6.4 Gooch crucibles, 25 mL (if 2.1 cm filter is used)
6.5 Evaporating dishes, porcelain, 100 mL volume. (Vycor or platinum dishes may be substituted)
6.6 Steam bath
6.7 Drying oven, 180°C ± 2°C
6.8 Desiccator
6.9 Analytical balance, capable of weighing to 0.1 mg

7.0 Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.
7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ± 50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ± 2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.
7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100 mL graduated cylinder. If total filterable residue is low, a larger volume may be filtered.
7.4 Filter the sample through the glass fiber filter, rinse with three 10 mL portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.
7.5 Transfer 100 mL (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.
7.6 Dry the evaporated sample for at least one hour at 180 plus or minus 2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8.0 Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in mL

9.0 Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

2540 C. Total Dissolved Solids Dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.[1] The filtrate from the total suspended solids determination (Section 2540D) may be used for determination of total dissolved solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

Apparatus listed in Section 2540B.2*a* - h is required, and in addition:

a. Glass-fiber filter disks#(1)* without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible,* 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-µm) fritted disk as filter support.#(2)†

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed.

Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. If volatile solids are to be determined, follow procedure in Section 2540E.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

6. Reference

1. SOKOLOFF, V.P. 1933. Water of crystallization in total solids of water analysis. *Ind. Eng. Chem.,* Anal. Ed. 5:336.

7. Bibliography

HOWARD, C.S. 1933. Determination of total dissolved solids in water analysis. *Ind. Eng. Chem.,* Anal. Ed. 5:4.

U.S. GEOLOGICAL SURVEY. 1974. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Techniques of Water-Resources Investigations, Book 5, Chap. A1. U.S. Geological Surv., Washington, D.C.

30:1066.

SMITH, A.L. & A.E. GREENBERG. 1963. Evaluation of methods for determining suspended solids in wastewater. *J. Water Pollut. Control Fed.* 35:940.

WYCKOFF, B.M. 1964. Rapid solids determination using glass fiber filters. *Water Sewage Works* 111:277.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1975. A Preliminary Review of Analytical Methods for the Determination of Suspended Solids in Paper Industry Effluents for Compliance with EPA-NPDES Permit Terms. Spec. Rep. No. 75-01. National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1977. A Study of the Effect of Alternate Procedures on Effluent Suspended Solids Measurement. Stream Improvement Tech. Bull. No. 291, National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

TREES, C.C. 1978. Analytical analysis of the effect of dissolved solids on suspended solids determination. *J. Water Pollut. Control Fed.* 50:2370.

Endnotes

1 (Popup - Footnote)

* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weigh; or other products that give demonstrably equivalent results. Practical filter diameters are 2.2 to 12.5 cm.

2 (Popup - Footnote)

† Gelman No. 4201 or equivalent.

PART 4:
ECOTEST CHANGES & SELECTED OPTIONS

PART 4 -
SECTION A. - PROCEDURE NOTES, STANDARD & REAGENT PREPARATIONS

PROCEDURE:

1. Set up vacuum filtration device: Side-Arm pyrex flask with Buchner funnel on top or Nalgene Filtration Assembly.. Connect vacuum pump hose to side arm.

NOTE 1: When stopping filtration, always disconnect hose from side-arm first. If pump is shut off first or vacuum is released at some other point, there will be a back flow through the vacuum hose into the side-arm flask with resulting contamination. This is a common problem with inexperience analysts and has caused problems in the past.

2.
a) Prepare Filters: use only Whatmann 934-AH glass-fiber filters, 5.5 cm diameter or larger. Place each filter in plastic Buchner funnel. Apply suction and rinse filter with 3 volumes of 20-30 mL deionized water. Stop vacuum and rinse out sid-arm flask with 3 rinses of DI water.

b) Prepare dishes as follows: Use pyrex glass dishes Corning No 3180, size 80 X 45. Wash dishes with Alconox and steel scouring wool. Rinse three times with DI water. Bake at 180 ^{o} C for 2 to 4 hours. Place in dessicator to cool. Weigh when cool.

3. Measure aliquot for filtration with graduate. This is 100 mL for drinking water and 50 mL for wastewaters. Smaller sample size may be required if salt content is high – "because excessive residue in the dish may form a water-trapping crust" a maximum of 0.2 grams (200 mg) should be the limit of dried residue in the dish.

4. After all sample has passed through filter, rinse the filter holder and the filter with two 10 mL portions of deionized water. This step is important with saltwater or other mineralized samples since unrinsed salt will result in loss of TDS.

6. All of the contents of the filtration flask must be transferred to prepared Evaporating Dish.

7. Place dishes in drying oven overnight at 90^{o} C. Next morning, turn temp up to 180 ^{o} C for 1 hour. Remove dishes directly to dessicators (drying crystals must be blue in dessicator). Allow dishes to cool for at least one hour. Weigh and perform calculation.

8. Calculate TDS, mg/L:

$$(B - A) \times 1000 \times \frac{1000}{C}$$

A = weight in grams of evaporating dish (dried) before addition of sample
B = weight in grams of evaporating dish after sample is evaporated and dish cooled in dessicator.
C= mL of sample filtered

Note 2: Do not touch dishes with fingers, use only forceps. Be careful not to make any holes or tears in filters. Discard damaged filters. Repeat sample if filter is damaged during analysis.
Note 3. Dishes to be weighed must be kept in dessicator at all times. Dried dishes quickly absorb moisture from the air and gain significant weight in a short time causing error. Weighings must be done quickly and dessicator kept closed whenever possible.
Note 4: Dessicant crystals in dessicator must be blue. If they are not, do not use the dessicator. Restore crystals to blue color by baking in 180^{o} C oven.
Note 5: Holding time is 7 days provided sample is stored at 6^{o} C in glass or plastic bottle. TSS cannot be run on a sample with preservative.

SECTION B - QUALITY CONTROL

GENERAL CALIBRATION AND STANDARDIZATION:

- Calibrate Balance daily with 2 weights as per normal balance requirements.
- Calibrate oven thermometers annually (if glass) quarterly if electronic as per normal thermometer requirements.

BATCH SPECIFIC QC:

- Temperature Control: Record temperature and time at beginning and end of each batch drying cycle. Thermometer bulb must be immersed in beaker of sand.

- Duplicates: perform two duplicates with each batch or every 20 samples whichever is more frequent. Chart results on range control chart.
- Reference sample: perform one reference sample per batch or every 20 samples whichever is more frequent. Chart results on control chart. Reference samples are purchased from VWR. Use Ricca brand, VWR No RC720032, 0.85% W/V. Use X10 Dilution: 10.0 mL + 90 mL Distilled Water. True value = 850 mg/L
- Blank: perform one blank by filtering 100 mL of distilled water through a prepared filter.
- Demonstration of Capability When an analyst performs test for the first time, he/she must perform minimum of 4 consecutive reference samples within acceptable limits. Thereafter DOC must be done annually. A single blind proficiency samples such as ELAP PT's may be used for annual DOC. NELAC form must be filled out, signed and raw data attached for all DOCs
- Spikes: Not applicable to method

SECTION C - DATA ASSESSMENT & ACCEPTANCE CRITERIA

Data from a batch are questionable and should be reanalyzed if following criteria are not met unless reason is known and has no impact on results.

- Duplicates: Control Limit is 3.27 X Standard Deviation (SD). SD is determined using results of 20 sets of duplicate samples. Use Excel spreadsheet Standard Deviation function to calculate SD.
- Reference Sample (QC Sample or Lab. Control Sample): Upper & Lower Control limits of 3 X SD should not be exceeded. Results are acceptable if Upper and Lower Warning Limits (2 X SD) are exceeded but Control limits are not exceeded.
- Spiked Sample: Not applicable to method
- Blanks (Laboratory Reagent Blank): Difference should not exceed 1.0 mg/L

SECTION D - OUT-OF-CONTROL DATA

1. Corrective Actions for Out-of-Control Data:

Data from a batch are questionable and should be reanalyzed if the criteria in "Quality Control" Section above are not met unless reason is known and has no impact on results. All practicable treatments of sample to eliminate interferences should be used. If QC values are still out-of-control the analyst should consult with supervisor for suggestions to solve problem. Review of analysts technique in all phases of the analysis should be performed if no reason can be determined for the problem. In some cases the problem may be with an individual sample in which case a duplicate and/or spike may be performed successfully on another sample.

2. Contingencies for Handling Out-of-Control Data:

If problem cannot be resolved by methods in section 1. above, QA Officer must be notified and the data must be flagged on final report with statement of the problem. Client should be contacted by QA Officer phone or fax to notify and discuss problem and possible solutions such as change of method or resampling. It should be determined from client what the purpose of the samples is. For example, samples for compliance monitoring for government regulations are usually the type of sample where QC compliance is the most critical. A file should be kept by QA Officer with record of all discussions and decisions regarding such problems and any resolutions thereof.

SECTION E - SAMPLE BOTTLES, PRESERVATION AND HOLDING TIME

Plastic or Glass Bottle. No Preservative, Store samples at 6^{o} C. Holding time is 7 days.

SECTION F - SAFETY

- Safety glasses are required for this procedure.
- Make sure to use drying oven that is vented to a hood which must be turned on. Avoid opening door of oven during drying.
- If particularly malodorous samples are being filtered or if sample contains potentially hazardous volatiles, set up side-arm vacuum apparatus under hood and make sure that vacuum pump outlet exhausts under hood as well.
- Consult "Chemical Hygiene Plan" for general safety measures.
- The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

SECTION G - WASTE DISPOSAL AND POLLUTION PREVENTION

- Normal nonhazardous wastewater samples require no special disposal.
- Industrial or liquid wastes require special disposal according to the nature of the waste
- Residue or rinsate from dried dish may have to be scraped or rinsed out in special container for disposal as hazardous waste.
- Consult "Waste Disposal" document for general disposal procedures.

ECOTEST LABORATORIES, INC. ENVIRONMENTAL TESTING

377 SHEFFIELD AVE. • N. BABYLON, N.Y. 11703 • (631) 422-5777 • FAX (631) 422-5770

STANDARD OPERATING PROCEDURE

METHOD PUBLISHED BY:
APHA, *Standard Methods for the Examination of Water And Wastewater*, 20th ed. 1999
&
US EPA, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA 600/R-03/100, Aug. 93.

METHOD NUMBERS: EPA 351.3 & APHA 4500 B

METHOD TITLE:
Nitrogen, Kjeldahl, Total (Colorimetric; Titrimetric; Potentiometric)

ECOTEST VERSION # 2 DATE: July 12, 2003
APPROVING AUTHORITY _____
Print Name: Thomas Powell

TABLE OF CONTENTS:

PART 1: NELAC STANDARDS:

NELAC Sec. 5.10.1.1 - Standard Operating Procedures (SOPs)

Laboratories shall maintain standard operating procedures that accurately reflect all phases of current laboratory activities (including) test methods.

a) These documents, for example, may be equipment manuals provided by the manufacturer, or internally written documents.

b) The test methods may be copies of published methods as long as any changes or selected options in the methods are documented and included in the methods manual (see 5.10.1.2).

c) Copies of all SOPs shall be accessible to all personnel.

d) The SOPs shall be organized .

e) Each SOP shall clearly indicate the effective date of the document, the revision number and the signature(s) of the approving authority.

NELAC Sec. 5.10.1.2 - Laboratory Method Manual(s)/ Standard Operating Procedures (SOPs)

a) The laboratory shall have and maintain an in-house methods manual(s) for each accredited analyte or test method.

b) This manual may consist of copies of published or referenced test methods or standard operating procedures that have been written by the laboratory. In cases where modifications to the published method have been made by the laboratory or where the referenced test method is ambiguous or provides insufficient detail, these changes or clarifications shall be clearly described. Each test method shall include or reference where applicable:

1) Identification of the test method
2) Applicable matrix or matrices
3) Detection limit
4) Scope and application, including components to be analyzed
5) Summary of the test method
6) Definitions
7) Interferences
8) Safety
9) Equipment and supplies
10) Reagents and standards
11) Sample collection, preservation, shipment and storage
12) Quality control
13) Calibration and standardization
14) Procedure
15) Calculations
16) Method performance
17) Pollution prevention
18) Data assessment and acceptance criteria for quality control measures
19) Corrective actions for out-of-control data
20) Contingencies for handling out-of-control or unacceptable data
21) Waste management
22) References
23) Tables, diagrams, flowcharts and validation data

PART 2: INDEX OF 23 NELAC REQUIRED SOP ITEMS

1) Identification of the test method; p1
2) Applicable matrix or matrices; Ground and surface and saline waters, domestic and industrial wastes. (Sec 1.0, p5)
3) Detection limit; 0.2 mg/L (280 mL aliquot can be used for 0.1 mg/L LRL)
4) Scope and application, including components to be analyzed; Sec 1.0, p5
5) Summary of the test method; Sec 3.0, p5
6) Definitions; Sec 2.0, p5
7) Interferences; Sec 5.0, p6
8) Safety; Sec 5, p21
9) Equipment and supplies; Sec 6.0., p6 & Sec 1, p18
10) Reagents and standards; Sec 7.0 , p6 & Sec1, p 18-19
11) Sample collection, preservation, shipment and storage; Sec 5, p21
12) Quality control; Sec 3, p20
13) Calibration and standardization; Titrants and Spiking Solutions are purchased with certificated of standardization, Sec 1, p18
14) Procedure; Sec 8.0, p7 & Sec 1, p18
15) Calculations; Sec 9, p9 & Sec 1-III, p19
17) Pollution prevention: Sec 6, p21
16) Method performance; Sec 10.0, p10
18) Data assessment and acceptance criteria for quality control measures; Sec 4, p21
19) Corrective actions for out-of-control data; Sec 7A, P22
20) Contingencies for handling out-of-control or unacceptable data; Sec 7B, P22
21) Waste management; Sec 6, P21
22) References; p11 & 16
23) Tables, diagrams, flowcharts and validation data; Sec 8.2 , p7 & 8.4, P8 &10.1,P10

PART 3: METHODS AS PUBLISHED

METHOD #: 351.3	Approved for NPDES (Editorial Revision 1974, 1978)
TITLE:	Nitrogen, Kjeldahl, Total (Colorimetric; Titrimetric; Potentiometric)
ANALYTE:	CAS # N Nitrogen 7727-37-9
INSTRUMENTATION:	Spectrophotometer
STORET No.	00625

1.0 Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/L.

1.3 This method is described for macro and micro glassware systems.

2.0 Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free- ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

3.0 Summary of Method

3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.

4.0 Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 mL of conc. H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic

nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5.0 Interference

5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

6.0 Apparatus

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 mL flasks and suction takeoff to remove SO_3 fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7.0 Reagents

7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
NOTE 1: All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 mL of 1:4 sulfuric acid (10.0 mL conc. H_2SO_4: 40 mL distilled water) and dilute to 100 mL with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 mL distilled water and 400 mL conc. H_2SO_4. Add 50 mL mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

7.6 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) 1 mL = 0.28 mg NH_3-N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 mL of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 mL of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg NH_3-N. Dilute 10.0 mL of the stock solution (7. 8) with distilled water to 1 liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 mL of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8.0 Procedure

8.1 The distillation apparatus should be pre steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 mL Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/L	Sample Size mL
0-5	500
5-10	250
10-20	100
20-50	50.0
50-500	25.0

Dilute the sample, if required, to 500 mL with distilled water, and add 100 mL sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 mL distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 mL of sodium hydroxide - thiosulfate solution (7.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the

aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 mL at the rate of 6-10 ml/min., into 50 mL of 2% boric acid (7.6) contained in a 500 mL Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 mL in the flask. These flasks should be marked at the 350 and the 500 mL volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/L, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/L.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 mL of sample or an aliquot diluted to 50 mL in a 100 mL Kjeldahl flask and add 10 mL sulfuric acid-mercuric sulfate- potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 mL distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 mL of sodium hydroxide thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 mL short-form Nessler tube.

8.3.4 Steam distill 30 mL at the rate of 6-10 ml/min., into 5 mL of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 mL. For concentrations above 1 mg/L the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/L.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 (7.7), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

mL of Standard 1.0 mL = 0.01 mg NH_3-N	mg NH_3-N/50.0 mL
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 mL with ammonia free water, add 1 mL of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg NH_3-N for the standard curve. Develop color in the 50 mL diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method,(350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled, and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9.0 Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weigh to nitrogen (14mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, } mg/L = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3-N read from curve.
B = mL total distillate collected including the H_3BO_3.
C = mL distillate taken for Nesslerization.
D = mL of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/L, as follows: Organic Kjeldahl Nitrogen = TKN--(NH_3-N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/L, in the original sample as follows:

$$\text{TKN, } mg/L = \frac{B}{D} \times A$$

where:

A = mg NH_3-N/L from electrode method standard curve.
B = volume of diluted distillate in mL.
D = mL of original sample taken.

10.0 Precision

10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	- 1.67	-0.08

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7-77-017.

4500-N_{org} A. Introduction

1. Selection of Method

The kjeldahl methods (B and C) determine nitrogen in the trinegative state. They fail to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime, and semi-carbazone. "Kjeldahl nitrogen" is the sum of organic nitrogen and ammonia nitrogen.

The major factor that influences the selection of a macro- or semi-micro-kjeldahl method to determine organic nitrogen is its concentration. The macro-kjeldahl method is applicable for samples containing either low or high concentrations of organic nitrogen but requires a relatively large sample volume for low concentrations. In the semi-micro-kjeldahl method, which is applicable to samples containing high concentrations of organic nitrogen, the sample volume should be chosen to contain organic plus ammonia nitrogen in the range of 0.2 to 2 mg.

The block digestion method (D) is a micro method with an automated analysis step capable of measuring organic nitrogen as low as 0.1 mg/L when blanks are carefully controlled.

2. Storage of Samples

The most reliable results are obtained on fresh samples. If an immediate analysis is not possible, preserve samples for kjeldahl digestion by acidifying to pH 1.5 to 2.0 with concentrated H_2SO_4 and storing at 4°C. Do not use $HgCl_2$ because it will interfere with ammonia removal.

3. Interferences

a. Nitrate: During kjeldahl digestion, nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the digested organic nitrogen, producing N_2O and resulting in a negative interference. When sufficient organic matter in a low state of oxidation is present, nitrate can be reduced to ammonia, resulting in a positive interference. The conditions under which significant interferences occur are not well defined and there is no proven way to eliminate the interference in conjunction with the kjeldahl methods described herein.

b. Inorganic salts and solids: The acid and salt content of the kjeldahl digestion reagent is intended to produce a digestion temperature of about 380°C. If the sample contains a very large quantity of salt or inorganic solids that dissolve during digestion, the temperature may rise above 400°C, at which point pyrolytic loss of nitrogen begins to occur. To prevent an excessive digestion temperature, add more H_2SO_4 to maintain the acid-salt balance. Not all salts cause precisely the same temperature rise, but adding 1 mL H_2SO_4/g salt in the sample gives reasonable results. Add the extra acid and the digestion reagent to both sample and reagent blank. Too much acid will lower the digestion temperature below 380°C and result in incomplete digestion and recovery. If necessary, add sodium hydroxide-sodium thiosulfate before the final distillation step to neutralize the excess acid.

Large amounts of salt or solids also may cause bumping during distillation. If this occurs, add more dilution water after digestion.

c. Organic matter: During kjeldahl digestion, H_2SO_4 oxidizes organic matter to CO_2 and H_2O. If a large amount of organic matter is present, a large amount of acid will be consumed, the ratio of salt to acid will increase, and the digestion temperature will increase. If enough organic matter is present, the temperature will rise above 400°C, resulting in pyrolytic loss of nitrogen. To prevent this, add to the digestion flask 10 mL conc H_2SO_4/3 g COD. Alternately, add 50 mL more digestion reagent/g COD. Additional sodium hydroxide-sodium thiosulfate reagent may be necessary to keep the distillation pH high. Because reagents may contain traces of ammonia, treat the reagent blank identically with the samples.

4. Use of a Catalyst

Mercury has been the catalyst of choice for kjeldahl digestion. Because of its toxicity and problems associated with legal disposal of mercury residues, a less toxic catalyst is recommended. Digestion of some samples may be complete or nearly complete without the use of a catalyst. Effective digestion results from the use of a reagent having a salt/acid ratio of 1 g/mL with copper as catalyst (¶ B.3*a*), and specified temperature (¶ B.2*a*) and time (¶ B.4*c*)). If a change is made in the reagent formula, report the change and indicate percentage recovery relative to the results for similar samples analyzed using the previous formula.

Before results are considered acceptable, determine nitrogen recovery from samples with known additions of nicotinic acid, to test completeness of digestion; and with ammonium chloride to test for loss of nitrogen.

4500-N_{org} B. Macro-Kjeldahl Method

1. General Discussion

a. Principle: In the presence of H_2SO_4, potassium sulfate (K_2SO_4), and cupric sulfate ($CuSO_4$) catalyst, amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined colorimetrically, by ammonia-selective electrode, or by titration with a standard mineral acid.

b. Selection of ammonia measurement method: The sensitivity of colorimetric methods makes them particularly useful for determining organic nitrogen levels below 5 mg/L. The titrimetric and selective electrode methods of measuring ammonia in the distillate are suitable for determining a wide range of organic nitrogen concentrations. Selective electrode methods and automated colorimetric methods may be used for measurement of ammonia in digestate without distillation. Follow equipment manufacturer's instructions.

2. Apparatus

a. Digestion apparatus: Kjeldahl flasks with a total capacity of 800 mL yield the best results. Digest over a heating device adjusted so that 250 mL water at an initial temperature of 25°C can be heated to a rolling boil in approximately 5 min. For testing, preheat heaters for 10 min if gas-operated or 30 min if electric. A heating device meeting this specification should provide the temperature range of 375 to 385°C for effective digestion.

b. Distillation apparatus: See Section 4500-NH_3.B.2*a*.

c. Apparatus for ammonia determination: See Section 4500-NH_3.C.2, 4500-NH_3.D.2, Section 4500-NH_3.F.2, or Section 4500-NH_3.G.2.

3. Reagents

Prepare all reagents and dilutions in ammonia-free water.

All of the reagents listed for the determination of Nitrogen (Ammonia), Section 4500-NH_3.C.3, Section 4500-NH_3.D.3, Section 4500-NH_3.F.3, or Section 4500-NH_3.G.3, are required, plus the following:

a. Digestion reagent: Dissolve 134 g K_2SO_4 and 7.3 g $CuSO_4$ in about 800 mL water. Carefully add 134 mL conc H_2SO_4. When it has cooled to room temperature, dilute the solution to 1 L with water. Mix well. Keep at a temperature close to 20°C to prevent crystallization.

b. Sodium hydroxide-sodium thiosulfate reagent: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in water and dilute to 1 L.

c. Borate buffer solution: See Section 4500-NH_3.B.3*b*.

d. Sodium hydroxide, NaOH, 6*N*.

4. Procedure

a. Selection of sample volume and sample preparation: Place a measured volume of sample in an 800-mL kjeldahl flask. Select sample size from the following tabulation:

Organic Nitrogen in Sample *mg/L*	Sample Size *mL*
0–1	500
1–10	250
10–20	100
20–50	50.0
50–100	25.0

If necessary, dilute sample to 300 mL, neutralize to pH 7, and dechlorinate as described in Section 4500-NH_3.B.4*b*.

b. Ammonia removal: Add 25 mL borate buffer and then 6*N* NaOH until pH 9.5 is reached. Add a few glass beads or boiling chips such as Hengar Granules #12 and boil off 300 mL. If desired, distill this fraction and determine ammonia nitrogen. Alternately, if ammonia has been determined by the distillation method, use residue in distilling flask for organic nitrogen determination.

For sludge and sediment samples, weigh wet sample in a crucible or weighing bottle, transfer contents to a kjeldahl flask, and determine kjeldahl nitrogen. Follow a similar procedure for ammonia nitrogen and organic nitrogen determined by difference. Determinations of organic and kjeldahl nitrogen on dried sludge and sediment samples are not accurate because drying results in loss of ammonium salts. Measure dry weight of sample on a separate portion.

c. Digestion: Cool and add carefully 50 mL digestion reagent (or substitute 6.7 mL conc H_2SO_4, 6.7 g K_2SO_4, and 0.365 g $CuSO_4$) to distillation flask. Add a few glass beads and, after mixing, heat under a hood or with suitable ejection equipment to remove acid fumes. Boil briskly until the volume is greatly reduced (to about 25 to 50 mL) and copious white fumes are observed (fumes may be dark for samples high in organic matter). Then continue to digest for an additional 30 min. As digestion continues, colored or turbid samples will become transparent and pale green. After digestion, let cool, dilute to 300 mL with water, and mix. Tilt flask away from personnel and carefully add 50 mL sodium hydroxide-thiosulfate reagent to form an alkaline layer at flask bottom. Connect flask to a steamed-out distillation apparatus and swirl flask to insure complete mixing. The pH of the solution should exceed 11.0.

d. Distillation: Distill and collect 200 mL distillate. Use 50 mL indicating boric acid as absorbent solution when ammonia is to be determined by titration. Use 50 mL 0.04*N* H_2SO_4 solution as absorbent for manual phenate or electrode methods. Extend tip of condenser well below level of absorbent solution and do not let temperature in condenser rise above 29°C. Lower collected distillate free of contact with condenser tip and continue distillation during last 1 or 2 min to cleanse condenser.

e. Final ammonia measurement: Use the titration, ammonia-selective electrode, manual phenate, or automated phenate method, Section 4500-NH_3.C, Section 4500-NH_3.D, Section 4500-NH_3.F, and Section 4500-NH_3.G, respectively.

f. Standards: Carry a reagent blank and standards through all steps of the procedure.

5. Calculation

See Section 4500-NH_3.C.5, Section 4500-NH_3.D.5, Section 4500-NH_3.F.5, or Section 4500-NH_3.G.5.

6. Precision and Bias

Two analysts in one laboratory prepared reagent water solutions of nicotinic acid and digested them by the macro-kjeldahl method. Ammonia in the distillate was determined by titration. Results are summarized in Table 4500-N_{org}:I.

7. Bibliography

KJELDAHL J. 1883. A new method for the determination of nitrogen in organic matter. *Z. Anal. Chem.* 22:366.

PHELPS, E.B. 1905. The determination of organic nitrogen in sewage by the Kjeldahl process. *J. Infect. Dis.* (Suppl.) 1:225.

MCKENZIE, H.A. & H.S. WALLACE. 1954. The Kjeldahl determination of nitrogen: A critical study of digestion conditions. *Aust. J. Chem.* 7: 55.

MORGAN, G.B., J.B. LACKEY & F.W. GILCREAS. 1957. Quantitative determination of organic nitrogen in water, sewage, and industrial wastes. *Anal. Chem.* 29:833.

BOLTZ, D.F., ed. 1978. Colorimetric Determination of Nonmetals. Interscience Publishers, New York, N.Y.

JONES, M. & D. BRADSHAW. 1989. Copper: An alternative to mercury; more effective than zirconium in kjeldahl digestion of ecological materials. *Commun. Soil Sci. Plant Anal.* 20:1513.

PART 4: ECOTEST CHANGES & SELECTED OPTIONS

1) PROCEDURE:

I)Digestion:

a) Selection of Sample Aliquot Volume: Normal aliquot is 140 mL. For final calculation this is considered a X2 dilution. Reporting limit will then be 0.2 mg/L. 280 mL aliquot (X1 dilution factor) can also be used to lower the reporting limit to 0.1 mg/L. For samples that are anticipated to be high in TKN, aliquots of 70 mL (X4) or 35 mL (X8) or smaller can be used.

b) Sample aliquote is poured into 500 mL, Long Neck (6"), Flat-Bottom digestion flasks.

NOTE 1: Digestion flasks are custom made by United Silica. Standard corning boiling flasks are purchased and sent to United Silica to have necks lengthened to 6 ".

c) Add boiling beads (6-10) to flask.

d) Add 25 mL TKN digestion reagent to flask

e) Preheat hotplates MAKE SURE HOOD IS ON WHEN YOU TURN ON HOTPLATES. If hood is off glass in door may oveerheat and crack.

f) Put flasks on hotplates. Close hood. Flasks will boil until all water has boiled off. Then boiling may slow or appear to stop. At this point dense white fumes should appear in the flask. This is when the actual digestion of the TKN begins to occur. These fumes are sulfuric acid fumes. The temperature of the hotplate should be such that these fumes continue to form but do not escape from the flasks. The long necks of the flasks are to allow the fumes to cool and recondense. Caution : There are usually hotspots on the hotplates that may cause overheating and loss of these fumes. This will result in excessively low results. Analyst should observe the behavior of the flasks on the hotplates until she/he becomes accustomed to their heating peculiarities and avoid placing flasks in spots that are too hot or too cold.

NOTE 2: It is best to avoid opening the hood as much as possible to avoid escape of acid fumes into the lab. If it is necessary to move flasks while they are being heated, open hood minimum possible, and move flasks with insulated gloves. DO NOT PUT HEAD INSIDE HOOD.

g) Once the heavy acid fumes have appeared in the flasks, continue the digestion until all flasks have been at this stage for at least 30 minutes. When digestion is complete, contents of flasks should appear clear and a pale green color. Some samples may need more than 30 minutes to digest. If a sample does not reach this point after an hour, there is probably too much organic matter for the amount of digestion reagent. It may be necessary to redigest a smaller aliquot (usually at least 4X less). It is OK to digest all of the samples for longer than 30 minutes while waiting for the last sample to be digested as long as acid fumes do not escape from flasks, i.e. it is not possible to "overidigest" a sample. This eliminates the need to open hood to remove flasks that are already done. Analyst should be able to start all flasks at same time, close hood and allow samples to digest, then turn off all hotplates at the same time when the last sampe is done. Samples should be allowed to cool on the hotplates. Do not shut off hood.

h) Once flasks have cooled to a warm temperature, add 25 mLs of ammonia-free water to each flask an swirl to mix.

NOTE 3: At this point, analysis can be stopped if necessary. Flasks can be parafilmed one they are at room temperature. Do not parafilm hot flasks as the parafilm will be sucked in and rupture as flasks cool. If flasks are well sealed with parafilm, they can be kept overnight if need be, to continue with distillation step the nex tday.

II) Distillation: Use VAP30 (yellow) Auto Still. Labconco can also be used with manual Alkali reagent addition; see note 4 below.
a) During digestion, all organic (primarily proteinaceous) nitrogen is transformed to ammonia. This is then distilled under conditions of high pH. To distill, transfer contents of TKN flask to distillation tube. Place tube on yellow (Vap30) automatic still. Under normal operating conditions still should dispense water and Alkali reagent to tubes. Before distillation starts place 250 mL flask under collection tube with tube submerged in boric acid indicator solution (50 mL). Begin distillation. Unit is time programmed to stop automatically. If TKN or Ammonia is present, color will change from purple/blue to green.

NOTE 4: If automated Alkali reagent feed is not functioning, add reagent manually to digestion tube immediately before placing tube on still. Pour reagent gently down side of tube. As tube is placed on still give it a swirl to mix. This minimizes loss of any ammonia.

b) Titrate sample immediately with 0.02N sulfuric acid titrant from green back to blue/purple. Purchase titrant from VWR or Fisher. Order certificate of analysis when ordering reagent. Keep cert. on file.

III) Calculation:

$$\text{TKN as N, mg/L} = \frac{280\ \text{mL}}{\text{Vol. Digested, mL}} \times \text{mL Titrant}$$

IV) Reagents:
a) Alkali Reagent:
Under hood, place 2000 mL pyrex beaker in water bath with ice packs. Add approx. 700 mL DI water (ammonia free). Add 500 g Sodium Hydroxide (NaOH) pellets slowly with mixing until dissolved. CAUTION: MIXTURE WILL BECOME EXTREMELY HOT. Add 25 g Sodium Thiosulfate crystals ($Na_2S_2O_2$). Mix until dissolved. Let cool. Dilute to 1.0 L.
b) Digestion reagent:
Dissolve 267 g K2SO4 (Potasssium Sulfate) in 1300 mL distilled water and 400 mL conc. H2SO4. Add 14.6 g $CuSO_4$ (Copper Sulfate) and dilute to 2 liters with distilled water.

V) Spike: Spike one sample per batch or every 20 samples whichever is less. Spike before digestion with Ammonium Chloride Solution, 0.1Molar (1400 mg/L) purchased from VWR or Fisher; Ricca brand, Cat no 627-16. Prepare a 5 mg/L spike by adding 0.5 mL of 0.1 Molar solution to sample. Request certificate of analysis when ordering solution. Keep certs. on file

VI) Reference or QC Sample: Prepare reference sample from analytical grade Glycine. Digest one QC sample per batch or every 20 samples whichever is less. Also perform one digested blank and one duplicate per batch.

VII) Cleaning glassware: clean with hot water, rinse 5X with DI water.

VIII) Soil samples should be started with 2.8 g + 40 to 50 mL water. This is a X100 dilution. Manual technique using bunsen burner with flask tipped into hood may be needed to boil off water without "bouncing" during boiling.

2) HOLDING TIME, PRESERVATIVES, BOTTLES:

Holding time 28 days, 1+1 Sulfuric Acid Preservative (0.5 mL per 6 oz bottle, 1.0 mL per 16 oz bottle), storage at 4° C required, glass or plastic bottle.

3) QUALITY CONTROL:

a) Duplicates: perform one duplicate each batch or every 20 samples whichever is more frequent. Chart results on range control chart. If no samples in batch are positive, perform a duplicate Spike.

b) Lab Control, Reference or QC sample:
Perform one QC (Glycine) sample per batch or every 20 samples whichever is more frequent. Chart results on control chart. .

c) Spike: Perform one spiked sample (Ammonium Chloride) per batch or every 20 samples whichever is more frequent. Chart results on control chart.

d) Blanks (Laboratory Reagent Blank): perform one blank with every batch. Chart results on control chart.

e) Demonstration of Capability When an analyst performs test for the first time, he/she must perform minimum of 4 consecutive reference samples within acceptable limits. Thereafter DOC must be done annually. A single blind proficiency samples such as ELAP PT's may be used for annual DOC. NELAC form must be filled out, signed and raw data attached for all DOCs

4) DATA ASSESSMENT AND ACCEPTANCE CRITERIA:

(Data from a batch are questionable and should be reanalyzed if following criteria are not met unless reason is known and has no impact on results)

a) Duplicates: Control Limit is 3.27 X Standard Deviation (SD). SD is determined using results of 20 sets of duplicate samples. If no samples in batch are positive, duplicate spikes should be performed.

b) Spikes Control Limit is +or- 3 X Standard Deviation (SD). Warning Limits is + or - 2 X SD. SD is determined using results of 5 to 20 spiked samples

c) QC Sample (or Lab Control or Reference Sample): Upper & Lower Control limits of 3 X SD should not be exceeded. Results are acceptable if Upper and Lower Warning Limits (2 X SD) are exceeded but Control limits are not exceeded.

d) Blanks (Laboratory Reagent Blank): If blank titrates higher than 0.1 mL this indicates laboratory or reagent contamination may have occurred. Corrective actions must be taken before continuing the analysis.

5) SAFETY:

Safety glasses, gloves and lab coat are required for this procedure due to use of corrosive chemicals and glassware. This is especially important when digesting samples and when preparing Alkali reagent.

Consult "Chemical Hygiene Plan" for general safety measures. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

6) WASTE DISPOSAL AND POLLUTION PREVENTION :

Unused acid-preserved samples must be pH neutralized with soda ash in building #2. Also collect analyzed aliquots and rinsates in plastic jars to be be pH neutralized with soda ash in building #2 . Consult "Waste Disposal" document for general disposal procedures.

7) OUT-OF-CONTROL DATA

A. Corrective Actions for Out-of-Control Data:

Data from a batch are questionable and should be reanalyzed if the criteria in "Quality Control" Section above are not met unless reason is known and has no impact on results. All practicable treatments of sample to eliminate interferences should be used. If QC values are still out-of-control the analyst should consult with supervisor for suggestions to solve problem. Review of analysts technique in all phases of the analysis should be performed if no reason can be determined for the problem. In some cases the problem may be with an individual sample in which case a duplicate and/or spike may be performed successfully on another sample.

B. Contingencies for Handling Out-of-Control Data:

If problem cannot be resolved by methods in section 1. above, the data must be flagged on final report with statement of the problem. Client should be contacted by phone or fax to notify and discuss problem and possible solutions such as change of method or resampling. It should be determined from client what the purpose of the samples is. For example, samples for compliance monitoring for government regulations are usually the type of sample where QC compliance is the most critical. A file should be kept with record of all discussions and decisions regarding such problems and any resolutions thereof.

STANDARD OPERATING PROCEDURE

METHOD PUBLISHED BY: EcoTest Laboratories Inc.

METHOD NUMBER: **8260B**

METHOD TITLE: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

ECOTEST VERSION #_2_ DATE 061103
APPROVING AUTHORITY _____
Print Name Thomas R. Treutlein

TABLE OF CONTENTS:

PART 1: NELAC STANDARDS:

NELAC Sec. 5.10.1.1 - Standard Operating Procedures (SOPs)

Laboratories shall maintain standard operating procedures that accurately reflect all phases of current laboratory activities (including) test methods.

a) These documents, for example, may be equipment manuals provided by the manufacturer, or internally written documents.

b) The test methods may be copies of published methods as long as any changes or selected options in the methods are documented and included in the methods manual (see 5.10.1.2).

c) Copies of all SOPs shall be accessible to all personnel.

d) The SOPs shall be organized .

e) Each SOP shall clearly indicate the effective date of the document, the revision number and the signature(s) of the approving authority.

NELAC Sec. 5.10.1.2 - Laboratory Method Manual(s)/ Standard Operating Procedures (SOPs)

a) The laboratory shall have and maintain an in-house methods manual(s) for each accredited analyte or test method.

b) This manual may consist of copies of published or referenced test methods or standard operating procedures that have been written by the laboratory. In cases where modifications to the published method have been made by the laboratory or where the referenced test method is ambiguous or provides insufficient detail, these changes or clarifications shall be clearly described. Each test method shall include or reference where applicable:

1) Identification of the test method
2) Applicable matrix or matrices
3) Detection limit
4) Scope and application, including components to be analyzed
5) Summary of the test method
6) Definitions
7) Interferences
8) Safety
9) Equipment and supplies
10) Reagents and standards
11) Sample collection, preservation, shipment and storage
12) Quality control
13) Calibration and standardization
14) Procedure
15) Calculations
16) Method performance
17) Pollution prevention
18) Data assessment and acceptance criteria for quality control measures
19) Corrective actions for out-of-control data
20) Contingencies for handling out-of-control or unacceptable data
21) Waste management
22) References
23) Tables, diagrams, flowcharts and validation data

PART 2: INDEX OF 23 NELAC REQUIRED SOP ITEMS

1) Identification of the test method 8260B
2) Applicable matrix or matrices See Part 3 Method 8260B , Section 1.0
3) Detection limit; Determined as per Appendix B to CFR Part 136. See Part 4 Appendix A for MDL studies. See Part 4 Appendix B for reporting limits.
4) Scope and application, including components to be analyzed; See Part 3 Method 8260 B, Section 1.0 and Part 4 Appendix C for list of Analytes
5) Summary of the test method; See Part 3 Method 8260 B, Section 2.0
6) Definitions; See Part 3 Method 524.2, Section 3.0
7) Interferences; See Part 3 Method 8260 B , Section 3.0
8) Safety; See Part 3 Method 524.2, Section 5.0 and Part 4 Appendix D
9) Equipment and supplies; See Part 3 Method 8260B, Section 4.0 and Part 3 Method 524.2, Section 6.0. Also see Appendix E
10) Reagents and standards; See Part 3 Method 8260B, Section 5.0
11) Sample collection, preservation, shipment and storage; See Part 3 Method 8260B, Section 6.0
12) Quality control; See part 3 Method 8260B, Section 8.0
13) Calibration and standardization; See Part 3 Method 8260B, Section 7.0 and Part 3 Method 524.2, Section 10.0
14) Procedure; See Part 3 Method 8260B, Section 7.0 and Part 4 Appendix H
15) Calculations; Instrument software calculates concentration without dilution factors or blank corrections. Analyst calculates for dilutions and blank corrections for final laboratory reported result. Also see Part 3 Method 8260B, Section 7.0
16) Method performance; See Part 3 Method 8260B, Section 9.0
17) Pollution prevention; See Part 3 Mehod 524.2, Section 14.0
18) Data assessment and acceptance criteria for quality control measures; See Part 4 Appendix I
19) Corrective actions for out-of-control data; See Part 4 Appendix L
20) Contingencies for handling out-of-control or unacceptable data; See Part 4 Appendix Q
21) Wasste management; See Part 3 Method 524.2, Section 15.0
22) References; See Part 3 Method 8260B, Section 10.0 and Part 3 Method 524.2, Section 16.0
23) Tables, diagrams, flowcharts and validation data; See Part 3 method 8260 Tables 1-33, Figures 1-4

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	I	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	I	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	I	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
I = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

10.0 REFERENCES

1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

2. Bellar, T.A., Lichtenberg, J.J, J. Amer. Water Works Assoc., 1974, 66(12), 739-744.

3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.

5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.

8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.

9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.

10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.

12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.

14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2'[c]	MDL[d] (µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2'[c]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

50

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Concentration Factor Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49		1.75
d_{14}-Diglyme	66	98,64	9.07
d_7-Dimethyl formamide	50	80	9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_5-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

TABLE 25 (cont.)

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[i] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	
Chlorobenzene-d_5	
4-Bromofluorobenzene (surrogate)	
Chlorobenzene	
Ethylbenzene	
Styrene	
1,1,2,2-Tetrachloroethane	
Tetrachloroethene	
Toluene	
Toluene-d_8 (surrogate)	
1,2,3-Trichloropropane	
Xylenes	

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit[a] (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

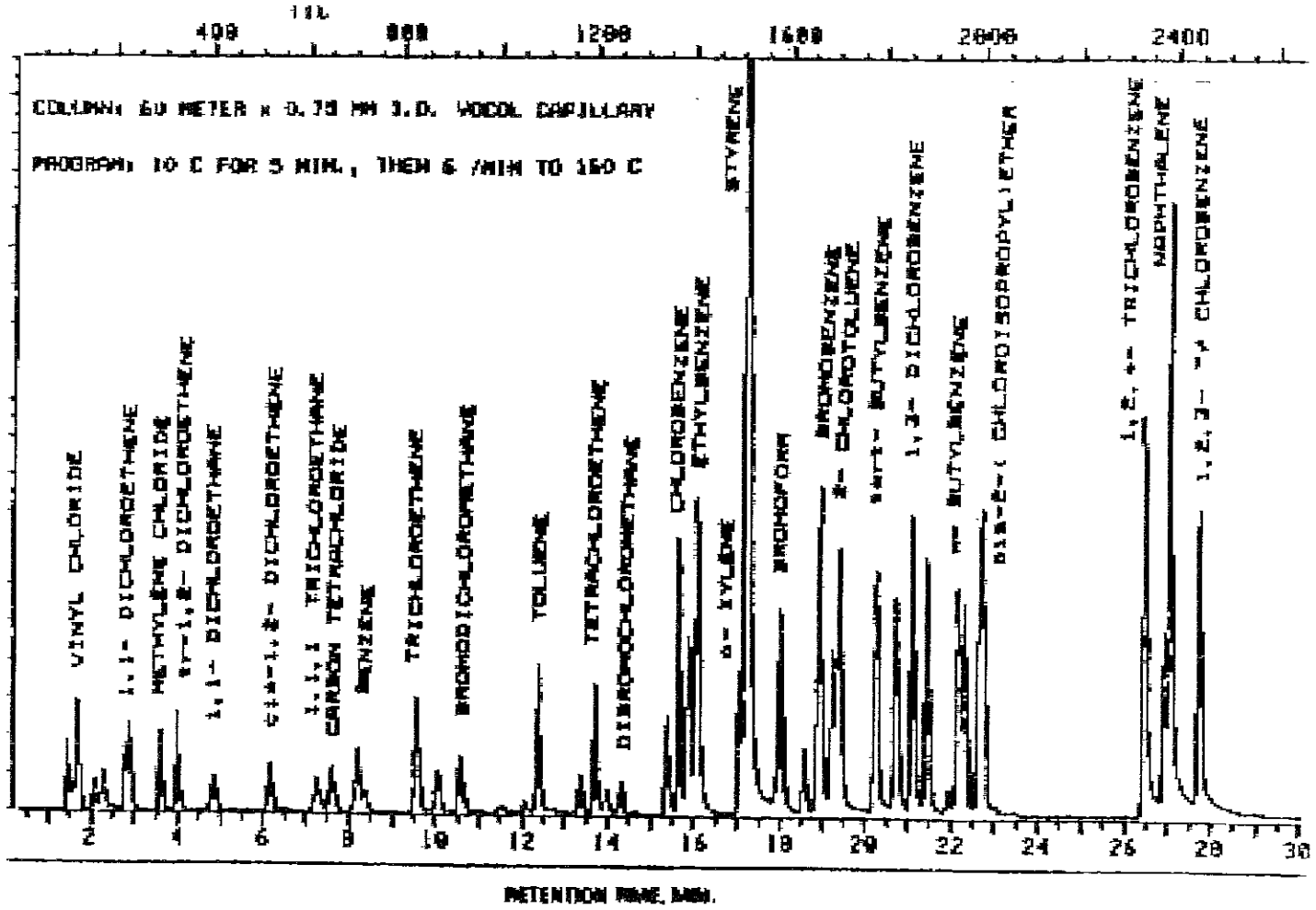


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

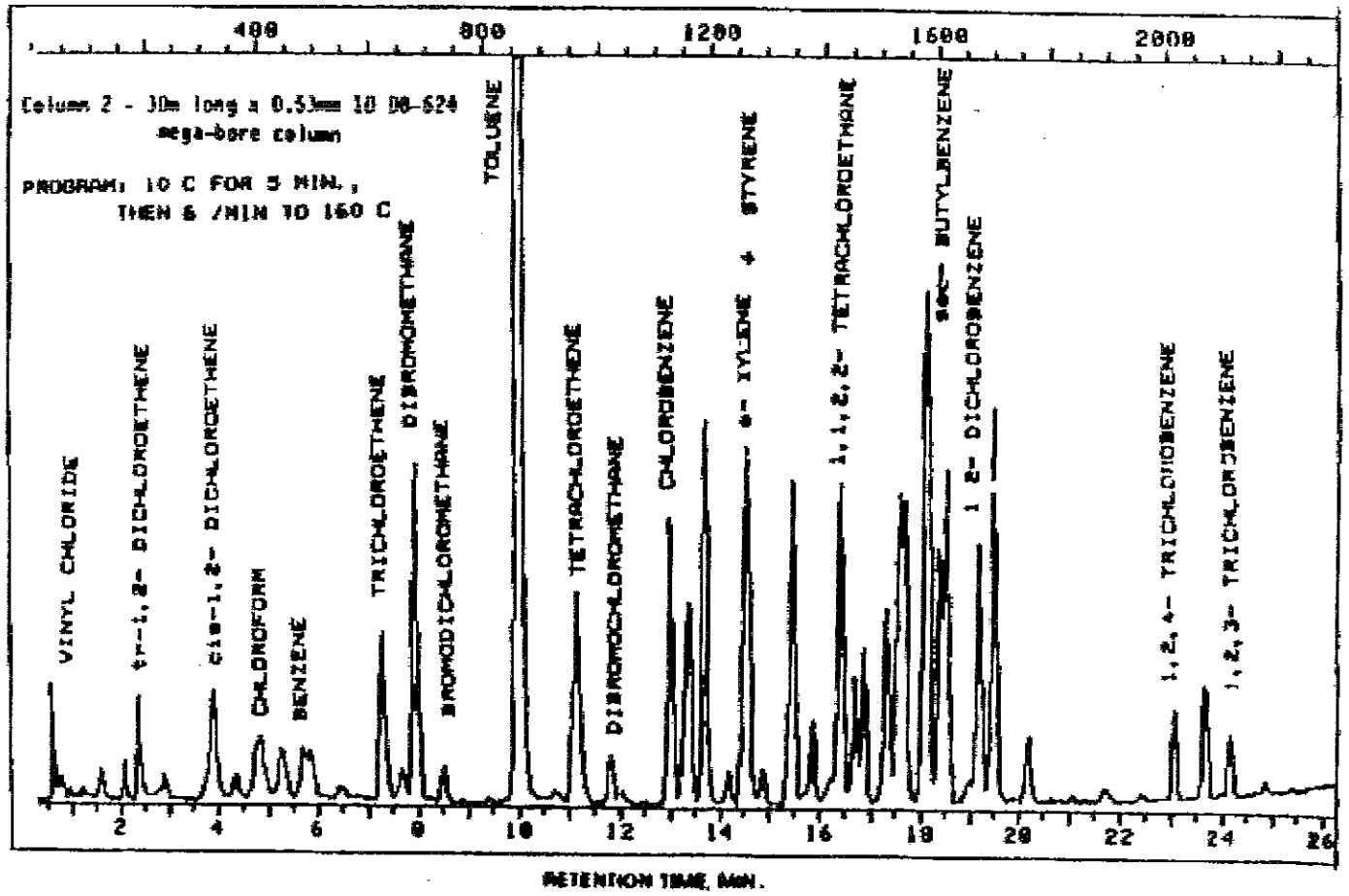


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

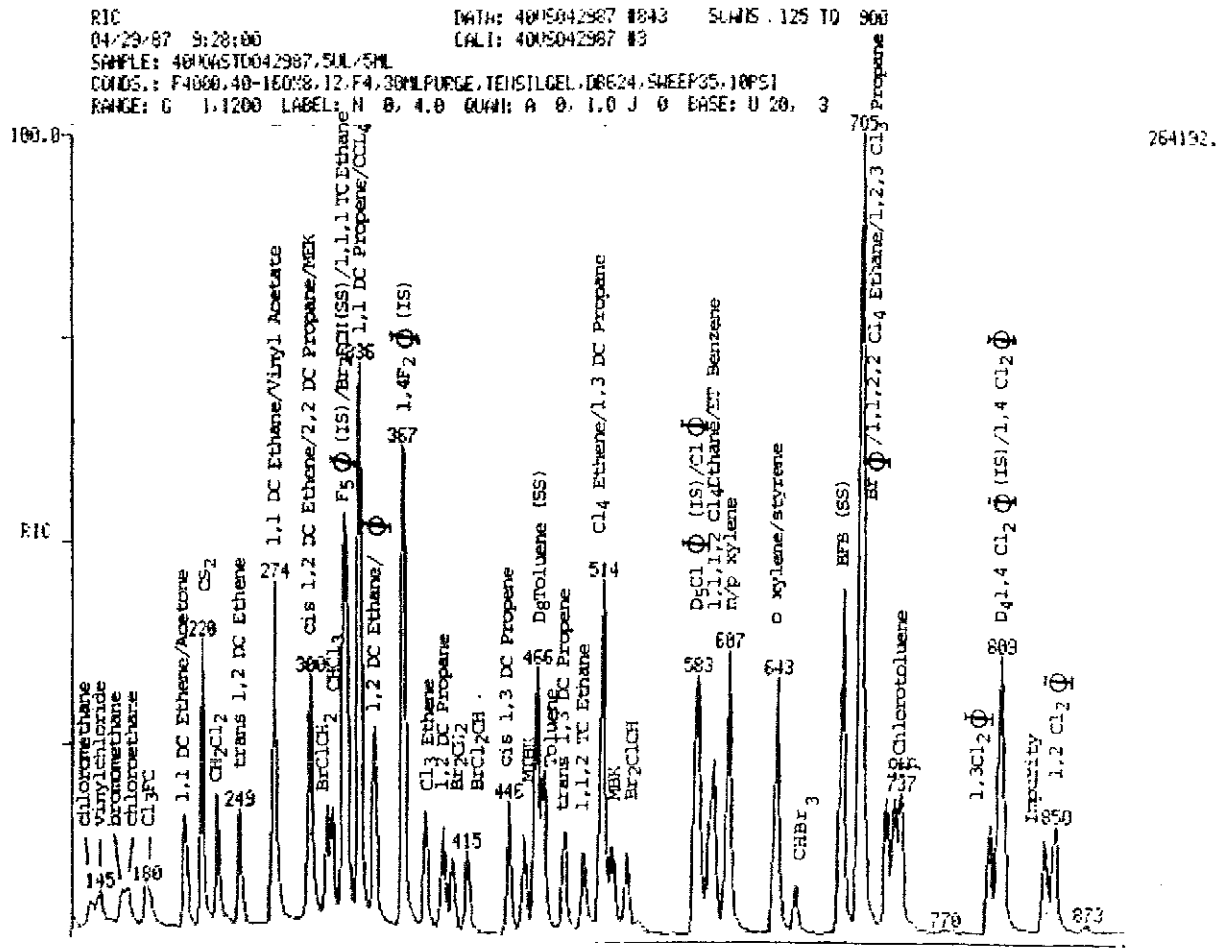
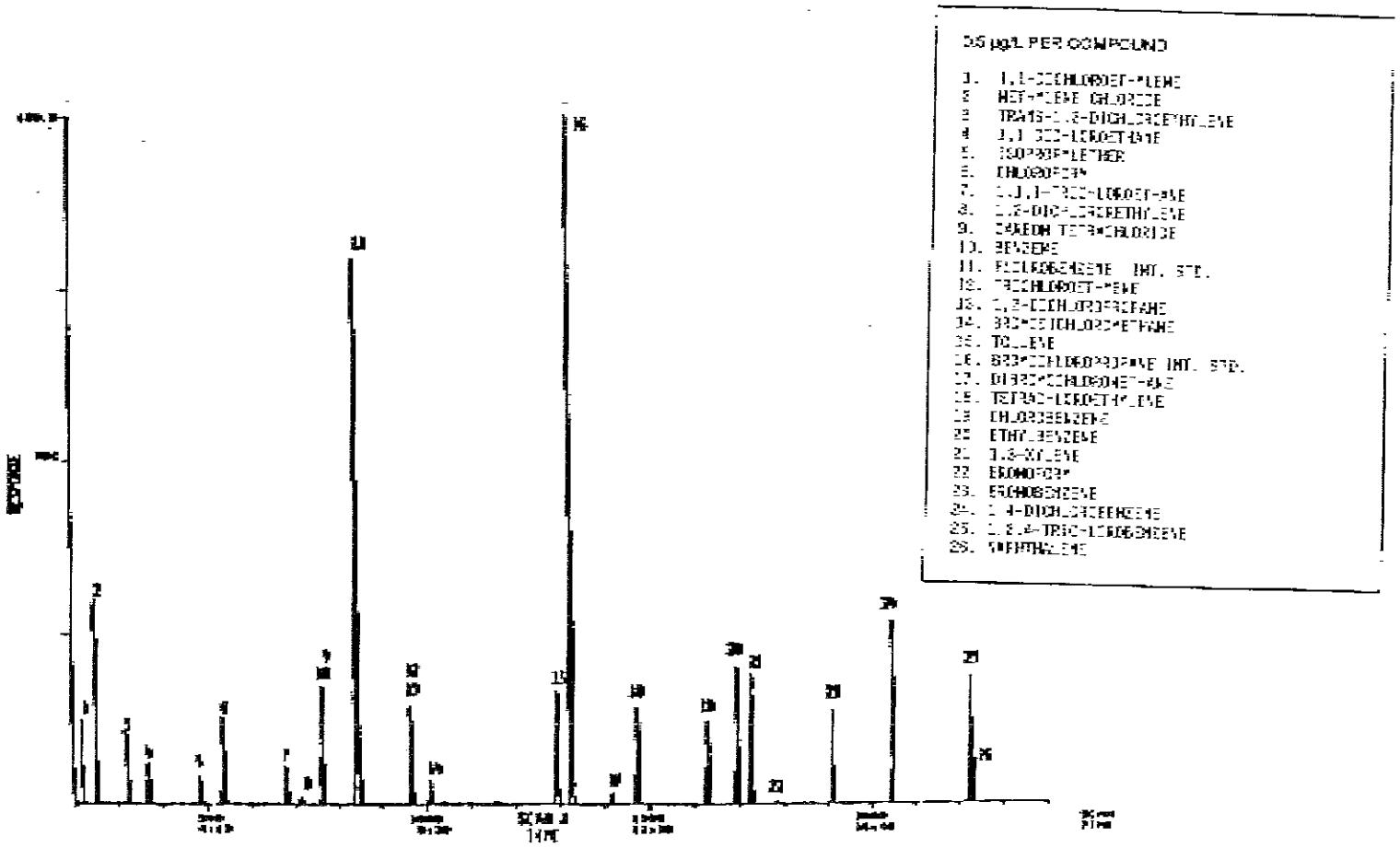
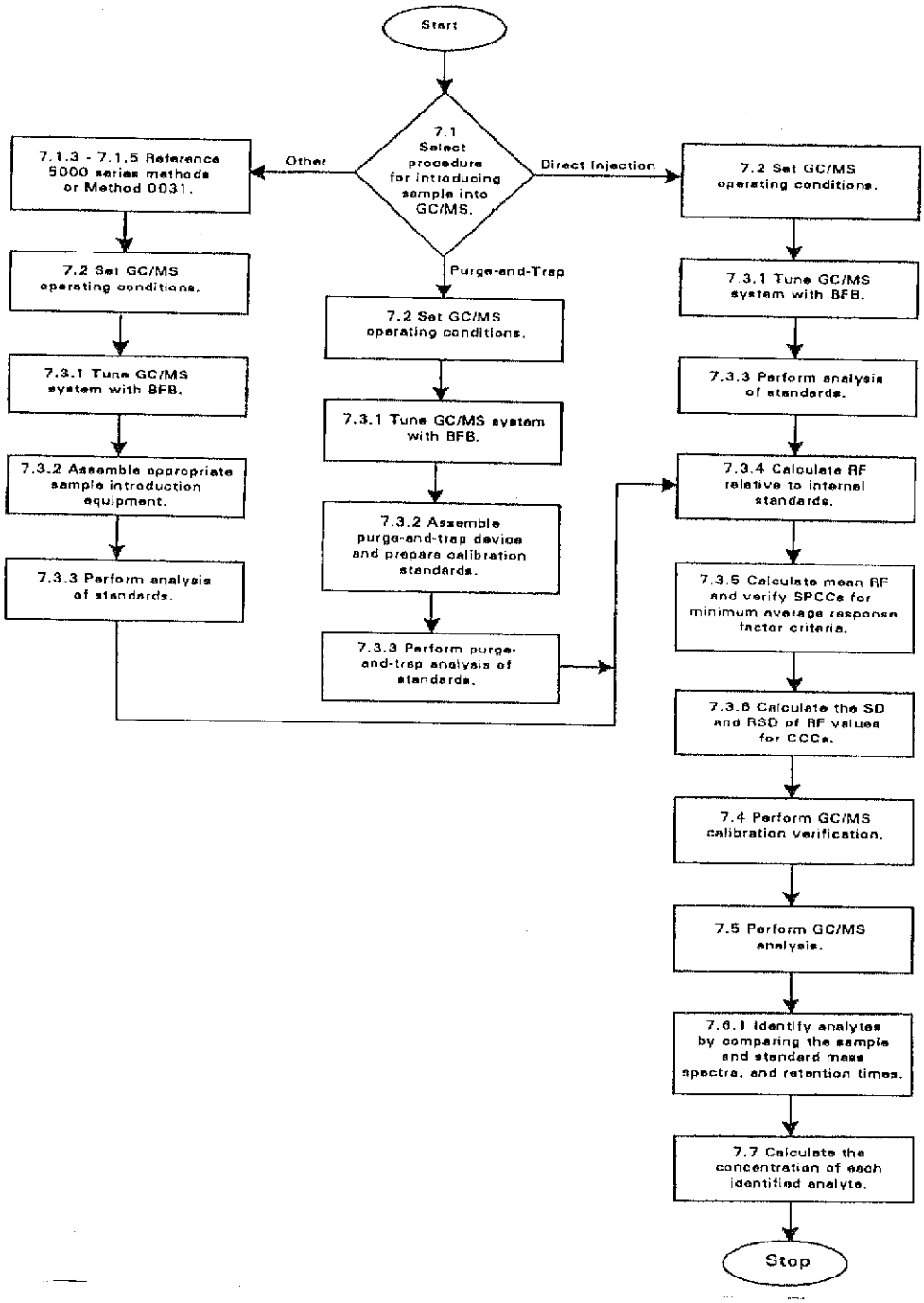


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Direct Injection
Purge-and-Trap
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 4.1

Edited by J.W. Munch (1995)

A. Alford-Stevens, J.W. Eichelberger, W.L. Budde - Method 524, Rev. 1.0 (1983)

R.W. Slater, Jr. - Revision 2.0 (1986)

J.W. Eichelberger, and W.L. Budde - Revision 3.0 (1989)

J.W. Eichelberger, J.W. Munch, and T.A. Bellar - Revision 4.0 (1992)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

89

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment[1,2]. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Analyte	Chemical Abstract Services Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl Chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon Disulfide*	75-15-0
Carbon Tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-Chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1

Analyte	Chemical Abstract Services Registry Number
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
trans-1,4-Dichloro-2-Butene*	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl Ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl Methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene Chloride	75-09-2
Methyl Iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-Pentanone*	108-10-1
Methyl-t-butyl Ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6

Analyte	Chemical Abstract Services Registry Number
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl Chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

*New compound in Revision 4.0.

1.2 Method detection limits (MDLs)[3] are compound, instrument and especially matrix dependent and vary from approximately 0.02-1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02-200 µg/L when a wide-bore thick-film capillary column is used. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02-20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and noninterfering quantitation ions (Table 1), can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar (Section 11.6.2). Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Section 11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (>2% solubility) and compounds with boiling points above 200°C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube

containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated using procedural standard calibration (Section 3.14). The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other

interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory Performance Check Solution (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock Standard Solution -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.14 Procedural Standard Calibration -- A calibration method where aqueous calibration standards are prepared and processed (e.g., purged,extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

4.4 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is

responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available[4-6] for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 Sample Containers -- 40-120 mL screw cap vials each equipped with a Teflon faced silicone septum. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

6.2 Purge and Trap System -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5 mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (<15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of <3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column. The use of a moisture control device is recommended to prohibit much of the trapped water vapor from entering the GC/MS and eventually causing instrumental problems.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: ⅓ of 2,6-diphenylene oxide polymer, ⅓ of silica gel, and ⅓ of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill ⅔ of the trap. Before initial use, the trap

should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 9.0, and provided the purge and desorption procedures specified in Section 11.0 of the method are not changed. Specifically, the purging time, the purge gas flow rate, and the desorption time may not be changed. Since many of the potential alternate sorbents may be thermally stable above 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in Section 11.0. If higher temperatures are used, the analyst should monitor the data for possible analyte and/or trap decomposition.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 lb/in^2 across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Figure 2 meets these criteria.

6.3 Gas Chromatography/Mass Spectrometer/Data System (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. If the column oven is to be cooled to 10°C or lower, a subambient oven controller will likely be required. If syringe injections of 4-bromofluorobenzene (BFB) will be used, a split/splitless injection port is required.

6.3.2 Capillary GC Columns -- Any gas chromatography column that meets the performance specifications of this method may be used (Section 10.2.4.1). Separations of the calibration mixture must be equivalent or better than those described in this method. Four useful columns have been evaluated, and observed compound retention times for these columns are listed in Table 2.

6.3.2.1 Column 1 - 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 µm film thickness.

Column 2 - 30 m x 0.53 mm ID DB-624 (J&W Scien-tific, Inc.) fused silica capillary with a 3 µm film thickness.

Column 3 - 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 µm film thickness.

Column 4 - 75 m x 0.53 mm id DB-624 (J&W Scien-tific, Inc.) fused silica capillary with a 3 µm film thickness.

6.3.3 Interfaces between the GC and MS -- The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore Columns 1, 2, and 4 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface[7] or an all-glass jet separator is an acceptable interface. Any interface can be used if the performance specifications described in this method (Sections 9.0 and 10.0) can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 When narrow-bore Column 3 is used, a cryogenic interface placed just in front of the column inlet is suggested. This interface condenses the desorbed sample components in a narrow band on an uncoated fused silica precolumn using liquid nitrogen cooling. When all analytes have been desorbed from the trap, the interface is rapidly heated to transfer them to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35-260 amu with a complete scan cycle time (including scan overhead) of two seconds or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average

spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Section 10.2.6 (or construction of a linear or second order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.0.

6.4 Syringe and Syringe Valves

6.4.1 Two 5 mL or 25 mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three two-way syringe valves with Luer ends.

6.4.3 Micro Syringes -- 10 µL and 100 µL.

6.4.4 Syringes -- 0.5 mL, 1.0 mL, and 5 mL, gas tight with shut-off valve.

6.5 Miscellaneous

6.5.1 Standard Solution Storage Containers -- 15 mL bottles with Teflon lined screw caps.

7.0 REAGENTS AND STANDARDS

7.1 Trap Packing Materials

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl Silicone Packing (Optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica Gel -- 35/60 mesh, Davison, Grade 15 or equivalent.

7.1.4 Coconut Charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 (or equivalent) by crushing through 26 mesh screen.

7.2 Reagents

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent Water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 minutes followed by a one-hour purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl Chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic Acid, ACS Reagent Grade, Granular.

7.2.6 Sodium Thiosulfate, ACS Reagent Grade, Granular.

7.3 Stock Standard Solutions -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10 mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100 µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5 mL valved gas-tight syringe with the standard to the 5.0 mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15 mL bottles equipped with Teflon lined screw caps. Methanol solutions of acrylonitrile, methyl iodide, and methyl acrylate are stable for only one week at 4°C. Methanol solutions prepared from other liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at <0°C; at room temperature, they must be discarded after one day.

7.4 Primary Dilution Standards (PDS) -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern in methanol or other suitable solvent. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Section 7.3.4 also apply to primary dilution standard solutions.

7.5 Fortification Solutions for Internal Standard and Surrogates

7.5.1 A solution containing the internal standard and the surrogate compounds is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each (any appropriate concentration is acceptable). A 5 µL aliquot of this solution added to a 25 mL water sample volume gives concentrations of 1 µg/L of each. A 5 µL aliquot of this solution added to a 5 mL water sample volume gives a concentration of 5 µg/L of each. Additional internal standards and surrogate analytes are optional. Additional surrogate compounds should be similar in physical and chemical characteristics to the analytes of concern.

7.6 Preparation of Laboratory Reagent Blank (LRB) -- Fill a 25 mL (or 5 mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject an appropriate volume of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Section 11.1.2.

7.7 Preparation of Laboratory Fortified Blank -- Prepare this exactly like a calibration standard (Section 7.8). This is a calibration standard that is treated as a sample.

7.8 Preparation of Calibration Standards (CAL)

7.8.1 The number of CALs needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern at a concentration of two to 10 times the method detection limit (Tables 4, 5, and 7) for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the method. Every CAL solution contains the internal standard and the surrogate compounds at the same concentration (5 µg/L suggested for a 5 mL sample; 1 µg/L for a 25 mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of acidified (pH 2) reagent water in a volumetric flask. Also add an appropriate volume of internal standard and surrogate compound solution from Section 7.5.1. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after one hour unless transferred to a sample bottle and sealed immediately. Alternately, aqueous calibration standards may be prepared in a gas tight, 5 mL or 25 mL syringe.

Note: If unacidified samples are being analyzed for THMs only, calibration standards should be prepared without acid.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Dechlorination

8.1.1 Collect all samples in duplicate. If samples, such as finished drinking water, are suspected to contain residual chlorine, add about 25 mg of ascorbic acid per 40 mL of sample to the sample bottle before filling. If analytes that are gases at room temperature (such as vinyl chloride), or analytes in Table 7 are not to be determined, sodium thiosulfate is recommended to reduce the residual chlorine. Three milligrams of sodium thiosulfate should be added for each 40 mL of water sample.

Note: If the residual chlorine is likely to be present >5 mg/L, a determination of the amount of the chlorine may be necessary. Diethyl-p-phenylenediamine (DPD) test kits are commercially available to determine residual chlorine in the field. Add an additional 25 mg of

ascorbic acid or 3 mg of sodium thiosulfate per each 5 mg/L of residual chlorine.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the flow to about 500 mL/min. and collect duplicate samples containing the desired dechlorinating agent from the flowing stream.

8.1.3 When sampling from an open body of water, partially fill a 1 q wide-mouth bottle or 1 L beaker with sample from a representative area. Fill duplicate sample bottles containing the desired dechlorinating agent with sample from the larger container.

8.1.4 Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed.

8.2 Sample Preservation

8.2.1 Adjust the pH of all samples to <2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample. Seal the sample bottles, Teflon face down, and mix for one minute. Exceptions to the acidification requirement are detailed in Sections 8.2.2 and 8.2.3.

Note: Do not mix the ascorbic acid or sodium thiosulfate with the HCl in the sample bottle prior to sampling.

8.2.2 **When sampling for THM analysis only**, acidification may be omitted if sodium thiosulfate is used to dechlorinate the sample. This exception to acidification does not apply if ascorbic acid is used for dechlorination.

8.2.3 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as "not acidified" and must be stored at 4°C or below. These samples must be analyzed within 24 hours of collection time if they are to be analyzed for any compounds other than THMs.

8.2.4 The samples must be chilled to about 4°C when collected and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.2 Sample Storage

8.2.1 Store samples at ≤4°C until analysis. The sample storage area must be free of organic solvent vapors and direct or intense light.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 Field Reagent Blanks (FRB)

8.3.1 Duplicate FRBs must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water and sample preservatives, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks. FRBs must remain hermetically sealed until analysis.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Section 8.1.1). The same batch of ascorbic acid and HCl should be used for the field reagent blanks as for the field samples.

9.0 QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. A MDL for each analyte must also be determined. Each laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbents, reagent water, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

9.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 2-5 µg/L depending upon the calibration range of the instrumentation.

9.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. It is recommended that a QCS from a source different than the calibration standards be used for this set of LFBs, since it will serve as a check to verify the accuracy of the standards used to generate the calibration curve. This is particularly useful

if the laboratory is using the method for the first time, and has no historical data base for standards. Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. Also add the appropriate amounts of internal standard and surrogates. If it is expected that field samples will contain a dechlorinating agent and HCl, then add these to the LFBs in the same amounts proscribed in Section 8.1.1. If only THMs are to be determined and field samples do not contain HCl, then do not acidify LFBs. Analyze each replicate according to the procedures described in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 Some analytes, particularly early eluting gases and late eluting higher molecular weight compounds, will be measured with less accuracy and precision than other analytes. However, the accuracy and precision for all analytes must fall within the limits expressed below. If these criteria are not met for an analyte of interest, take remedial action and repeat the measurements for that analyte until satisfactory performance is achieved. For each analyte, the mean accuracy must be 80-120% (i.e., an accuracy of ±20%). The precision of the recovery (accuracy) for each analyte must be <20%. These criteria are different than the ±30% response factor criteria specified in Section 10.3.5. The criteria differ, because the measurements in Section 9.3.3 as part of the initial demonstration of capability are meant to be more stringent than the continuing calibration measurements in Section 10.3.5.

9.3.4 To determine the MDL, analyze a minimum of seven LFBs prepared at a low concentration. MDLs in Table 5 were calculated from samples fortified from 0.1-0.5 µg/L, which can be used as a guide, or use calibration data to estimate a concentration for each analyte that will yield a peak with a three to five signal to noise response. Analyze the seven replicates as described in Section 11.0, and on a schedule that results in the analyses being conducted over several days. Calculate the mean accuracy and standard deviation for each analyte. Calculate the MDL using the equation in Section 13.0.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting surrogate recoveries is an especially valuable activity because surrogates are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates (Table 1) in all samples, continuing calibration checks, and

blanks. These should remain reasonably constant over time. An abrupt change may indicate a matrix effect or an instrument problem. If a cryogenic interface is utilized, it may indicate an inefficient transfer from the trap to the column. These samples must be reanalyzed or a laboratory fortified duplicate sample analyzed to test for matrix effect. A more gradual drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected.

9.5 Laboratory Reagent Blanks (LRB) -- With each batch of samples processed as a group within a work shift, analyze a LRB to determine the background system contamination.

9.6 Assessing Laboratory Performance -- Use the procedures and criteria in Sections 10.3.4 and 10.3.5 to evaluate the accuracy of the measurement of the laboratory fortified blank (LFB), which must be analyzed with each batch of samples that is processed as a group within a work shift. If more than 20 samples are in a work shift batch, analyze one LFB per 20 samples. Prepare the LFB with the concentration of each analyte that was used in the Section 9.3.3 analysis. If the acceptable accuracy for this measurement (±30%) is not achieved, the problem must be solved before additional samples may be reliably analyzed. Acceptance criteria for the IS and surrogate given in Section 10.3.4 also applies to this LFB.

Since the calibration check sample in Section 10.3.5 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as a calibration check in Section 10.3.5. Add the results of the LFB analysis to the control charts to document data quality.

9.7 If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination.

9.8 At least quarterly, replicate LFB data should be evaluated to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, or ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required unless the criteria in Section 9.4 are not met. If matrix effects are observed or suspected to be causing low recoveries, analyze a laboratory fortified matrix

sample for that matrix. The sample results should be flagged and the LFM results should be reported with them.

9.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards.

Note: Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.6, may be used here as a calibration check sample.

10.2 Initial Calibration

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.2.2.

10.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Section 11.0. If the spectrum does not meet all criteria in Table 3, the MS must be returned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

10.2.3 Purge a medium CAL solution, (e.g., 10-20 µg/L) using the procedure given in Section 11.0.

10.2.4 Performance criteria for calibration standards. Examine the stored GC/MS data with the data system software. Figures 3 and 4 shown acceptable total ion chromatograms.

10.2.4.1 GC performance -- Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are unusually broad, or if there is poor resolution between peaks, the wrong

column has been selected or remedial action is probably necessary (Section 10.3.6).

10.2.4.2 MS sensitivity -- The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Section 10.3.6.

10.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

10.2.6 Calculate a response factor (RF) for each analyte and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Section 6.3.5), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion of the internal standard
Q_x = quantity of analyte purged in nanograms or concentration units
Q_{is} = quantity of internal standard purged in ng or concentration units

10.2.6.1 For each analyte and surrogate, calculate the mean RF from analyses of CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance Section 10.3.6). Surrogate compounds are present at the same concentration on every sample, calibration standard, and all types of blanks.

10.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available

software to generate a linear or second order regression calibration curve, by plotting A_x/A_{is} vs. Q_x.

10.3 Continuing Calibration Check -- Verify the MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed using the following procedure. Additional periodic calibration checks are good laboratory practice. It is highly recommended that an additional calibration check be performed at the end of any cycle of continuous instrument operation, so that each set of field samples is bracketed by calibration check standards.

10.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng or less of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 3), the MS must be returned and adjusted to meet all criteria before proceeding with the continuing calibration check.

10.3.2 Purge a CAL solution and analyze with the same conditions used during the initial calibration. Selection of the concentration level of the calibration check standard should be varied so that the calibration is verified at more than one point over the course of several days.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte of concern and surrogate compound from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear or second order regression is used, the concentration measured using the calibration curve must be within 30% of the true value of the concentration in the calibration solution. If these conditions do not exist, remedial action must be taken which may require recalibration. All data from field samples obtained after the last successful calibration check standard, should be considered suspect. After remedial action has been taken, duplicate samples should be analyzed if they are available.

10.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner. This applies only if the injection liner is an integral part of the system.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a slight change in retention times. Analyst may need to redefine retention windows.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10.3.6.9 Replace the trap, especially when only a few compounds fail the criteria in Section 10.3.5 while the majority are determined successfully. Also check for gas leaks in the purge and trap unit as well as the rest of the analytical system.

10.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

10.4.1 Fill the purging device with 25.0 mL (or 5 mL) of reagent water or aqueous calibration standard.

10.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 µL and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL

of room air or carrier gas. Inject the gaseous standard before five minutes of the 11-minute purge time have elapsed.

10.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)\ (V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L
C = Concentration of gaseous standard in mg/L (v/v)
V = Volume of standard injected in mL

11.0 PROCEDURE

11.1 Sample Introduction and Purging

11.1.1 This method is designed for a 25 mL or 5 mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the helium purge gas flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25 mL (or 5 mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25 mL (or 5 mL). To all samples, blanks, and calibration standards, add 5 µL (or an appropriate volume) of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11 minutes at ambient temperature.

11.1.4 Standards and samples must be analyzed in exactly the same manner. Room temperature must be reasonably constant, and changes in excess of 10°F will adversely affect the accuracy and precision of the method.

11.2 Sample Desorption

11.2.1 Non-Cryogenic Interface -- After the 11-minute purge, place the purge and trap system in the desorb mode and preheat the trap to 180°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at a flow rate suitable for the column being used (optimum desorb flow rate is 15 mL/min.) for about four minutes, begin the GC temperature program, and start data acquisition.

11.2.2 Cryogenic Interface -- After the 11-minute purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is a -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/min. for about five minutes. At the end of the five minutes desorption cycle, rapidly heat the cryogenic trap to 250°C, and simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.3 While the trapped components are being introduced into the gas chromatograph (or cryogenic interface), empty the purging device using the sample syringe and wash the chamber with two 25 mL flushes of reagent water. After the purging device has been emptied, leave syringe valve open to allow the purge gas to vent through the sample introduction needle.

11.3 Gas Chromatography/mass Spectrometry -- Acquire and store data over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of two seconds or less. If water, methanol, or carbon dioxide cause a background problem, start at 47 or 48 m/z. If ketones are to be determined, data must be acquired starting at m/z 43. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Suggested temperature programs are provided below. Alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide-bore Columns 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to within the capacity of the separator, or about 15 mL/min. The column temperature is reduced 10°C and held for five minutes from the beginning of desorption, then programmed to 160°C at 6°C/min., and held until all components have eluted.

11.3.2 Multi-ramp temperature program for wide-bore Column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced to 10°C and held for six minutes from the beginning of desorption, then heated to 70°C at 10°/min., heated to 120°C at 5°/min., heated to 180° at 8°/min., and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow-bore Column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced to 10°C and held for five minutes from the beginning of vaporization from the cryogenic trap, programmed at 6°/min. for 10 minutes, then 15°/min. for five minutes to 145°C, and held until all components have eluted.

11.3.4 Multi-ramp temperature program for wide-bore Column 4 with the open split interface. Adjust the helium carrier gas flow rate to about 7.0 mL/min. The column temperature is -10°C and held for six minutes. from beginning of desorption, then heated to 100°C at 10°C/min., heated to 200°C at 5°C/min. and held at 200°C for eight minutes or until all compounds of interest had eluted.

11.4 Trap Reconditioning -- After desorbing the sample for four minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. Maintain the moisture control module, if utilized, at 90°C to remove residual water. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 Termination of Data Acquisition -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 Identification of Analytes -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously

represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. If the response for any analyte exceeds the linear range of the calibration established in Section 10.0, obtain and dilute a duplicate a duplicate sample. Do not extrapolate beyond the calibration range.

12.1.1 Calculate analyte and surrogate concentrations, using the multi-point calibration established in Section 10.0. Do not use the daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)\ (Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample
A_x = integrated abundance of the quantitation ion of the analyte in the sample
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample
V = original water sample volume in mL
RF = mean response factor of analyte from the initial calibration

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear or second order regression curve established in Section 10.0. Do not use the daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at concentrations between 0.1 and 5 µg/L. Results were obtained using the four columns specified (Section 6.3.2.1) and the open split or jet separator (Section 6.3.3.1), or the cryogenic interface (Sect. 6.3.3.2). These data are shown in Tables 4-8.

13.2 With these data, method detection limits were calculated using the formula[3]:

$$MDL = S\ t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates

S = the standard deviation of the replicate analyses

14.0 POLLUTION PREVENTION

14.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

15.0 WASTE MANAGEMENT

15.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

16.0 REFERENCES

1. J.W. Munch, J.W. Eichelberger. "Evaluation of 48 Compounds for Possible Inclusion in USEPA Method 524.2, Revision 3.0: Expansion of the Method Analyte List to a Total of 83 Compounds", J. Chro. Sci. ,30, 471,1992.

2. C. Madding. "Volatile Organic Compounds in Water by Purge and Trap Capillary Column GC/MS", Proceedings of the Water Quality Technology Conference, American Water Works Association, Denver, CO, December 1984.

3. J.A. Glaser, D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde. "Trace Analyses for Wastewaters", Environ. Sci. Technol., 15, 1426, 1981.

4. "Carcinogens-Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry", (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. R.F. Arrendale, R.F. Severson, and O.T. Chortyk. "Open Split Interface for Capillary Gas Chromatography/Mass Spectrometry", Anal. Chem. 1984, 56, 1533.

8. J.J. Flesch, P.S. Fair. "The Analysis of Cyanogen Chloride in Drinking Water", Proceedings of Water Quality Technology Conference, American Water Works Association, St. Louis, MO., November 14-16, 1988.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal Standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174, 176
1,2-Dichlorobenzene-d4	150	152	115, 150
Target Analytes			
Acetone	58	43	58
Acrylonitrile	53	52	53
Allyl Chloride	76	76	49
Benzene	78	78	77
Bromobenzene	156	156	77, 158
Bromochloromethane	128	128	49, 130
Bromodichloromethane	162	83	85, 127
Bromoform	250	173	175, 252
Bromomethane	94	94	96
2-Butanone	72	43	57, 72
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Caron Disulfide	76	76	--
Carbon Tetrachloride	152	117	119
Chloroacetonitrile	75	48	75
Chlorobenzene	112	112	77, 114
1-Chlorobutane	92	56	49
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155, 157
1,2-Dibromoethane	186	107	109, 188
Dibromomethane	172	93	95, 174
1,2-Dichlorobenzene	146	146	111, 148

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
1,3-Dichlorobenzene	146	146	111, 148
1,4-Dichlorobenzene	146	146	111, 148
trans-1,4-Dichloro-2-Butene	124	53	88, 75
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65, 83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61, 63
cis-1,2-Dichloroethene	96	96	61, 98
trans-1,2-Dichloroethene	96	96	61, 98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97
1,1-Dichloropropene	110	75	110, 77
1,1-Dichloropropanone*	126	43	83
cis-1,3-Dichloropropene	110	75	110
trans-1,3-Dichloropropene	110	75	110
Diethyl Ether	74	59	45, 73
Ethylbenzene	106	91	106
Ethyl Methacrylate	114	69	99
Hexachlorobutadiene	258	225	260
Hexachloroethane	234	117	119, 201
2-Hexanone	100	43	58
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134, 91
Methacrylonitrile	67	67	52
Methyl Acrylate	86	55	85
Methylene Chloride	84	84	86, 49
Methyl Iodide	142	142	127
Methylmethacrylate	100	69	99
4-Methyl-2-Pentanone	100	43	58, 85
Methyl-t-butyl Ether	88	73	57
Naphthalene	128	128	– –
Nitrobenzene	123	51	77
2-Nitropropane	89	46	– –
Pentachloroethane	200	117	119, 167
Propionitrile	55	54	– –
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133, 119
1,1,2,2-Tetrachloroethane	166	83	131, 85
Tetrachloroethene	164	166	168, 129

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Tetrahydrofuran	72	71	72, 42
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99, 61
1,1,2-Trichloroethane	132	83	97, 85
Trichloroethene	130	95	130, 132
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

[a]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SET OF CONDITIONS[a]

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
Internal Standard					
Fluorobenzene	8:49	6:27	14:06	8:03	22:00
Surrogates					
4-Bromofluorobenzene	18:38	15:43	23:38		31:21
1,2-Dichlorobenzene-d4	22:16	19:08	27:25		35:51
Target Analytes					
Acetone					16:14
Acrylonitrile					17:49
Allyl Chloride					16:58
Benzene	8:14	5:40	13:30	7:25	21:32
Bromobenzene	18:57	15:52	24:00	16:25	31:52
Bromochloromethane	6:44	4:23	12:22	5:38	20:20
Bromodichloromethane	10:35	8:29	15:48	9:20	23:36
Bromoform	17:56	14:53	22:46	15:42	30:32
Bromomethane	2:01	0:58	4:48	1:17	12:26
2-Butanone					19:41
n-Butylbenzene	22:13	19:29	27:32	17:57	35:41
sec-Butylbenzene	20:47	18:05	26:08	17:28	34:04
tert-Butylbenzene	20:17	17:34	25:36	17:19	33:26
Caron Disulfide					16:30
Carbon Tetrachloride	7:37	5:16	13:10	7:25	21:11
Chloroacetonitrile					23:51
Chlorobenzene	15:46	13:01	20:40	14:20	28:26
1-Chlorobutane					21:00
Chloroethane	2:05	1:01		1:27	
Chloroform	6:24	4:48	12:36	5:33	20:27
Chloromethane	1:38	0:44	3:24	0:58	9:11
2-Chlorotoluene	19:20	16:25	24:32	16:44	32:21
4-Chlorotoluene	19:30	16:43	24:46	16:49	32:38
Cyanogen Chloride[8]				1:03	
Dibromochloromethane	14:23	11:51	19:12	12:48	26:57
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02	38:20
1,2-Dibromoethane	14:44	11:50	19:24	13:36	27:19
Dibromomethane	10:39	7:56	15:26	9:05	23:22
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47	35:55

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SET OF CONDITIONS[a]

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28	34:31
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38	34:45
trans-1,4-Dichloro-2-Butene					31:44
Dichlorodifluoromethane	1:33	0:42	3:08	0:53	7:16
1,1-Dichloroethane	4:51	2:56	10:48	4:02	18:46
1,2-Dichloroethane	8:24	5:50	13:38	7:00	21:31
1,1-Dichloroethene	2:53	1:34	7:50	2:20	16:01
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04	19:53
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32	17:54
1,2-Dichloropropane	10:05	7:40	15:12	8:56	23:08
1,3-Dichloropropane	14:02	11:19	18:42	12:29	26:23
2,2-Dichloropropane	6:01	3:48	11:52	5:19	19:54
1,1-Dichloropropanone					24:52
1,1-Dichloropropene	7:49	5:17	13:06	7:10	21:08
cis-1,3-Dichloropropene	11:58		16:42		24:24
trans-1,3-Dichloropropene	13:46		17:54		25:33
Diethyl Ether					15:31
Ethylbenzene	15:59	13:23	21:00	14:44	28:37
Ethyl Methacrylate					25:35
Hexachlorobutadiene	26:59	23:41	32:04	19:14	42:03
Hexachloroethane					36:45
Hexanone					26:23
Isopropylbenzene	18:04	15:28	23:18	16:25	30:52
4-Isopropyltoluene	21:12	18:31	26:30	17:38	34:27
Methacrylonitrile					20:15
Methyl Acrylate					20:02
Methylene Chloride	3:36	2:04	9:16	2:40	17:18
Methyl Iodide					16:21
Methylmethacrylate					23:08
4-Methyl-2-Pentanone					24:38
Methyl-t-butyl Ether					17:56
Naphthalene	27:10	23:31	32:12	19:04	42:29
Nitrobenzene					39:02
2-Nitropropane					23:58
Pentachloroethane					33:33
Propionitrile					19:58
n-Propylbenzene	19:04	16:25	24:20	16:49	32:00
Styrene	17:19	14:36	22:24	15:47	29:57
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44	28:35
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47	31:35
Tetrachloroethene	13:44	11:09	18:36	13:12	26:27

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SET OF CONDITIONS[a]

Compound	Retention Time (min:sec) Col. 1[b]	Col. 2[b]	Col. 2[c]	Col. 3[d]	Col. 4[e]
Tetrahydrofuran					20:26
Toluene	12:26	10:00	17:24	11:31	25:13
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14	43:31
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50	41:26
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46	20:51
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59	25:59
Trichloroethene	9:35	7:16	14:48	9:01	22:42
Trichlorofluoromethane	2:16	1:11	6:12	1:46	14:18
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16	31:47
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19	33:33
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59	32:26
Vinyl Chloride	1:43	0:47	3:56	1:02	10:22
o-Xylene	17:07	14:31	22:16	15:47	29:56
m-Xylene	16:10	13:41	21:22	15:18	28:53
p-Xylene	16:07	13:41	21:18	15:18	28:53

[a]Columns 1-4 are those given in Sectioin 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (Columns 1-2, and 4) or from the beginning of thermal release from the cryogenic interface (Column 3).
[b]GC conditions given in Section 11.3.1.
[c]GC conditions given in Section 11.3.2.
[d]GC conditions given in Section 11.3.3.
[e]GC conditions given in Section 11.3.4.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15-40% of Mass 95
75	30-80% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5-9% of Mass 95
173	<2% of Mass 174
174	>50% of Mass 95
175	5-9% of Mass 174
176	>95% but <101% of Mass 174
177	5-9% of Mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon Tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-Chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2-Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit[b] (µg/L)
Methylene Chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl Chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a]Data obtained by using Column 1 with a jet separator interface and a quadrupole mass spectrometer (Section 11.3.1) with analytes divided among three solutions.
[b]Replicate samples at the lowest concentration listed in Column 2 of this table were analyzed. These results were used to calculate MDLs.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW-BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Benzene	0.1	99	6.2	0.03
Bromobenzene	0.5	97	7.4	0.11
Bromochloromethane	0.5	97	5.8	0.07
Bromodichloromethane	0.1	100	4.6	0.03
Bromoform	0.1	99	5.4	0.20
Bromomethane	0.1	99	7.1	0.06
n-Butylbenzene	0.5	94	6.0	0.03
sec-Butylbenzene	0.5	90	7.1	0.12
tert-Butylbenzene	0.5	90	2.5	0.33
Carbon Tetrachloride	0.1	92	6.8	0.08
Chlorobenzene	0.1	91	5.8	0.03
Chloroethane	0.1	100	5.8	0.02
Chloroform	0.1	95	3.2	0.02
Chloromethane	0.1	99	4.7	0.05
2-Chlorotoluene	0.1	99	4.6	0.05
4-Chlorotoluene	0.1	96	7.0	0.05
Cyanogen Chloride[b]		92	10.6	0.30
Dibromochloromethane	0.1	99	5.6	0.07
1,2-Dibromo-3-Chloropropane	0.1	92	10.0	0.05
1,2-Dibromoethane	0.1	97	5.6	0.02
Dibromomethane	0.1	93	6.9	0.03
1,2-Dichlorobenzene	0.1	97	3.5	0.05
1,3-Dichlorobenzene	0.1	99	6.0	0.05
1,4-Dichlorobenzene	0.1	93	5.7	0.04
Dichlorodifluoromethane	0.1	99	8.8	0.11
1,1-Dichloroethane	0.1	98	6.2	0.03
1,2-Dichloroethane	0.1	100	6.3	0.02
1,1-Dichloroethene	0.1	95	9.0	0.05
cis-1,2-Dichloroethene	0.1	100	3.7	0.06
trans-1,2-Dichloroethene	0.1	98	7.2	0.03
1,2-Dichloropropane	0.1	96	6.0	0.02
1,3-Dichloropropane	0.1	99	5.8	0.04
2,2-Dichloropropane	0.1	99	4.9	0.05
1,1-Dichloropropene	0.1	98	7.4	0.02
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW-BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Isopropylbenzene	0.5	98	6.4	0.10
4-Isopropyltoluene	0.5	87	13.0	0.26
Methylene Chloride	0.5	97	13.0	0.09
Naphthalene	0.1	98	7.2	0.04
n-Propylbenzene	0.1	99	6.6	0.06
Styrene	0.1	96	19.0	0.06
1,1,1,2-Tetrachloroethane	0.1	100	4.7	0.04
1,1,2,2-Tetrachloroethane	0.1	100	12.0	0.20
Tetrachloroethene	0.1	96	5.0	0.05
Toluene	0.1	100	5.9	0.08
1,2,3-Trichlorobenzene	0.1	98	8.9	0.04
1,2,4-Trichlorobenzene	0.1	91	16.0	0.20
1,1,1-Trichloroethane	0.1	100	4.0	0.04
1,1,2-Trichloroethane	0.1	98	4.9	0.03
Trichloroethene	0.1	96	2.0	0.02
Trichlorofluoromethane	0.1	97	4.6	0.07
1,2,3-Trichloropropane	0.1	96	6.5	0.03
1,2,4-Trimethylbenzene	0.1	96	6.5	0.04
1,3,5-Trimethylbenzene	0.1	99	4.2	0.02
Vinyl Chloride	0.1	96	0.2	0.04
o-Xylene	0.1	94	7.5	0.06
m-Xylene	0.1	94	4.6	0.03
p-Xylene	0.1	97	6.1	0.06

[a]Data obtained by using Column 3 with a cryogenic interface and a quadrupole mass spectrometer (Section 11.3.3).
[b]Reference 8.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	–	–	–	–
Surrogates					
4-Bromofluorobenze	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d_4	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon Tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	[d]	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-Chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	[d]	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,2-Dichloropropene[c]					
trans-1,2-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene Chloride	27	[e]		[e]	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl Chloride	36	104	3.5	115	14.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	[f]		[f]	
p-Xylene	61	98	2.3	103	1.4

[a]Data obtained using Column 2 with the open split interface and an ion trap mass spectrometer (Section 11.3.2) with all method analytes in the same reagent water solution.
[b]Designation in Figures 1 and 2.
[c]Not measured; authentic standards were not available.
[d]Not found at 0.2 µg/L.
[e]Not measured; methylene chloride was in the laboratory reagent blank.
[f]m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING WIDE-BORE CAPILLARY COLUMN 4[a]

Compound	True Conc. (µg/L)	Mean Conc. Detected (µg/L)	Rel. Std. Dev. (%)	Method Detect. Limit (µg/L)
Acetone	1.0	1.6	5.7	0.28
Acrylonitrile	1.0	0.81	8.7	0.22
Allyl Chloride	1.0	0.90	4.7	0.13
2-Butanone	2.0	2.7	5.6	0.48
Carbon Disulfide	0.20	0.19	15	0.093
Chloroacetonitrile	1.0	0.83	4.7	0.12
1-Chlorobutane	1.0	0.87	6.6	0.18
trans-Dichloro-2-Butene	1.0	1.3	8.7	0.36
1,1-Dichloropropanone	5.0	4.2	7.7	1.0
cis-1,3-Dichloropropene	0.20	0.20	3.1	0.020
trans-1,3-Dichloropropene	0.10	0.11	14	0.048
Diethyl Ether	1.0	0.92	9.5	0.28
Ethyl Methacrylate	0.20	0.23	3.9	0.028
Hexachloroethane	0.20	0.18	10	0.057
2-Hexanone	1.0	1.1	12	0.39
Methacrylonitrile	1.0	0.92	4.2	0.12
Methylacrylate	1.0	1.2	12	0.45
Methyl Iodide	0.20	0.19	3.1	0.019
Methylmethacrylate	1.0	1.0	13	0.43
4-Methyl-2-Pentanone	0.40	0.56	9.7	0.090
Methyl-tert-Butylether	0.40	0.52	5.6	1.2
Nitrobenzene	2.0	2.1	18	0.16
2-Nitrobenzene	1.0	0.83	6.2	0.14
Pentachloroethane	0.20	0.23	20	0.14
Propionitrile	1.0	0.87	5.3	1.6
Tetrahydrofuran	5.0	3.9	13	

[a]Data obtained using Column 4 with the open split interface and an ion trap mass spectrometer.

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L[a]

	Reagent Water			Raw Water			Tap Water		
Compound	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Acetone	19	12%	95%	21	3.7%	105%	22	8.2%	110%
Acrylonitrile	20	4.7%	100%	22	3.4%	110%	21	1.3%	105%
Allyl Chloride	20	5.1%	100%	20	2.8%	100%	19	3.5%	95%
2-Butanone	17	11%	85%	19	7.3%	95%	17	5.6%	85%
Carbon Disulfide	19	6.4%	95%	18	2.5%	90%	18	3.0%	90%
Chloroacetonitrile	20	4.1%	100%	23	4.7%	115%	23	1.3%	115%
1-Chlorobutane	18	6.4%	90%	19	2.2%	95%	17	2.2%	85%
t-1,2-Dichloro-2-Butene	19	4.1%	95%	22	2.9%	110%	21	0.90%	105%
1,1-Dichloropropanone	20	5.6%	100%	22	6.4%	110%	21	7.7%	105%
Diethyl Ether	18	6.7%	90%	22	3.4%	110%	22	2.6%	110%
Ethyl Methacrylate	20	3.7%	100%	23	2.6%	115%	22	1.8%	110%
Hexachloroethane	20	6.1%	100%	21	2.5%	105%	21	2.0%	105%
2-Hexanone	19	6.3%	95%	21	3.8%	105%	21	4.0%	105%
Methacrylonitrile	20	3.4%	100%	23	2.9%	115%	22	2.0%	110%
Methylacrylate	20	3.7%	100%	22	3.1%	110%	21	2.1%	105%

TABLE 8. ACCURACY AND PRECISION FROM FOUR DETERMINATIONS OF METHOD ANALYTES IN THREE WATER MATRICES FORTIFIED AT 20 µG/L[a]

	Reagent Water			Raw Water			Tap Water		
Compound	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)	Mean (µg/L)	Dev. (%)	(% of True Value)
Methyl Iodide	20	4.4%	100%	19	3.8%	95%	19	3.0%	95%
Methylmethacrylate	20	3.7%	100%	23	3.3%	115%	23	2.7%	115%
4-Methyl-2-Pentanone	19	8.7%	95%	21	5.5%	105%	22	7.2%	110%
Methyl-tert-Butylether	19	3.5%	95%	22	2.5%	110%	22	3.6%	110%
Nitrobenzene	20	5.4%	100%	22	4.8%	110%	21	2.4%	105%
2-Nitropropane	20	6.1%	100%	23	5.1%	115%	22	3.2%	110%
Pentachloroethane	19	5.2%	95%	21	2.6%	105%	22	1.7%	110%
Propionitrile	20	4.5%	100%	23	3.9%	115%	23	2.4%	115%
Tetrahydrofuran	20	2.8%	100%	24	3.2%	120%	21	2.9%	105%

[a]Data obtained using Column 4 with the open-split interface and an ion trap mass spectrometer with all Table 8 analyses in the same reagent water solution.[1]

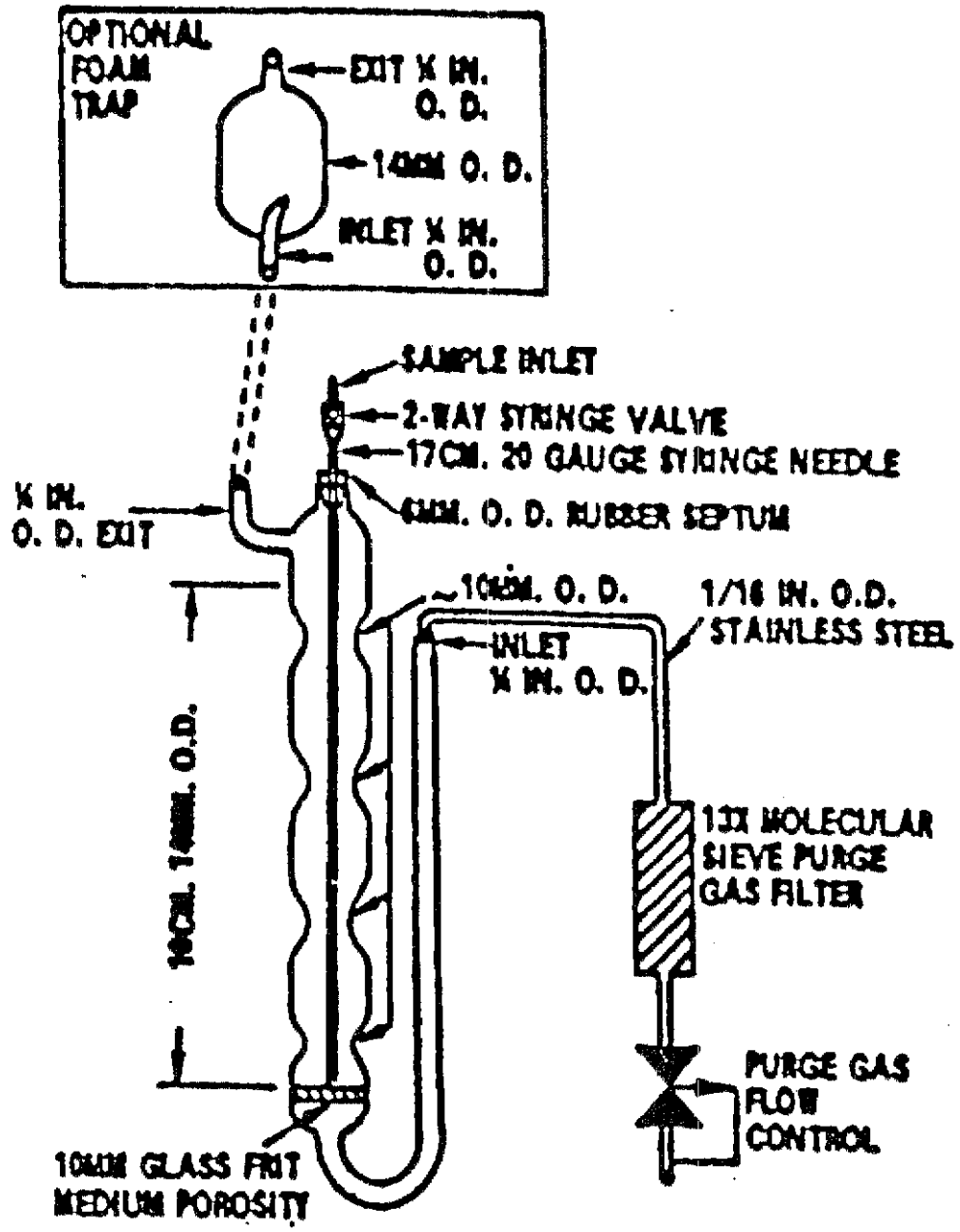


FIGURE 1. PURGING DEVICE

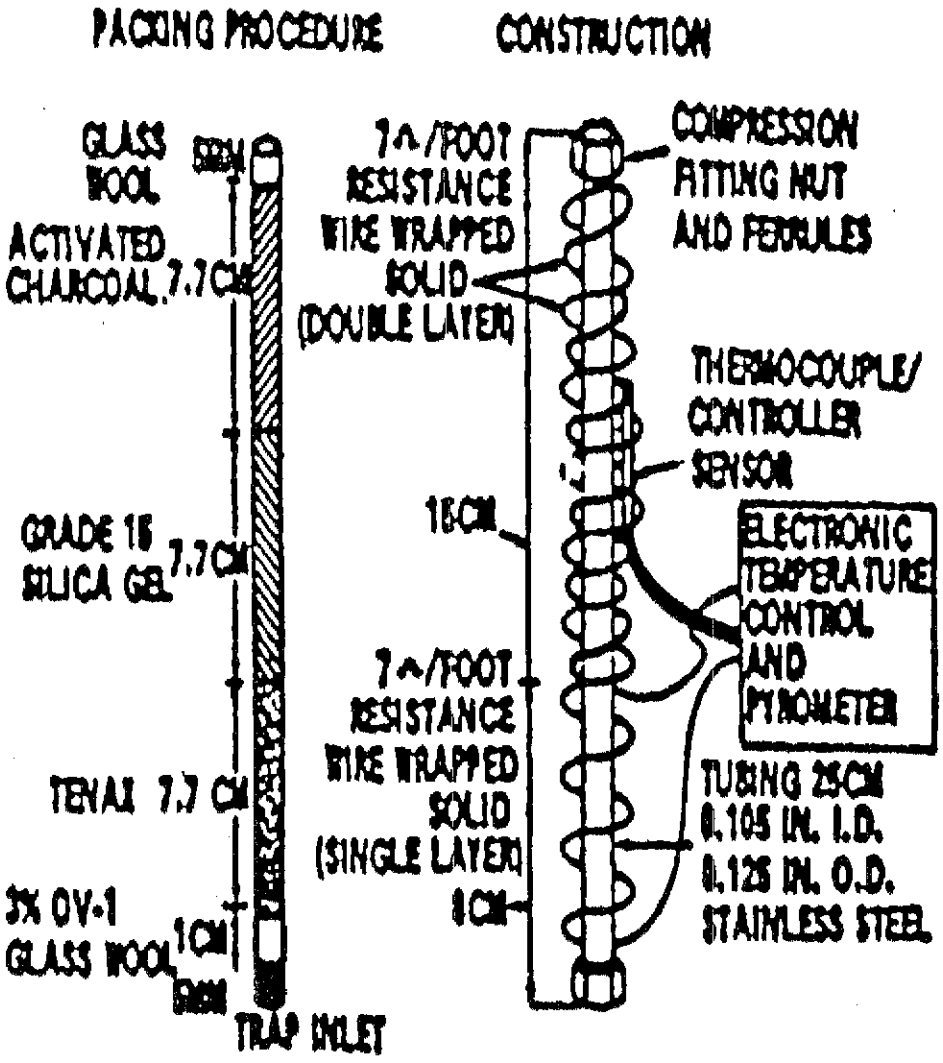


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

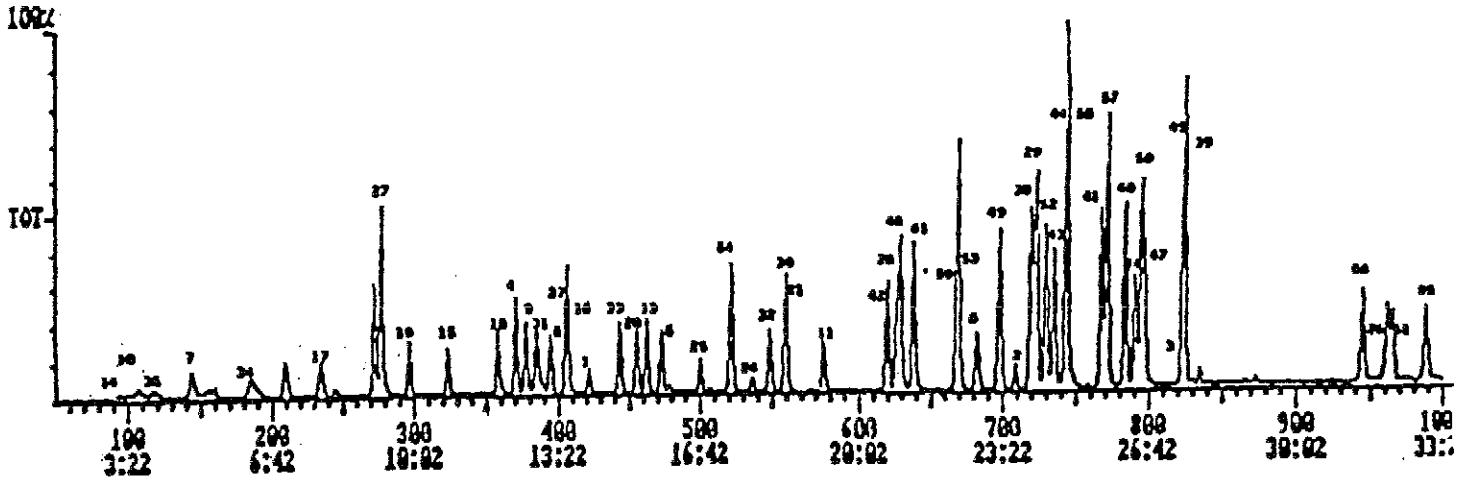
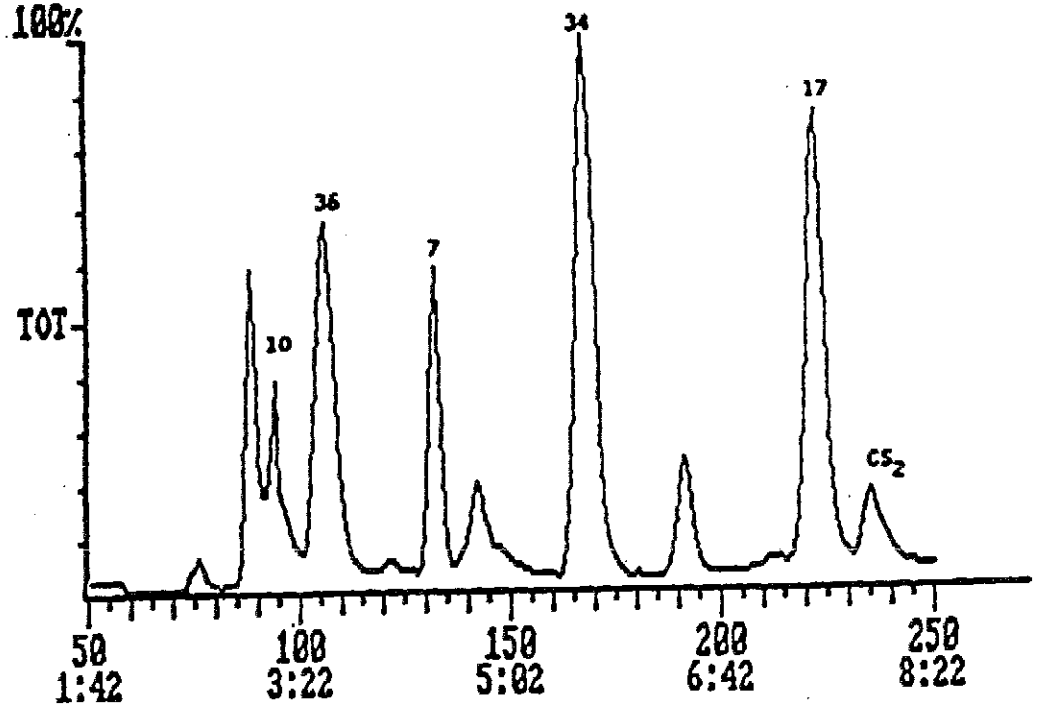


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



Appendix A Method Detectin Limits (MDL) for GCMSV#3

WATER

Compound	MDL (ug/L)
dichlorodifluoromethane	0.23
chlorodifluoromethane	0.15
chloromethane	0.76
vinyl chloride	0.39
bromomethane	0.52
chloroethane	0.12
trichlorofluoromethane	0.27
freon	0.19
acetone	1.84
1,1-dichloroethene	0.25
methylene chloride	0.26
carbon disulfide	0.26
tert-butylmethylether	0.14
trans-1,2-dichloroethene	0.35
vinyl acetate	1.12
1,1-dichloroethane	0.20
methyl ethyl ketone	1.77
2,2-dichloropropane	0.34
cis-1,2-dichloroethene	0.17
chloroform	0.23
bromochloromethane	0.19
1,1,1-trichloroethane	0.22
1,1-dichloropropene	0.45
carbon tetrachloride	0.61
1,2-dichloroethane	0.18
benzene	0.17
trichloroethene	0.29
1,2-dichloropropane	0.16
bromodichloromethane	0.23
dibromomethane	0.26
2-chloroethylvinylether	0.50
4-methyl-2-pentanone	6.48
cis-1,3-dichloropropene	0.10
toluene	0.29
trans-1,3-dichloropropene	0.20
1,1,2-trichloroethane	0.17
2-hexanone	0.96
1,3-dichloropropane	0.11
tetrachloroethene	0.16
dibromochloromethane	0.15
1,2-dibromoethane	0.19
chlorobenzene	0.17
1,1,1,2-tetrachloroethane	0.22
ethylbenzene	0.19
m+p-xylene	0.37
o-xylene	0.23
styrene	0.14
bromoform	0.13
isopropylbenzene	0.16
1,1,2,2-tetrachloroethane	0.30
1,2,3-trichloropropane	0.40
n-propylbenzene	0.24
bromobenzene	0.30
p-ethyltoluene	0.18
1,3,5-trimethylbenzene	0.20
2-chlorotoluene	0.17
4-chlorotoluene	0.13
tert-butylbenzene	0.30
1,2,4-trimethylbenzene	0.18
sec-butylbenzene	0.20
4-isopropyltoluene	0.17
1,3-dichlorobenzene	0.19
1,4-dichlorobenzene	0.19
n-butylbenzene	0.20
p-diethylbenzene	0.20
1,2-dichlorobenzene	0.17
1,2,4,5-tetramethylbenzene	0.12
1,2-dibromo-3-chloropropane	0.39
1,2,4-trichlorobenzene	0.18
hexachlorobutadiene	0.45
naphthalene	0.16
1,2,3-trichlorobenzene	0.25

SOIL

Compound	MDL (ug/L)
dichlorodifluoromethane	0.42
chlorodifluoromethane	0.69
chloromethane	0.75
vinyl chloride	0.24
bromomethane	0.55
chloroethane	0.43
trichlorofluoromethane	0.41
freon	0.36
acetone	1.63
1,1-dichloroethene	0.40
methylene chloride	0.42
carbon disulfide	0.43
tert-butylmethylether	0.18
trans-1,2-dichloroethene	0.40
vinyl acetate	2.01
1,1-dichloroethane	0.32
methyl ethyl ketone	2.61
2,2-dichloropropane	0.66
cis-1,2-dichloroethene	0.21
chloroform	0.31
bromochloromethane	0.30
1,1,1-trichloroethane	0.39
1,1-dichloropropene	0.64
carbon tetrachloride	0.50
1,2-dichloroethane	0.27
benzene	0.41
trichloroethene	0.30
1,2-dichloropropane	0.34
bromodichloromethane	0.70
dibromomethane	0.27
2-chloroethylvinylether	0.81
4-methyl-2-pentanone	0.54
cis-1,3-dichloropropene	0.21
toluene	0.22
trans-1,3-dichloropropene	0.17
1,1,2-trichloroethane	0.12
2-hexanone	1.79
1,3-dichloropropane	0.16
tetrachloroethene	0.42
dibromochloromethane	0.35
1,2-dibromoethane	0.28
chlorobenzene	0.23
1,1,1,2-tetrachloroethane	0.20
ethylbenzene	0.24
m+p-xylene	0.37
o-xylene	0.26
styrene	0.12
bromoform	0.21
isopropylbenzene	0.30
1,1,2,2-tetrachloroethane	0.27
1,2,3-trichloropropane	0.06
n-propylbenzene	0.36
bromobenzene	0.16
p-ethyltoluene	0.49
1,3,5-trimethylbenzene	0.32
2-chlorotoluene	0.35
4-chlorotoluene	0.31
tert-butylbenzene	0.32
1,2,4-trimethylbenzene	0.24
sec-butylbenzene	0.39
4-isopropyltoluene	0.44
1,3-dichlorobenzene	0.25
1,4-dichlorobenzene	0.22
n-butylbenzene	0.65
p-diethylbenzene	0.44
1,2-dichlorobenzene	0.16
1,2,4,5-tetramethylbenzene	0.26
1,2-dibromo-3-chloropropane	0.31
1,2,4-trichlorobenzene	0.57
hexachlorobutadiene	0.58
naphthalene	0.19
1,2,3-trichlorobenzene	0.33

Appendix B Practical Quantitation Limits (PQL) for GCMSV#3

WATER

Compound	PQL (ug/L)
dichlorodifluoromethane	1.00
chlorodifluoromethane	1.00
chloromethane	1.00
vinyl chloride	1.00
bromomethane	1.00
chloroethane	1.00
trichlorofluoromethane	1.00
freon	1.00
acetone	10.00
1,1-dichloroethane	1.00
methylene chloride	1.00
carbon disulfide	1.00
tert-butylmethylether	1.00
trans-1,2-dichloroethene	1.00
vinyl acetate	10.00
1,1-dichloroethane	1.00
methyl ethyl ketone	10.00
2,2-dichloropropane	1.00
cis-1,2-dichloroethene	1.00
chloroform	1.00
bromochloromethane	1.00
1,1,1-trichloroethane	1.00
1,1-dichloropropene	1.00
carbon tetrachloride	1.00
1,2-dichloroethane	1.00
benzene	1.00
trichloroethene	1.00
1,2-dichloropropane	1.00
bromodichloromethane	1.00
dibromomethane	1.00
2-chloroethylvinylether	1.00
4-methyl-2-pentanone	10.00
cis-1,3-dichloropropene	1.00
toluene	1.00
trans-1,3-dichloropropene	1.00
1,1,2-trichloroethane	1.00
2-hexanone	10.00
1,3-dichloropropane	1.00
tetrachloroethene	1.00
dibromochloromethane	1.00
1,2-dibromoethane	1.00
chlorobenzene	1.00
1,1,1,2-tetrachloroethane	1.00
ethylbenzene	1.00
m+p-xylene	2.00
o-xylene	1.00
styrene	1.00
bromoform	1.00
isopropylbenzene	1.00
1,1,2,2-tetrachloroethane	1.00
1,2,3-trichloropropane	1.00
n-propylbenzene	1.00
bromobenzene	1.00
p-ethyltoluene	1.00
1,3,5-trimethylbenzene	1.00
2-chlorotoluene	1.00
4-chlorotoluene	1.00
tert-butylbenzene	1.00
1,2,4-trimethylbenzene	1.00
sec-butylbenzene	1.00
4-isopropyltoluene	1.00
1,3-dichlorobenzene	1.00
1,4-dichlorobenzene	1.00
n-butylbenzene	1.00
p-diethylbenzene	1.00
1,2-dichlorobenzene	1.00
1,2,4,5-tetramethylbenzene	1.00
1,2-dibromo-3-chloropropane	1.00
1,2,4-trichlorobenzene	1.00
hexachlorobutadiene	1.00
naphthalene	1.00
1,2,3-trichlorobenzene	1.00

SOIL

Compound	PQL (ug/L)
dichlorodifluoromethane	1.00
chlorodifluoromethane	1.00
chloromethane	1.00
vinyl chloride	1.00
bromomethane	1.00
chloroethane	1.00
trichlorofluoromethane	1.00
freon	1.00
acetone	10.00
1,1-dichloroethene	1.00
methylene chloride	1.00
carbon disulfide	1.00
tert-butylmethylether	1.00
trans-1,2-dichloroethene	1.00
vinyl acetate	10.00
1,1-dichloroethane	1.00
methyl ethyl ketone	10.00
2,2-dichloropropane	1.00
cis-1,2-dichloroethene	1.00
chloroform	1.00
bromochloromethane	1.00
1,1,1-trichloroethane	1.00
1,1-dichloropropene	1.00
carbon tetrachloride	1.00
1,2-dichloroethane	1.00
benzene	1.00
trichloroethene	1.00
1,2-dichloropropane	1.00
bromodichloromethane	1.00
dibromomethane	1.00
2-chloroethylvinylether	1.00
4-methyl-2-pentanone	10.00
cis-1,3-dichloropropene	1.00
toluene	1.00
trans-1,3-dichloropropene	1.00
1,1,2-trichloroethane	1.00
2-hexanone	10.00
1,3-dichloropropane	1.00
tetrachloroethene	1.00
dibromochloromethane	1.00
1,2-dibromoethane	1.00
chlorobenzene	1.00
1,1,1,2-tetrachloroethane	1.00
ethylbenzene	1.00
m+p-xylene	2.00
o-xylene	1.00
styrene	1.00
bromoform	1.00
isopropylbenzene	1.00
1,1,2,2-tetrachloroethane	1.00
1,2,3-trichloropropane	1.00
n-propylbenzene	1.00
bromobenzene	1.00
p-ethyltoluene	1.00
1,3,5-trimethylbenzene	1.00
2-chlorotoluene	1.00
4-chlorotoluene	1.00
tert-butylbenzene	1.00
1,2,4-trimethylbenzene	1.00
sec-butylbenzene	1.00
4-isopropyltoluene	1.00
1,3-dichlorobenzene	1.00
1,4-dichlorobenzene	1.00
n-butylbenzene	1.00
p-diethylbenzene	1.00
1,2-dichlorobenzene	1.00
1,2,4,5-tetramethylbenzene	1.00
1,2-dibromo-3-chloropropane	1.00
1,2,4-trichlorobenzene	1.00
hexachlorobutadiene	1.00
naphthalene	1.00
1,2,3-trichlorobenzene	1.00

Appendix C List of Analytes

WATER

Compound
dichlorodifluoromethane
chlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
chloroethane
trichlorofluoromethane
freon
acetone
1,1-dichloroethene
methylene chloride
carbon disulfide
tert-butylmethylether
trans-1,2-dichloroethene
vinyl acetate
1,1-dichloroethane
methyl ethyl ketone
2,2-dichloropropane
cis-1,2-dichloroethene
chloroform
bromochloromethane
1,1,1-trichloroethane
1,1-dichloropropene
carbon tetrachloride
1,2-dichloroethane
benzene
trichloroethene
1,2-dichloropropane
bromodichloromethane
dibromomethane
2-chloroethylvinylether
4-methyl-2-pentanone
cis-1,3-dichloropropene
toluene
trans-1,3-dichloropropene
1,1,2-trichloroethane
2-hexanone
1,3-dichloropropane
tetrachloroethene
dibromochloromethane
1,2-dibromoethane
chlorobenzene
1,1,1,2-tetrachloroethane
ethylbenzene
m+p-xylene
o-xylene
styrene
bromoform
isopropylbenzene
1,1,2,2-tetrachloroethane
1,2,3-trichloropropane
n-propylbenzene
bromobenzene
p-ethyltoluene
1,3,5-trimethylbenzene
2-chlorotoluene
4-chlorotoluene
tert-butylbenzene
1,2,4-trimethylbenzene
sec-butylbenzene
4-isopropyltoluene
1,3-dichlorobenzene
1,4-dichlorobenzene
n-butylbenzene
p-diethylbenzene
1,2-dichlorobenzene
1,2,4,5-tetramethylbenzene
1,2-dibromo-3-chloropropane
1,2,4-trichlorobenzene
hexachlorobutadiene
naphthalene
1,2,3-trichlorobenzene

SOIL

Compound
dichlorodifluoromethane
chlorodifluoromethane
chloromethane
vinyl chloride
bromomethane
chloroethane
trichlorofluoromethane
freon
acetone
1,1-dichloroethene
methylene chloride
carbon disulfide
tert-butylmethylether
trans-1,2-dichloroethene
vinyl acetate
1,1-dichloroethane
methyl ethyl ketone
2,2-dichloropropane
cis-1,2-dichloroethene
chloroform
bromochloromethane
1,1,1-trichloroethane
1,1-dichloropropene
carbon tetrachloride
1,2-dichloroethane
benzene
trichloroethene
1,2-dichloropropane
bromodichloromethane
dibromomethane
2-chloroethylvinylether
4-methyl-2-pentanone
cis-1,3-dichloropropene
toluene
trans-1,3-dichloropropene
1,1,2-trichloroethane
2-hexanone
1,3-dichloropropane
tetrachloroethene
dibromochloromethane
1,2-dibromoethane
chlorobenzene
1,1,1,2-tetrachloroethane
ethylbenzene
m+p-xylene
o-xylene
styrene
bromoform
isopropylbenzene
1,1,2,2-tetrachloroethane
1,2,3-trichloropropane
n-propylbenzene
bromobenzene
p-ethyltoluene
1,3,5-trimethylbenzene
2-chlorotoluene
4-chlorotoluene
tert-butylbenzene
1,2,4-trimethylbenzene
sec-butylbenzene
4-isopropyltoluene
1,3-dichlorobenzene
1,4-dichlorobenzene
n-butylbenzene
p-diethylbenzene
1,2-dichlorobenzene
1,2,4,5-tetramethylbenzene
1,2-dibromo-3-chloropropane
1,2,4-trichlorobenzene
hexachlorobutadiene
naphthalene
1,2,3-trichlorobenzene

Appendix D

SAFETY :

- < Safety glasses are reguired at all times for all lab procedures.
- < Wear lab coat when handling corrosives or when heating or distilling.
- < Use particular care with flammables to avoid sparks, flames or spills.
- < Transport solvents in protective carrying containers.
- < Do not allow solvent, acid, ammonium hydroxide, or other chemical vapors to escape from hood into lab air.
- < Consult "Chemical Hygene Plan" for general safety measures.

WASTE DISPOSAL :

- < Unused portions of preserved samples are disposed of to sewer after pH neutralization with soda ash in building #2.
- < Aqueous sample aliquots are disposed of under hood to sewer unless hazardous levels of reagents have been added. If this is the case, waste aliquots are held in small containers for transfer to appropriate drums.
- < Consult "Waste Disposal" document for general disposal procedures.

APPENDIX E

EQUIPMENT AND SUPPLIES

Instrument : Hewlett Packard 5971 Mass Selective Detector
Hewlett Packard 5890 Series II Gas Chromatography Oven
Restek MTX-624 Capillary GC Column
Tekmar 3100 Concentrator
Tekmar Solatek 72 Autosampler
Comp U.S.A. Computer
Hewlett Packard Laserjet 1100 Printer

Gases : High Purity Helium

Consumables Restek MTX-624 Capillary GC Column
11mm diameter Thermolite Septa- cat. # 20365
Agilent Filament Assembly for 5971-Part # 05971-60140
Purg K trap for 3000 concentrator-cat. # 24920-U
Inlet (pre-silanized by Ecotest Labs, Inc.)

APPENDIX F
Reagents and Standard Preparation
EPA 8260B

This SOP is applicable to the preparation of standard solutions for all Ecotest Laboratory 8260B target compound list (see Appendix C).

Calibration and Running Standard

Ecotest Prepared Stock Solutions(in methanol):

HSL 2000 ug/ml

Std#	Name
1	Acetone
69	Vinyl Acetate
34	Methyl Ethyl Ketone
35	Methyl Isobutyl Ketone
119	2-Hexanone

cis+trans- 1,3-Dichloropropene 2000ug/ml

25	cis+trans-1,3-Dichloropropene

VOC Supplemental 2000ug/ml

3	Carbon Disulfide
73	Freon 113
56	tert-Butylmethylehter
16	2-Chlorovinylether
90	1,2,3-trimethylbenzene
48	p-Ethyltoluene
44	p-Diethylbenzene
20	1,2,4,5-Tetramethylbenzene

Chlorodifluoromethane 2000ug/ml

Chlorodifluoromathane (diluted from 50,000ug/ml stock std. from purged gas)

Purchased Stock Solutions (in methanol):

Supelco Organic Compounds Mix 6 2000 ug/ml catalog # 48799-U
Supelco 8260 Volatiles Calibration Mix 2000ug/ml catalog # 5-00607

Stock solutions are combine in to a 100 ug/ml "working standard" for all analysis by the following method:

Dilute each of the following up to 2ml in a 2ml teflon cap vial:

100ul	cis+trans-1,3-Dichloropropene 2000ug/ml std.
100ul	Voc Supplemental 2000ug/ml std.
100ul	Chlorodifluoromethane 2000ug/ml std.
100ul	Supelco Organic Compounds Mix 6 2000ug/ml std.
100ul	Supelco 8260 Volatiles Calibration Mix 2000ug/ml std.
500ul	HSL 2000ug/ml std.

To make a 5 point calibration curve using the 100 ug/ml "working standard" do the following:

5 ug/ml std.	dilute 5ul of 100ug/ml std. up to 100ml of reagent free water.
10ug/ml std.	dilute 5ul of 100ug/ml std. up to 50ml of reagent free water.
20ug/ml std.	dilute 10ul of 100ug/ml std. up to 50ml of reagent free water.
50ug/ml std.	dilute 25ul of 100ug/ml std. up to 50ml of reagent free water.
100ug/ml std.	dilute 50ul of 100ug/ml std. up to 50ml of reagent free water.

Invert each standard 3 times slowly to ensure proper mixing. Each standard is then poured in to a 40ml septa cap vial for analysis.

A 20 ppb continuing calibration standard is used every 12 hours after a BFB is run. The 20ppb continuing calibration standard is made the same way as the 20ug/ml standard above.

Bromofluorobenzene Tuning Standard

Bromofluorobenzene 500ug/ml std.

std#	name
9	Bromofluorobenzene

To make a 50ug/ml "working standard" of bromofluorobenzene dilute 100ul of 500ug/ml stock standard up to 1ml of methanol.

1ul directly injected onto GC column is equivalent to 50ng.
10 ul of 50ug/ml "working standard" in 50ml of reagent free water for analysis is equivalent to 50ng.

Reference Standard

At the end of each run a reference standard made from mostly neat compounds at a different concentration from the Calibration and Running Standard is analyzed.

See attached sheet for Reference Standard Stock Soluions and Concentration. Additional Standards:

EPA Purgeable C 200ug/ml-catalog # 4-8853
Dichlorodifluoromethane 200ug/ml-catalog # 4-8623
Chlorodifluoromethane 2000ug/ml-Same as Calibration and Running std.

To make a 10ug/ml "working standard" from the stock solutions dilute each of the following up to 2ml in a 2ml teflon cap vial:

Standard #1	40ul
Standard #2	40ul
Standard #3	40ul
Standard #4	40ul
Standard #5	80ul
Standard #6	40ul
Purgeable C	100ul
Dichlorodifluoromethane	100ul
Chlorodifluoromethane (2000ug/ml)	10ul

To make a 10ppb Reference standard dilute 50ul of the "working standard" in 50 ml of reagent free water. Invert 3 times to ensure proper mixing. Pour standard solution in to 40ml teflon cap vial for analysis.

Internal Standards

Internal standards are added to all blanks, running standards, check standards, and samples. Internal standard is not added to BFB vials due to interference with 4-bromofluorobenzene.

Internal standard stock. Solution (5000 ug/ml)

Name
Pentaflurorbenzene
1,4-diflurorbenzene
Chlorobenzene-d5
1,4-dichlorobenzene-d4
1,2-dichloroehtane-d4
Toluene-d8
4-bromofluorobenzene

For the Solatek 72 Multi-matrix Autosampler. Dilute 200ul of the 5000 ug/ml stock standard up to 20ml of methanol to make a 50ug/ml "working standard". Put the working standard in to one of the internal standard vials on the instrument. To add 50ppb of the internal standards to all appropriate sample, use 5ul aliquots.

REFERENCE STANDARD STOCK SOLUTIONS

std#	std #1 500ug/mL	ul
86F	TRICHLOROFLUOROMETHANE	6.7
73	FREON 113	6.4
16	2-CHLOROETHYLVINYLETHER	9.5
22F	1,1-DICHLOROETHENE	8.0
58F	trans-1,2-DICHLOROETHENE	8.0
15F	cis-1,2-DICHLOROETHENE	7.8
87F	1,1-DICHLOROPROPENE	8.6
	01/21/03 btb	55.0

	std#2 500ug/mL	
33	METHYLENE CHLORIDE	7.5
3	CARBON DISULFIDE	7.9
56	tert-BUTYL METHYL ETHER	13.5
21	1,1-DICHLOROETHANE	8.5
28	2,2-DICHLOROPROPANE	9.2
12	CHLOROFORM	6.7
6	BROMOCHLOROMETHANE	5.0
62	1,1,1-TRICHLOROETHANE	7.8
10	CARBON TETRACHLORIDE	6.3
32	1,2-DICHLOROETHANE	8.0
2	BENZENE	11.4
59	TRICHLOROETHYLENE	6.9
24	1,2-DICHLOROPROPANE	8.6
74	BROMODICHLOROMETHANE	5.1
17	DIBROMOMETHANE	4.0
25	(cis-1,3-DICHLOROPROPENE & trans-1,3-DICHLOROPROPENE)	16.4
	01/23/03 btb	132.8

	std#3 500ug/mL	
61	TOLUENE	11.5
63	1,1,2-TRICHLOROETHANE	7.0
81	1,3-DICHLOROPROPANE	8.4
57	TETRACHLOROETHYLENE	6.1
13	DIBROMOCHLOROMETHANE	4.1
31	1,2-DIBROMOETHANE	4.6
11	CHLOROBENZENE	9.0
79	1,1,1,2-TETRACHLOROETHANE	6.3
30	ETHYL BENZENE	11.5
36	M-XYLENE	11.5
50	P-XYLENE	11.6
43	O-XYLENE	11.4
54	STYRENE	11.0
7	BROMOFORM	3.5
14	ISOPROPYLBENZENE	11.0
53	1,1,2,2-TETRACHLOROETHANE	6.3
66	1,2,3-TRICHLOROPROPANE	7.2
	01/21/03 btb	141.9

	std#4 500ug/mL	
40	N-PROPYLBENZENE	11.6
5	BROMOBENZENE	6.7
48	P-ETHYL TOLUENE	11.6
68	1,3,5-TRIMETHYLBENZENE	11.6
41	2-CHLOROTOLUENE	9.2
60	4-CHLOROTOLUENE	9.3
55	tert-BUTYLBENZENE	11.5
67	1,2,4-TRIMETHYLBENZENE	11.4
52	sec-BUTYLBENZENE	11.6
49	P-ISOPROPYLTOLUENE	11.7
82	1,3-DICHLOROBENZENE	7.7
45,46	1,4-DICHLOROBENZENE	1000.0
39	N-BUTYLBENZENE	11.6
44	P-DIETHYLBENZENE	11.6
42	1,2-DICHLOROBENZENE	7.7
20	1,2,4,5-TETRAMETHYLBENZENE	1000.0
113	1,2-DIBROMO-3-CHLOROPROPANE	4.8
84	1,2,4-TRICHLOROBENZENE	6.9
83	HEXACHLOROBUTADIENE	6.0
37,38	NAPHTHALENE	1000.0
64,65	1,2,3-TRICHLOROBENZENE	1000.0
	01/21/03 btb	4162.5

	std #5 2500ug/mL	
1	ACETONE	63.2
69	VINYL ACETATE	53.5
34	METHYL ETHYL KETONE	62.1
35	METHYL ISOBUTYL KETONE	62.4
119	2-HEXANONE	60.2
	01/21/03 btb	301.4

	std. #6 500ug/L	
16	2-CHLOROETHYLVINYLETHER	9.5
90	1,2,3-TRIMETHYLBENZENE	11.5
	02/26/03 btb	21.0

APPENDIX G

Quality Control :

1. Matrix spike/dup spike are analyzed at a rate of 1 per 12 samples for each matrix run.
2. Initial calibriation verification standard is run following 5 point initial calibration curve update.
3. 50ng Bromofluorobenzene (BFB) tune calibration run every 12 hours.
4. Continuing calibration standard run immediately after 50ng BFB every 12 hours.
5. Method blank is analyzed immediately following continuing calibration standard or for each new matrix that is run.
6. A reference standard (10ppb) is analyzed at the end of every 12 hour run.

APPENDIX H

GCMS Procedure

Make sure the HP5971 Mass Selective detector is operational
>Vacuum gauge pressure should be less than 4 x 10exp-5 torr.
>Run a 50ng BFB sample to ensure the MS is properly tuned

Make sure the HP 5890 Series II Gas Chromatography oven is operational.
>Glass Jet Separator vacuum gauge should read between .8-1.2 torr.
>Injector A temperature should read 120 celcius.
>Detector A temperature should read 220 celcuis.
>Detector B temperaute should read 250 celcius.

Make sure the Tekmar 3100 Concentrator is operational.
>Concentrator should read "Purge Ready" before analysis can begin.
>System Pressure should read 20psi.
>Trap Pressure Control has been disabled on GCMSV#2.
>Inspect glassware for cracks
>Inspect all connections for leaks using a leak detector or "snoop"

Make sure the Solatek 72 Multi-matrix Autosampler is operational.
>Digital display should read "end method" at the end of previous run.
>System pressure should read 16-18psi.
>Make sure there is sufficient Internal Standard for analysis.
>Make sure the water reservoir is full.

Computer start up
>Turn on computer and wait for password screen to appear
>Press OK button to enter windows operating system
>Open GC-top, ENVDA, and Solatek software from desktop shortcuts.

Tuning HP5971 Mass Selective Detector,
>In GC-top make a new schedule starting with method "bfb"
>Run method and inject 1ul of 10ug/ml standardof BFB solution.
>If tune passes, continue with run.
>If tune fails, use auto-tune and target-tune software until BFB tune passes

Procedure for GCMSV#2

>Direct injection is only used for BFB analysis at the beginnig of the day.
>All samples are purged in 5ml aliquots.
>A 20ppb continuing calibration standard is run by diluting 10ul of 100ug/ml "working standard" up to 50ml reagent free water (prepared daily).
>All Response Factors are automatically calculated by data analysis software.
>Continuing calibration check standard acceptable limits are 20% RSD as compared to initial calibration curve.
>System performance check is performed using all target analytes immediately after initial calibration.
>5ul of mixed internal standard plus surrogate compounds is added by the Solatek 72 autosampler automatically (50ppb).
>Samples are spiked with 20ppb spiking solution.
>Laboratory Control Sample (LCS) or reference sample is run at a concentration of 10ppb, 100ppb ketones at the end of every 12 hour run.

APPENDIX I

Acceptance Criteria for Quality Control Measures

< Tuning Calibration

Mass Selective Detector must be properly tuned before analysis using auto tune and target tune software in GC-top.

Mass selective detector is properly tuned when 50 ng BFB passes all tune criteria. This is run every 12 hours.

< Initial Calibration

A 5 point curve of concentrations 5ppb, 10ppb, 20ppb, 50ppb and 100ppb is run for initial start up of machine, when continuing calibration fails, after new BFB tuning, and after any alterations to system configuration.

All RSD results for 5 point curve must be less than 15%.

< Continuing Calibration

A 20ppb continuing calibration standard is run every 12 hours after a BFB tune check

"Limits" are established as follows : All non ketone values must be within 20% deviation from the initial calibration curve. All ketones must be between 50% and 200%.

< Matrix Spikes :

"Limits" are established as follows: Upper warning limits are the average of thirty readings, plus 2 times the Standard Deviation of those thirty readings.
Lower warning limits are the average of thirty readings, minus 2 times the Standard Deviation of those thirty readings.
Upper control limits are the average of thirty readings, plus 3 times the Standard Deviation of those thirty readings.
Lower control limits are the average of thirty readings, minus 3 times the Standard Deviation of those thirty readings.

LCS

"Limits" are established as follows: Upper warning limits are the average of thirty readings, plus 2 times the Standard Deviation of those thirty readings.
Lower warning limits are the average of thirty readings, minus 2 times the Standard Deviation of those thirty readings.
Upper control limits are the average of thirty readings, plus 3 times the Standard Deviation of those thirty readings.
Lower control limits are the average of thirty readings, minus 3 times the Standard Deviation of those thirty readings.

APPENDIX L

Corrective action for out-of-control data

Initial Calibration

>If any compound has greater than 15% RSD, plots of compounds are analyzed to expose any errors in standard preparation or instrument error.

>If standard preparation is the cause, a new standard will be run. If machine error is the cause, corrective action is taken and a new 5 point curve is run.

>Immediately run an Initial Calibration Verification Standard (ICVS) to verify the 5 point curve is acceptable.

Continuing calibration

>If any continuing calibration compound is more than 20% out of range compared to the initial calibration curve, then a new CC will be analyzed.

>If continuing calibration compounds unable to pass 20% deviation from initial calibration curve, a new initial calibration 5 point curve is run.

Matrix Spike/Dup Spike

>If any target compounds in the matrix spike are out of linear Initial Calibration range, the LCS will be used to demonstrate the machine is able to accurately operate.

>If one spike does not work properly, check to see if it was properly sampled and if the internal standard was added correctly. If sampling error was the cause, use the LCS to verify proper analysis has occurred and re-run spikes.

>Check that the concentration of the matrix spike/dup spike addition is significant compared to the unspiked sample. If it is not, re-run spikes.

>If after re-analysis of the duplicate spikes the samples still do not meet criteria, notify the volatiles dapartment supervisor or laboratory director for further instructions.

Laboratory Control Sample (reference)

>If LCS is out of accepted range, check to see if it was properly sampled and the internal standard was added correctly. If machine error was the cause, re-run the LCS.

>If the LCS fails a second time for analytes in the run and the continuing calibration standard is passing, the possibility exists for contamination of the LCS standard or an unacceptable initial calibration.

>Prepare and run a new LCS standard.

>If the new LCS standard fails, re-calibrate the instrument.

>If re-calibration fails to correct the problem, contact the volatiles supervisor or laboratory director for further instructions.

APPENDIX Q

ICVS Fails Acceptance Criteria

If ICVS for an analyte does not pass, no data for that analyte may be reported unless specifically permitted in Section 3.

CCVS OR LCS Fails

If the LCVS fails for an analyte, the analyst may not report any data for that analyte unless specifically permitted in Section 3.

The Laboratory Director may permit data to be reported for an analyte which has not passed the CCVS or LCS criteria if it can be demonstrated to his satisfaction that the cause of the out of control result was due to loss of sample during unattended operation, or due to contamination of the working LCVS solution, or due to some other problem which would not indicate a loss of calibration of the instrument.

Duplicate/Duplicate Spike (Precision) Sample Fail Acceptance Criteria

If the Duplicate/Duplicate Spike samples do not meet acceptance criteria, the analyst may not report any data for t he effected analytes and samples covered by these duplicates.

The Laboratory Director may permit data to be reported for an analyte which as failed the precision acceptance criteria if it can be demonstrated that the failure was due to:

Loss of sample during unattended operation and there is evidence that there is no diminution in the precision of the analytical system.

Loss of internal standard during unattended operation and there is no indication that the loss effected samples for which the data is to be accepted.

If the failed precision data is based on duplicate spikes and the spike added is insignificant compared to the unspiked concentration, and there is no other indication of loss of precision in the analytical system.

If the failed precision data is based on duplicate spikes and the spiked sample must be diluted in order to be within the linear calibration range of the instrument, and there is no other indication of loss precision in the analytical system.

APPENDIX Q

If the failed precision data is traced to a contamination of the sample during preparation or analysis and it can be demonstrated that the sample data to be accepted was not effected by the contamination.

If the failed precision data is traced to a non-homogeneous sample or samples.

If Spike Sample (Recovery) Data Is Not Within Acceptance Criteria

If the recovery samples do not meet acceptance criteria the analyst may not report any data for the effected analytes and samples covered by this recovery data.

The Laboratory Director may permit data to be reported for an analyte which has failed the recovery acceptance criteria if it can be demonstrated the failure was due to:

Loss of sample during unattended operation and there is evidence that there is no diminution in the recovery of the analytical system.

Loss of internal standard during unattended operation and there is no indication that the loss effected samples for which the data is to be accepted.

If the failed recovery data is based on a spike sample in which one or more analytes had spikes added which were insignificant compared to the unspiked concentration and there is no other indication of loss of recovery in the analytical system.

If the failed recovery data is based on a spiked sample where the sample must be diluted so that the concentration of the analyte in questions is within the linear calibration range of the instrument, and there is no other indication of loss of recovery in the analytical system.

If the failed recovery data is traced to a contamination in the sample during preparation or analysis and it can be demonstrated that the sample data to be accepted was not effected by the contamination.

If the failed recovery data is traced to a non homogeneous sample.

In all of the above cases if the Laboratory Director decides that data should be accepted he should initial and annotate the data sheets with the reason for accepting the data.

He should also enter the reasons for accepting the data in the "Director's Remarks" section of the electronic record.

ATTACHMENT 3

Example Chain of Custody Form (EcoTest)

ECO TEST LABORATORIES, INC. • ENVIRONMENTAL TESTING
377 Sheffield Avenue, North Babylon, New York 11703
(631) 422-5777 • FAX (631) 422-5770

CHAIN OF CUSTODY RECORD

Client:	
Address:	
Phone:	FAX:
Person receiving report:	
Sampled by:	
Source:	
Job No.:	

MATRIX (Soil, Water, etc.)	COLLECTED DATE	COLLECTED TIME	SAMPLE IDENTIFICATION	TOTAL NUMBER OF CONTAINERS	TYPE & NUMBER OF CONTAINERS	REMARKS–TESTS REQUIRED, SPECIAL TURNAROUND, SPECIAL Q.C. etc

Relinquished by: *(Signature)*	DATE/TIME	SEAL INTACT ?	Received by: *(Signature)*	Relinquished by: *(Signature)*	DATE/TIME	SEAL INTACT ?	Received by: *(Signature)*
Representing:		YES NO NA	Representing:	Representing:		YES NO NA	Representing:
Relinquished by: *(Signature)*	DATE/TIME	SEAL INTACT ?	Received by: *(Signature)*	Relinquished by: *(Signature)*	DATE/TIME	SEAL INTACT ?	Received by: *(Signature)*
Representing:		YES NO NA	Representing:	Representing:		YES NO NA	Representing:

ATTACHMENT 4

Decontamination Procedures

DECONTAMINATION PROCEDURES

Field sampling equipment will be decontaminated prior to sampling and in between sample locations (e.g., between wells). The decontamination activities will be completed on-site. Procedures for decontaminating any non-disposable field sampling equipment will be conducted as described below. If a submersible pump is dedicated to a monitoring well, then decontamination of the equipment will not be necessary.

1. Rinse equipment with Micro-90 low-phosphate detergent (or equivalent) and potable water solution and scrub with a brush.

2. Rinse equipment with distilled/deionized rinse water.

ARCADIS

Appendix S

Remedial Investigation Report – Well Data Summary and Water Level Measurements Tables

Table 2-1
Well Data Summary
Pelham Bay Landfill
Bronx, New York

	Date Installed	Depth (ft)	Diameter (in)	Length of Screen (ft)	Estimated Yield (gpm)	Well Type	Screened Material	Riser Material	Ground Elevation (ft above BD)	Metal Casing Elevation (ft above BD)	Riser Elevation (ft above BD)	Riser Height (ft above GRD)	Screen Elevation Top (ft)	Screen Elevation Bottom (ft)	Northing	Easting	Bedrock Elevation (ft above BD)
1992 WELLS																	
MW-113	26-May-92	12.08	4	5	<0.5	stickup	overburden	sch 40 PVC	8.22	11.42	11.07	2.85	3.99	-1.01	29070.315	-19814.674	-9.78
MW-113B	11-Jun-92	83.98	4	20	~1.5	stickup	bedrock	sch 80 PVC	7.09	10.59	10.20	3.11	-53.78	-73.78	29081.229	-19818.601	-9.91
MW-114	27-May-92	11.87	4	10	< 0.5	flush mount	overburden	sch 80 PVC	7.96	8.26	8.01	0.05	6.14	-3.86	28402.734	-20517.931	-
MW-114B	7-Jul-92	91.48	4	10	< 0.5	flush mount	bedrock	sch 40 PVC	7.62	7.72	7.32	-0.30	-74.16	-84.16	28390.178	-20537.285	-23.38
MW-115	8-Jun-92	42.50	6	20	> 5.0	stickup	overburden	sch 40 PVC	18.44	21.64	20.34	1.90	-2.16	-22.16	27911.455	-20754.435	-22.56
MW-115B	8-Jun-92	72.41	8 & 6	18.41' open hole	> 5.0	stickup	bedrock	8" to 6" (54')	17.71	20.11	open hole	-	-33.89	-52.30	27904.201	-20755.529	-28.29
MW-116	29-May-92	12.20	4	5	<1.0	stickup	sed./fill	sch 80 PVC	10.97	14.27	13.92	2.95	6.72	1.72	26940.256	-20658.534	0.97
MW-116B	29-Jun-92	73.37	4	10	<0.5	stickup	bedrock	sch 80 PVC	11.71	14.11	13.79	2.08	-49.58	-59.58	26901.876	-20656.069	-0.29
MW-117	1-Jun-92	19.66	4	10	0.5	stickup	overburden	sch 80 PVC	5.18	7.49	7.33	2.15	-2.33	-12.33	26639.141	-20177.984	-12.82
MW-117B	29-Jun-92	79.13	4	10	0.5	stickup	bedrock	sch 80 PVC	4.62	6.52	6.40	1.78	-62.73	-72.73	26615.782	-20186.704	-11.38
MW-118	3-Jun-92	17.19	4	10	<1.0	stickup	fill	sch 80 PVC	10.83	13.73	13.19	2.36	6.00	-4.00	26728.412	-19287.747	-
MW-118B	19-Jun-92	112.20	4	20	<0.5	stickup	bedrock	sch 80 PVC	11.00	13.30	13.09	2.09	-79.11	-99.11	26729.859	-19250.687	-39.00
MW-119	10-Jun-92	31.21	4	10	>0.5	stickup	riprap	sch 80 PVC	11.52	13.92	13.78	2.26	-7.43	-17.43	27200.090	-18950.844	-40.48
MW-119B	24-Jun-92	113.51	4	10	<0.5	stickup	bedrock	sch 80 PVC	11.63	14.63	14.29	2.66	-89.22	-99.22	27171.359	-18948.976	-37.37
MW-120	10-Jun-92	55.58	6	20	>10	stickup	overburden	sch 40 PVC	9.05	12.45	11.61	2.56	-23.97	-43.97	27776.950	-18994.003	-43.95
MW-120B	22-May-92	79.70	4	10	<0.5	stickup	bedrock	sch 40 PVC	9.09	10.99	10.84	1.75	-58.86	-68.86	27791.700	-18995.120	-46.91
MW-121	29-May-92	40.71	4	10	>10	stickup	overburden	sch 80 PVC	10.85	13.45	13.10	2.25	-17.61	-27.61	28578.134	-19121.503	-
MW-121B	27-May-92	69.25	4	10	<0.5	stickup	bedrock	sch 80 PVC	11.06	14.66	13.54	2.48	-45.71	-55.71	28587.134	-19126.776	-31.94
MW-122	2-Jun-92	38.15	4	10	>5	stickup	overburden	sch 80 PVC	9.54	12.04	11.68	2.14	-16.47	-26.47	28967.060	-19311.343	-
MW-122B	29-May-92	80.25	4	20	<1.0	stickup	bedrock	sch 80 PVC	9.57	11.37	11.17	1.60	-49.08	-69.08	28975.330	-19321.196	-30.43
MW-123	2-Jul-92	14.50	4	10	<0.5	flush mount	overburden	sch 80 PVC	12.96	13.41	13.23	0.27	8.73	-1.27	27295.939	-21322.259	-
MW-124	2-Jul-92	13.27	4	10	< 0.5	flush mount	overburden	sch 40 PVC	22.14	22.24	22.12	-0.02	18.85	8.85	26498.996	-20818.821	7.64
MW-124B	7-Jul-92	69.67	4	10	<0.5	flush mount	bedrock	sch 40 PVC	20.90	21.00	20.60	-0.30	-39.07	-49.07	26520.305	-20800.748	7.90
MW-125	13-Jul-92	19.58	4	10	~3.0	flush mount	overburden	sch 80 PVC	5.58	6.03	5.92	0.34	-3.66	-13.66	28452.426	-20675.673	-
MW-125B	6-Jul-92	103.04	4	20	~8.0	flush mount	bedrock	sch 40 PVC	5.95	6.15	5.90	-0.05	-77.14	-97.14	28462.816	-20669.218	-45.05
MW-126 (PZ5)	1-Jul-92	140.00	4	20	>2.0	stickup	fill	sch 40 SS	124.12	125.23	124.68	0.56	4.68	-15.32	27770.025	-19860.461	-23.88
PZ-1F	19-May-92	78.42	2	10	-	stickup	fill	sch 40 PVC	80.40	82.60	82.33	1.93	13.91	3.91	28602.070	-19719.777	-
PZ-1B	19-May-92	106.22	2	10	-	stickup	bedrock	sch 40 PVC	79.95	82.35	82.08	2.13	-14.14	-24.14	28607.553	-19715.618	1.45
PZ-2F	13-May-92	97.73	2	10	-	stickup	fill	sch 40 PVC	92.00	95.60	95.48	3.48	7.75	-2.25	28062.389	-20214.844	-10.00
PZ-3F	5-Jun-92	136.00	2	10	-	stickup	fill	iron	127.36	129.26	129.10	1.74	3.10	-6.90	27353.441	-19573.734	-
PZ-3S	29-May-92	160.00	2	10	-	stickup	overburden	iron	126.89	129.49	129.46	2.57	-20.54	-30.54	27352.641	-19567.616	-33.11
PZ-3B	12-Jun-92	172.00	2	5	-	stickup	bedrock	iron	128.82	131.32	130.93	2.11	-36.07	-41.07	27356.313	-19597.121	-28.68
PZ-4F	21-May-92	77.83	2	10	-	stickup	fill	sch 40 PVC	79.31	81.81	81.27	1.96	13.44	3.44	28055.269	-19373.243	-2.69
PZ-5B	17-Jun-92	165.00	2	5	-	stickup	bedrock	iron	123.40	126.20	126.08	2.68	-33.92	-38.92	27773.634	-19882.983	-24.60
CP-1	21-Jun-92	44.35	2	20	-	stickup	overburden	sch 40 PVC	20.72	23.82	23.62	2.90	-0.73	-20.73	27940.300	-20746.521	-42.78
CP-2	16-Jun-92	41.07	2	20	-	flush mount	overburden	sch 40 PVC	18.32	18.42	18.18	-0.14	-2.89	-22.89	27914.767	-20768.121	-37.18
CB-1	30-Jun-92	77.72	2	10	-	stickup	bedrock	sch 40 PVC	19.79	21.89	21.77	1.98	-45.95	-55.95	27922.866	-20747.965	-41.21
HP-1	23-Jun-92	45.40	2	10	-	stickup	overburden	sch 40 PVC	8.40	11.00	10.89	2.49	-24.51	-34.51	27766.674	-18992.946	-37.60
HP-2	25-Jun-92	48.24	2	10	-	stickup	bedrock	sch 40 PVC	9.15	11.55	11.39	2.24	-26.85	-36.85	27748.104	-18989.605	-36.85
HP-3	9-Jul-92	25.19	2	10	-	flush mount	fill	sch 40 PVC	8.63	8.73	8.53	-0.10	-6.66	-16.66	27780.225	-18975.657	-
TB-1	29-Jun-92	56.00	Abandoned Test boring		-	-	-	-	~11	-	-	-	-	-	-	-	~ - 27.00
TB-2	14-Jul-92	20.00	Abandoned Test Boring		-	-	-	-	~11	-	-	-	-	-	-	-	-

Table 2-1
Well Data Summary
Pelham Bay Landfill
Bronx, New York

	Date Installed	Depth (ft)	Diameter (in)	Length of Screen (ft)	Estimated Yield (gpm)	Well Type	Screened Material	Riser Material	Ground Elevation (ft above BD)	Metal Casing Elevation (ft above BD)	Riser Elevation (ft above BD)	Riser Height (ft above GRD)	Screen Elevation Top (ft)	Screen Elevation Bottom (ft)	Northing	Easting	Bedrock Elevation (ft above BD)
1989 WELLS																	
MW-101	1-Dec-89	45.00	4	10	-	flush mount	fill	sch 80 PVC	80.02	-	-	-	-	-	28590.892	-19452.983	-
MW-102	5-Dec-89	56.00	4	10	-	flush mount	fill	sch 80 PVC	78.79	78.89	78.43	-0.36	32.43	22.43	27086.164	-19724.929	-
MW-103	27-Nov-89	13.62	4	10	>5	flush mount	overburden	sch 80 PVC	9.43	9.73	9.43	0.00	5.81	-4.19	28946.055	-19300.926	-
MW-104	21-Nov-89	15.35	4	10	~0.6	flush mount	overburden	sch 80 PVC	9.75	9.85	9.55	-0.20	4.20	-5.80	28179.490	-19030.697	-
MW-105	28-Nov-89	17.40	4	10	>5	flush mount	overburden	sch 80 PVC	9.99	10.30	9.99	0.00	2.59	-7.41	27518.177	-18974.661	-
MW-106	28-Nov-89	17.47	4	10	>5	flush mount	overburden	sch 80 PVC	10.05	10.25	9.86	-0.19	2.39	-7.61	26742.231	-18980.711	-23
MW-107	20-Nov-89	15.83	4	5	<0.1	flush mount	overburden	sch 80 PVC	5.03	5.43	5.19	0.16	-5.64	-10.64	26630.328	-20189.235	-
MW-108	21-Nov-89	Destroyed during IRM 5/92			-	flush mount	-	-	-	-	-	-	-	-	-	-	-
MW-109	10-Nov-89	16.75	4	10	<0.1	flush mount	overburden	sch 80 PVC	17.16	17.26	16.96	-0.20	10.21	0.21	28784.326	-20169.171	-5.84
MW-110	30-Nov-89	16.89	4	10	>5	flush mount	overburden	sch 80 PVC	11.39	11.69	11.34	-0.05	4.45	-5.55	26731.688	-19689.792	-
MW-111	1-Dec-89	34.86	4	10	~0.3	flush mount	overburden	sch 80 PVC	20.36	20.86	20.71	0.35	-4.15	-14.15	27930.200	-20744.629	-
MW-112	7-Dec-89	12.00	4	10	<0.1	flush mount	overburden	sch 80 PVC	10.64	10.84	10.54	-0.10	8.54	-1.46	29031.043	-19812.714	-

Notes:
BD = Bronx Datum = 2.608 ft. above mean sea level
SS = Stainless Steel
GRD = Ground
gpm = gallons per minute
HP-2 was damaged during the weekend of 8/8/92
Well depth measured from top of inner riser

Prepared by: DAD
Checked by: PGN
92C4087

Table 2-4
Water Level Measurements
Pelham Bay Landfill
Bronx, New York

Well Number	AUGUST 4, 1992 LOW TIDE AT 1103				AUGUST 12, 1992 HIGH TIDE AT 1208				NOVEMBER 5, 1992 LOW TIDE AT 1420			
	Time	Depth to Water (ft)	Elevation of PVC (ft)	Water Table Elevation (ft)	Time	Depth to Water (ft)	Elevation of PVC (ft)	Water Table Elevation (ft)	Time	Depth to Water (ft)	Elevation of PVC (ft)	Water Table Elevation (ft)
MW-103	omitted		9.43		1244	8.2	9.43	1.23	1433	14.55	9.43	-5.12
MW-104	1114	8.95	9.55	0.60	1212	8.68	9.55	0.87	1442	9.08	9.55	0.47
MW-105	1109	8.87	9.99	1.12	1230	8.80	9.99	1.19	1425	8.89	9.99	1.10
MW-106	1100	14.25	9.86	-4.39	1229	8.10	9.86	1.76	1435	9.04	9.86	0.82
MW-107	1103	6.59	5.19	-1.40	omitted		5.19		1420	5.54	5.19	-0.35
MW-109	1015	10.50	16.96	6.46	1138	10.80	16.96	6.16	1420	11.58	16.96	5.38
MW-110	1113	12.89	11.34	-1.55	omitted		11.34		1445	13.32	11.34	-1.98
MW-111									1508	16.67	20.71	4.04
MW-112	1109	8.39	10.54	2.15	1221	8.74	10.54	1.80	1424	8.96	10.54	1.58
MW-113	1108	9.66	11.07	1.41	Aquistar power failure		11.07		1423	9.97	11.07	1.10
MW-113B	1105	10.12	10.20	0.08	1220	7.53	10.20	2.67				
MW-114	1031	4.27	8.01	3.74	1327	3.07	8.01	4.94	1420	4.45	8.01	3.56
MW-114B	1030	3.45	7.32	3.87	omitted		7.32					
MW-115	1354	16.08	20.34	4.26	pump test		20.34		1431	15.95	20.34	4.39
MW-115B	1351	15.80	21.77	5.97	pump test		21.77					
MW-116	1408	8.15	13.92	5.77	1516	8.36	13.92	5.56	1435	7.51	13.92	6.41
MW-116B	1410	57.70	13.79	-43.91	1548	62.00	13.79	-48.21				
MW-117	1108	8.73	7.33	-1.40	1220	6.82	7.33	0.51	1421	7.7	7.33	-0.37
MW-117B	1104	8.08	6.40	-1.68	1208	6.70	6.40	-0.30				
MW-118	1116	15.62	13.19	-2.43	Aquistar power failure		13.19		1440	13.94	13.19	-0.75
MW-118B	1117	20.02	13.09	-6.93	development		13.09					
MW-119	1106	18.95	13.78	-5.17	1231	12.70	13.78	1.08	1430	18.52	13.78	-4.74
MW-119B	1104	16.20	14.29	-1.91	1238	15.63	14.29	-1.34				
MW-120	development		11.61		1209	11.33	11.61	0.28	1420	12.13	11.61	-0.52
MW-120B	1111	14.42	10.84	-3.58	1239	10.77	10.84	0.07				
MW-121	development		13.10		1215	12.18	13.10	0.92	1437	17.35	13.10	-4.25
MW-121B	development		13.54		1215	66.92	13.54	-53.38				
MW-122	1117	15.28	11.68	-3.60	1217	10.42	11.68	1.26	1427	15.07	11.68	-3.39
MW-122B	1115	15.00	11.17	-3.83	1217	9.75	11.17	1.42				
MW-123	1358	6.70	13.23	6.53	1515	6.90	13.23	6.33	1440	6.55	13.23	6.68
MW-124	1405	10.55	22.12	11.57	1526	10.92	22.12	11.20	1430	11.98	22.12	10.14
MW-124B	1404	12.80	20.60	7.80	1526	9.18	20.60	11.42				
MW-125	1024	3.90	5.92	2.02	1300	3.05	5.92	2.87	1424	3.98	5.92	1.94
MW-125B	1023	3.90	5.90	2.00	omitted		5.90					
MW-126	1304	118.00	124.68	6.68	1425	120.37	124.68	6.31	1443	115.15	124.68	9.53
PZ-1B	1244	77.90	82.08	4.18	1426	78.02	82.08	4.06				
PZ-1F	1251	77.00	82.33	5.33	1428	76.18	82.33	6.15	1510	76.25	82.33	6.08
PZ-2F	1257	94.78	95.48	0.70	1437	dry	95.48	dry	1500	97.6	95.48	-2.12
PZ-3B	1344	132.20	130.93	-1.27	1457	132.40	130.93	-1.47				
PZ-3F	1336	124.70	129.10	4.40	1457	132.40	129.10	-3.30	1454	121.66	129.10	7.44
PZ-3S	1340	131.36	129.46	-1.90	1458	131.60	129.46	-2.14				
PZ-4F	1157	dry	81.27	dry	1505	dry	81.27	dry	1500	Well Dry	81.27	
PZ-5B	1310	121.58	126.08	4.50	1347	133.28	126.08	-7.20				

Note: Elevations are referenced to the Bronx Datum which is 2.608 feet above mean tide level at Sandy Hook, NJ

Prepared by: KNS
Checked by: TRP
92C4087

ARCADIS

Appendix T

Well Construction Logs

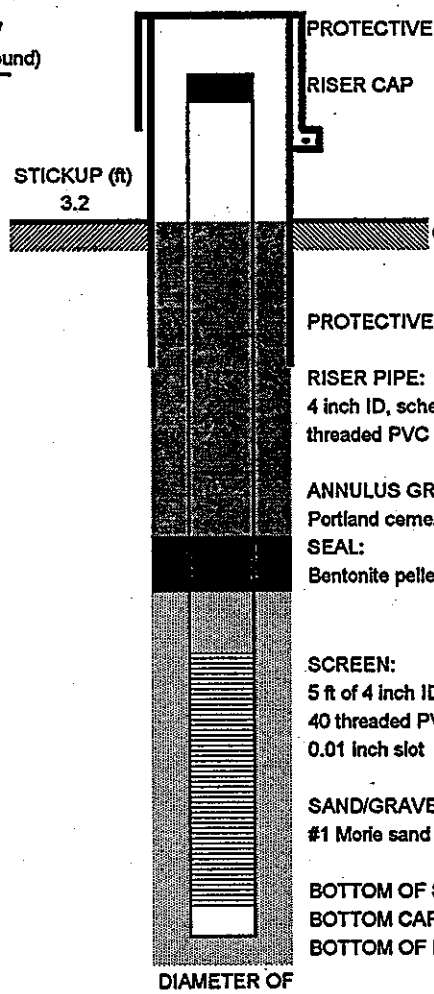
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-113**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.068 ft. above MSL
Drilling company WARREN-GEORGE INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 8.22 ft
Date and time of completion 5/26/92	*Northing* 29070.315	*Top of protective steel casing elevation* 11.42 ft
Inspector D. Davidson	*Easting* -19814.674	*Top of riser pipe elevation* 11.07 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below / above ground)
	11.07	A	2.85
	8.22	B	0
0-10 inches: Brown organic soil. 11"- 13ft.: Sand, silt, gravel, and decomposed rock.			
13-14 ft.: Dk-med. grey SILT.	6.72	C	1.5
14-18 ft.: Decomposed ROCK.	5.72	D	2.5
	3.72	E	4.5
18-22 ft.: Fine biotite GNEISS with garnet.			
22-23 ft.: Coarse grained PEGMATITE DIKE.	-1.28	F	9.5
	-1.28	G	9.5
23-28 ft.: White and black biotite-feldspar GNEISS with garnet, quartz.	-19.78	H	28



REMARKS (Installation, development) :

MATERIALS: 10 FT. OF 4" SCH 40 PVC RISER, 5 FT. OF SCC 40 PVC SCREEN, 2 BOTTOM/TOP CAPS, 4 BAGS #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 2 BAGS OF PORTLAND CEMENT, 1 4" STICK UP.

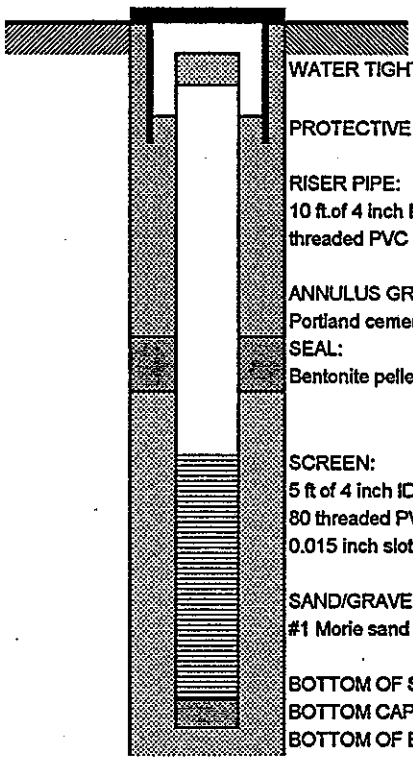
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-114**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL
Drilling company WARREN-GEORGE	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 7.96 ft
Date and time of completion 5/27/92	*Northing* 28402.734	*Top of protective steel casing elevation* 8.26 ft
Inspector D. Davidson	*Easting* -20517.931	*Top of riser pipe elevation* 8.01 ft

A = Ground Surface
B = Top of Riser
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	7.96	A	0
	8.01	B	0.05
0-8 ft.: Dk. brown gravelly sandy organic soil.			
	8.01	C	0.05
	7.14	D	0.82
	6.14	E	1.82
8-12 ft.: Orange-brown and green-brown micaceous varved SILT.			
12-22 ft.: Brown to olive green fine-coarse silty SAND w/ gravel, decomposed mica-ceous rock. Very green color at 18 ft. (chlorite?) Varved mica. silt stringers at 20 ft.	-3.86	F	11.82
	-3.86	G	11.82
	-5.54	H	13.5



REMARKS (Installation, development) :

MATERIALS: 5 FT. OF 4" SCH 80 PVC SCREEN,10 FT OF 4" SCH 80 PVC RISER, 1 BOTTOM CAP, 3 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 1 BAG OF PORTLAND CEMENT,1 FLUSH MOUNT CASING.

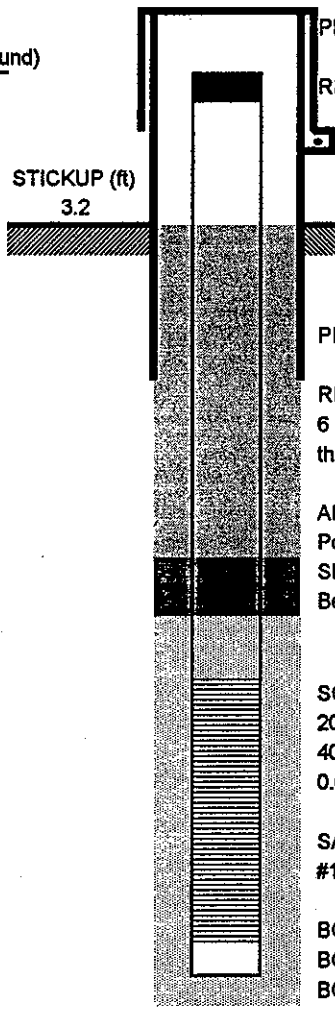
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-115**

Project name & location	*Well lock No.*	*Elevation datum*
PELHAM BAY LANDFILL, BRONX, NEW YORK	3220	Bronx Datum (BD) 2.608 ft above MSL
Drilling company	***Surveyor***	***Ground elevation***
WARREN-GEORGE INC.	ETTLINGER & ETTLINGER	18.44 ft
Date and time of completion	***Northing***	***Top of protective steel casing elevation***
6/8/92	27911.455	21.64 ft
Inspector	***Easting***	***Top of riser pipe elevation***
B. Atkinson	-20754.435	20.34 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	20.34	A	1.9
			STICKUP (ft) 3.2
	18.44	B	0
0-6 ft.: Lt. brown cuttings.			
6-16 ft.: Black cuttings.			
16-41 ft.: Lt. brown-brown fine SAND w/ mica and gravel.	9.44	C	9
	1.44	D	17
	-2.56	E	21
	-22.56	F	41
	-22.56	G	41
	-22.56	H	41



PROTECTIVE STEEL CAP WITH LOCK
RISER CAP
GROUND SURFACE
PROTECTIVE STEEL CASING CEMENTED
RISER PIPE:
6 inch ID, schedule 40 threaded PVC
ANNULUS GROUTED WITH:
Portland cement
SEAL:
Bentonite pellets
SCREEN:
20 ft of 6 inch ID, schedule 40 threaded PVC, 0.01 inch slot
SAND/GRAVEL PACK:
#1 Morie sand
BOTTOM OF SCREEN
BOTTOM CAP
BOTTOM OF BOREHOLE
DIAMETER OF BOREHOLE:
6"

REMARKS (Installation, development) :
MATERIALS: 22 ft. OF 6" SCH 40 PVC RISER, 20 FT. OF 6" SCH 40 WIRE WRAPPED PVC SCREEN, 8 BAGS OF # 1 SAND, 1 1/2 BUCKETS OF BENTONITE PELLETS, 4 BAGS OF CEMENT.

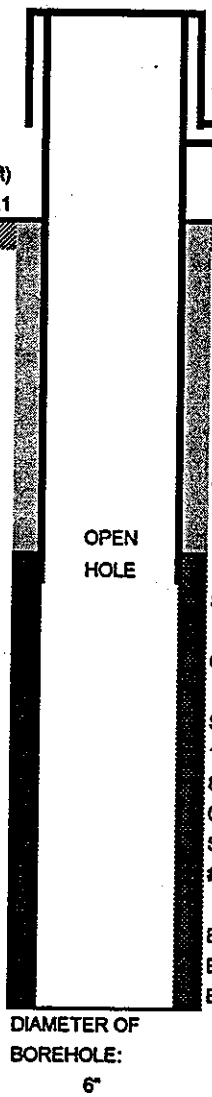
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-115B**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	***Well lock No.*** 3220	***Elevation datum*** Bronx Datum (BD) 2.608 ft. above MSL
Drilling company WARREN-GEORGE, INC.	***Surveyor*** ETTLINGER & ETTLINGER	***Ground elevation*** 19.79 ft
Date and time of completion 6/8/92	***Northing*** 27904.201	***Top of protective steel casing elevation*** 21.89 ft
Inspector B. Atkinson	***Easting*** -20755.529	***Top of riser pipe elevation*** 21.77 ft

A = Top of Riser
B = Ground Surface
C = Top of Bedrock
D = Bottom of 8" Casing
E = Bottom of Borehole

	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	21.77	A	1.98
GENERALIZED SOIL DESCRIPTION			STICKUP (ft) 2.1
	19.79	B	0
0-1.5 ft. Black to brown silty SAND & FILL			
1.5-40 ft. Black FILL			
	-26.21	C	46
	-34.21	D	54
40-74 ft.Competent Bedrock: Biotite-Garnet SCHIST.			
	-54.21	E	74



PROTECTIVE STEEL CAP WITH LOCK
RISER CAP
GROUND SURFACE
8" STEEL CASING CEMENTED IN PLACE
RISER PIPE:
4 inch ID, schedule 80
threaded PVC
ANNULUS GROUTED WITH:
Portland cement
SEAL: Bentonite pellets
6" DIAMETER BORE HOLE
SCREEN:
10 ft of 4 inch ID, schedule
80 threaded PVC,
0.015 inch slot
SAND/GRAVEL PACK:
#1 Morie sand
BOTTOM OF SCREEN
BOTTOM CAP
BOTTOM OF BOREHOLE
DIAMETER OF BOREHOLE:
6"

REMARKS (Installation, development) :
Open bedrock hole 54 - 74 feet. MATERIALS: 10 FT OF 4" SCH 80 PVC SCREEN, 104 FT OF SCH 80 PVC RISER, 21 FT OF 8" STEEL CASING,1 BOTTOM CAP, 6 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 10 BAGS OF PORTLAND CEMENT, 1 6 " STICK UP CASING.

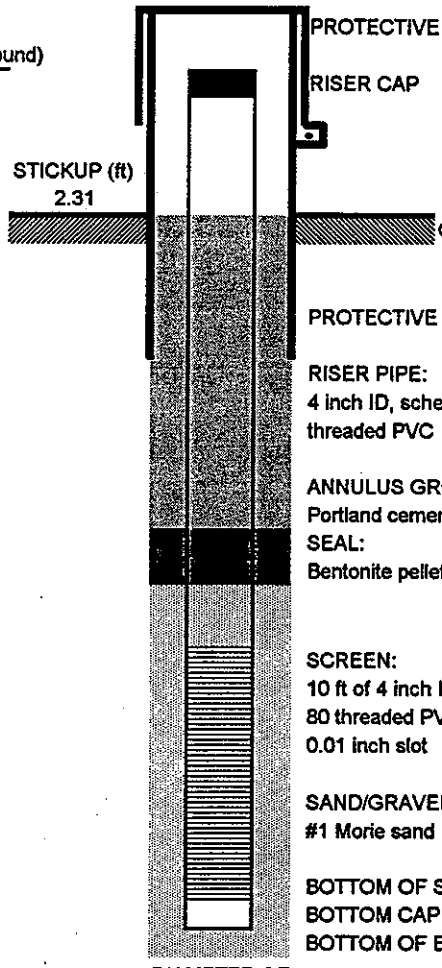
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-117**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft above MSL
Drilling company WARREN-GEORGE, INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 5.18 ft
Date and time of completion 6/1/92	*Northing* 26639.141	*Top of protective steel casing elevation* 7.49 ft
Inspector D. Davidson	*Easting* -20177.984	*Top of riser pipe elevation* 7.33 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	7.33	A	2.15
	5.18	B	0
0-2 ft.: Highly organic sandy, silty soil.			
2-9 ft.: Crushed SLAG			
	1.18	C	4
	-0.82	D	6
	-2.82	E	8
9-11 ft.: Lt. gray highly organic SILT.			
11-18 ft.: Decomposed ROCK w/ silt and sand.			
18-28 ft. NX core: Competent bedrock Biotite-feldspar GNEISS w/ quartz and garnet.	-12.82	F	18
	-12.82	G	18
	-12.82	H	18



REMARKS (Installation, development) :

MATERIALS: 10 FT OF 4" SCH 80 PVC SCREEN, 10 FT OF 4" SCH 80 PVC RISER, 1 BOTTOM CAP, 2 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 2 BAGS OF PORTLAND CEMENT, 1 6" STICK UP CASING.

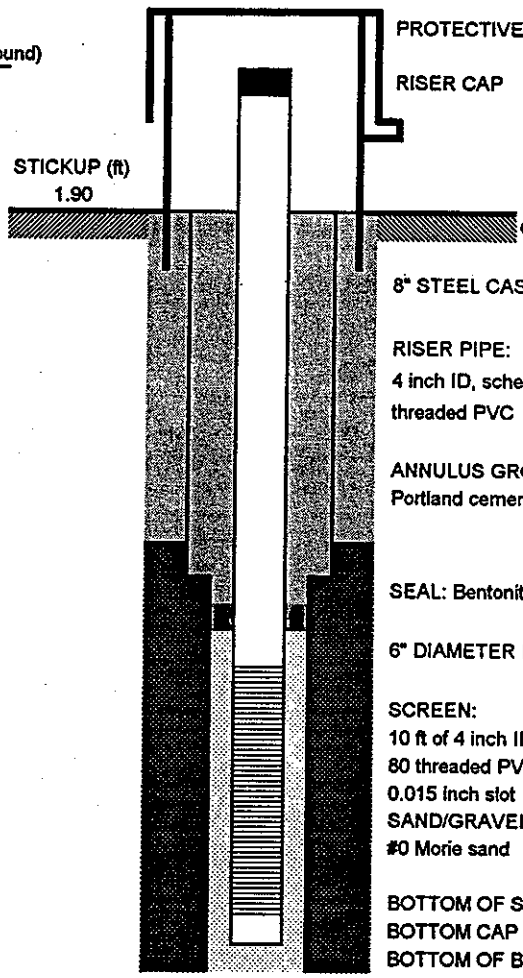
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-117B**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL
Drilling company WARREN-GEORGE, INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 4.62 ft
Date and time of completion 6/29/92	*Northing* 26615.782	*Top of protective steel casing elevation* 6.52 ft
Inspector R. Costa	*Easting* -20186.704	*Top of riser pipe elevation* 6.40 ft

A = Top of Riser
B = Ground Surface
C = Top of Bedrock
D = Bottom of 8" Casing
E = Top of Bentonite Seal
F = Top of Sand Pack
G = Top of Screen
H = Bottom of Screen
I = Bottom of PVC/Steel
J = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above MSL)		DEPTHS (ft below/ above ground)
	6.40	A	1.78
0-16 ft.: Brown med. SAND and SILT.			
16-24.5 ft.: Decomposed biotite SCHIST.			
	-19.88	C	24.5
24.5-78 ft.: Competent Bedrock: Biotite-garnet SCHIST.	-21.38	D	26
	-25.38	E	30
	-27.38	F	32
	-63.38	G	68
	-73.38	H	78
	-73.38	I	78
	-73.38	J	78



REMARKS (Installation, development) :

MATERIALS: 26 FT OF 8" STEEL CASING; 1 BOTTOM PLUG; 10 FT OF SCH 80 4" PVC SCREEN 0.015 SLOT; 70 FT OF 4" SCH 80 PVC RISER; 6 BAGS #0 MORIE SAND; 1/2 BUCKET BENTONITE PELLETS, 4 BAGS PORTLAND CEMENT; 1 STANDPIPE W/ LOCK.

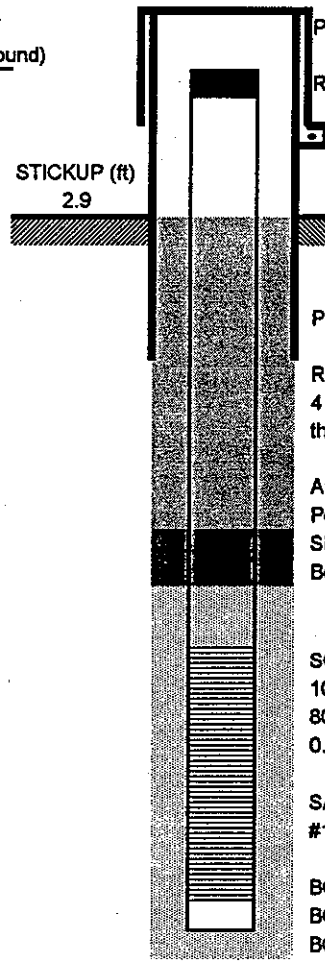
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-118**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL
Drilling company WARREN-GEORGE, INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 10.83 ft
Date and time of completion 6/3/92	*Northing* 26728.412	*Top of protective steel casing elevation* 13.73 ft
Inspector D. Davidson	*Easting* -19287.747	*Top of riser pipe elevation* 13.19 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	13.19	A	2.36
			STICKUP (ft) 2.9
	10.83	B	0
0-6 ft.: Sand, silt, gravel, and decomposed rock.			
6-15 ft.: FILL			
	8.83	C	2
	7.33	D	3.5
	5.83	E	5
	-4.17	F	15
	-4.17	G	15
	-4.71	H	15



PROTECTIVE STEEL CAP WITH LOCK

RISER CAP

GROUND SURFACE

PROTECTIVE STEEL CASING CEMENTED

RISER PIPE:
4 inch ID, schedule 80 threaded PVC

ANNULUS GROUTED WITH:
Portland cement

SEAL:
Bentonite pellets

SCREEN:
10 ft of 4 inch ID, schedule 80 threaded PVC, 0.01 inch slot

SAND/GRAVEL PACK:
#1 Morie sand

BOTTOM OF SCREEN
BOTTOM CAP
BOTTOM OF BOREHOLE

DIAMETER OF BOREHOLE:
11 1/2"

REMARKS (Installation, development) :
MATERIALS: 10 FT OF 4" SCH 80 PVC SCREEN, 10 FT OF 4" SCH 80 PVC RISER,1 BOTTOM CAP, 6 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 3 BAGS OF PORTLAND CEMENT,1 6" STICK UP CASING.

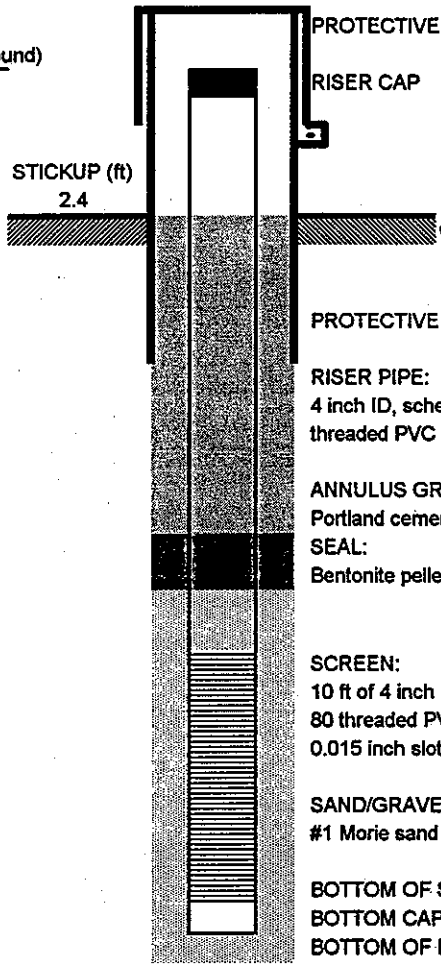
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-119**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL.
Drilling company WARREN-GEORGE INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 11.52 ft
Date and time of completion 6/10/92	*Northing* 27200.09	*Top of protective steel casing elevation* 13.92 ft
Inspector D. Davidson	*Easting* -18950.844	*Top of riser pipe elevation* 13.78 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	13.78	A	2.26
	11.52	B	0
0-27 ft.: FILL.			
	-0.48	C	12
	-2.48	D	14
	-6.48	E	18
27-52 ft.: RIP-RAP			
52-58.5 ft.: White and black biotite feldspar GNEISS w/ muscovite, quartz, and garnet.			
	-16.48	F	28
	-16.48	G	28
	-40.48	H	52



REMARKS (Installation, development) :

MATERIALS: 10 FT OF 4" SCH 80 PVC SCREEN, 20 FT OF 4" SCH 80 PVC RISER, 1 BOTTOM CAP, 4 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS, 3 BAGS OF PORTLAND CEMENT, 1 6" STICK UP CASING.

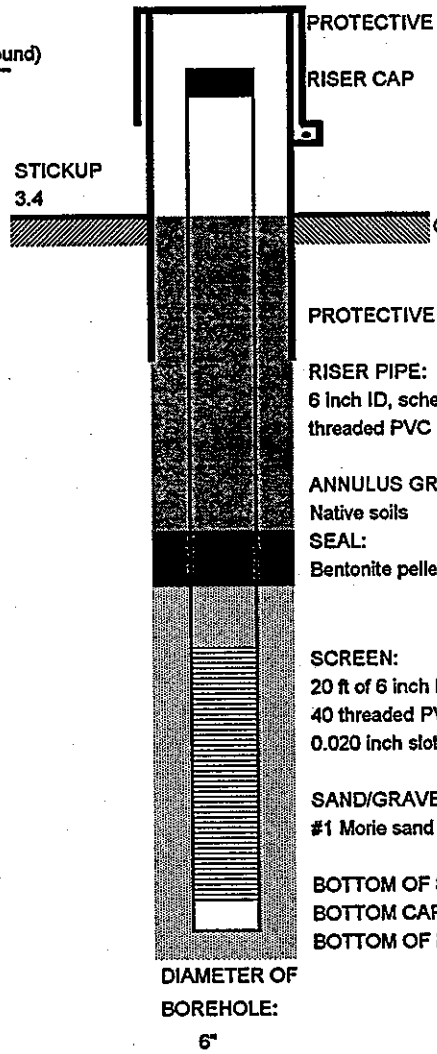
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-120**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL.
Drilling company WARREN-GEORGE, INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 9.05 ft
Date and time of completion 6/10/92	*Northing* 27776.950	*Top of protective steel casing elevation* 12.45 ft
Inspector B. Atkinson	*Easting* -18994.003	*Top of riser pipe elevation* 11.61 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	11.16	A	2.56
	9.05	B	0
0-6 ft.: Brown cuttings.			
6-30 ft.: Black cuttings, abundant gravel.			
30-46 ft.: Dark grey, silty CLAY.	-20.31	C	31
	-22.31	D	33
	-22.31	E	33
46-53 ft.: Lt. brown fine SAND.			
	-42.31	F	53
	-42.31	G	53
	-44.89	H	55.58



REMARKS (Installation, development) :

MATERIALS: 20 FT OF 6" SCH 40 PVC SCREEN, 36 FT OF 6" SCH 40 PVC RISER, 1 BOTTOM CAP, 9 BAGS OF #1 SAND, 1 BUCKET OF BENTONITE PELLETS.

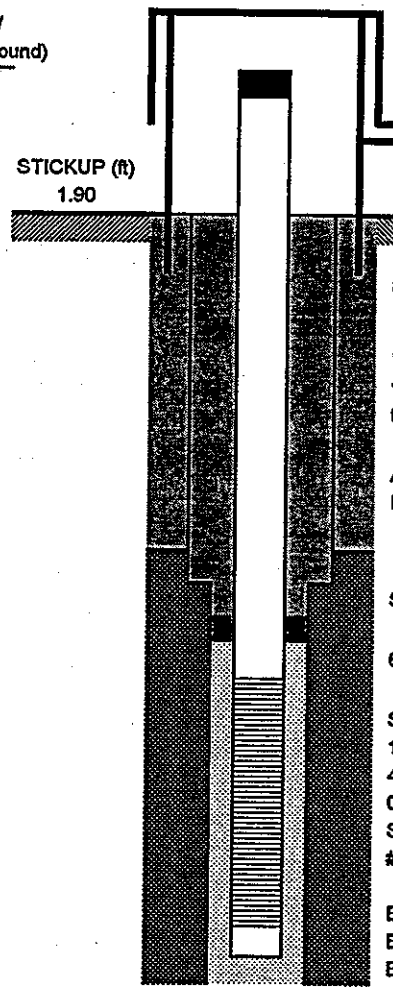
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-120B**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft. above MSL
Drilling company WARREN-GEORGE, INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 9.09 ft
Date and time of completion 5/22/92	*Northing* 27791.700	*Top of protective steel casing elevation* 10.99 ft
Inspector J. Prunetti	*Easting* -18995.120	*Top of riser pipe elevation* 10.84 ft

A = Top of Riser
B = Ground Surface
C = Top of Bedrock
D = Bottom of 8" Casing
E = Top of Bentonite Seal
F = Top of Sand Pack
G = Top of Screen
H = Bottom of Screen
I = Bottom of PVC/Steel
J = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	10.84	A	1.75
	9.09	B	0
0-45 ft.: Dark grey cuttings and fluids; unconsolidated material. (FILL?)			
45-56 ft.: Tan cuttings, very soft material. (Glacial Sediment?)	-46.95	C	56
	-54.95	D	64
	-55.95	E	65
56-79 ft.: Lt. grey cuttings; BEDROCK.	-57.95	F	67
	-59.95	G	69
	-69.95	H	79
	-69.95	I	79
	-69.95	J	79



REMARKS (Installation, development) :
8" casing driven to 64 ft.; borehole advanced to 79 ft. to set well.

MATERIALS: 10 FT 4" SCH 40 PVC SCREEN; 70 FT 4" SCH 40 PVC RISER; 65 FT 8" STEEL CASING; 3 BAGS #1 MORIE SAND; 11 BAGS PORTLAND CEMENT; 1 BUCKET BENTONITE PELLETS; 1 BOTTOM CAP; 1 STANDPIPE W/ LOCK.

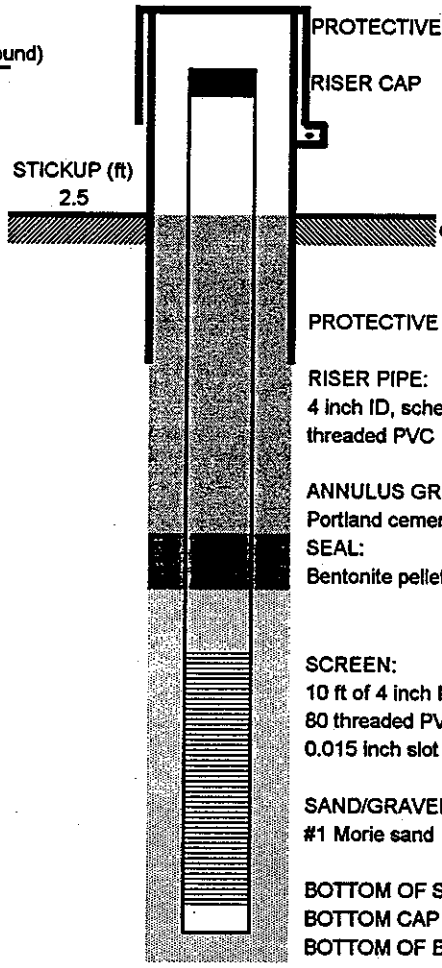
WOODWARD-CLYDE CONSULTANTS
Consulting Engineers, Geologists and Environmental Scientists

CONSTRUCTION OF WELL / PIEZOMETER **MW-122**

Project name & location PELHAM BAY LANDFILL, BRONX, NEW YORK	*Well lock No.* 3220	*Elevation datum* Bronx Datum (BD) 2.608 ft, above MSL.
Drilling company WARREN-GEORGE INC.	*Surveyor* ETTLINGER & ETTLINGER	*Ground elevation* 9.54 ft
Date and time of completion 6/2/92	*Northing* 28967.069	*Top of protective steel casing elevation* 12.04 ft
Inspector B. Atkinson	*Easting* -19311.343	*Top of riser pipe elevation* 11.68 ft

A = Top of Riser
B = Ground Surface
C = Top of Bentonite Seal
D = Top of Sand Pack
E = Top of Screen
F = Bottom of Screen
G = Bottom of PVC/Steel
H = Bottom of Borehole

GENERALIZED SOIL DESCRIPTION	ELEV. (ft above/ below BD)		DEPTHS (ft below/ above ground)
	11.68	A	2.14
	9.54	B	0
0-26 ft.: Brownish-dk. grey gravelly cuttings.			
26-28 ft.: Dk. grey-black SILT.	-11.46	C	21
	-14.46	D	24
	-17.46	E	27
28-37 ft.: Lt. brown fine SAND.			
	-27.46	F	37
	-27.46	G	37
	-27.46	H	37



REMARKS (Installation, development) :
30 FT. OF SCH 80 4" PVC RISER, 10 FT. OF SCH 80 4" PVC SCREEN, 1 BUCKET OF BENTONITE PELLETS, 5 BAGS OF #1 SAND, 4 BAGS OF PORTLAND CEMENT, 2 SCH 80 PVC BOTTOM/TOP CAPS.

ARCADIS

Appendix U

Groundwater Well Sampling Log

MONITORING WELL INFORMATION

Date: **Sampler:**

Monitoring Well Characteristics

Well No.	**Well Diameter:**	**Gallons/Ft.**
Depth of Well, (Ft.)		
Depth to Water, (Ft.)		
Depth of Water, (Ft.)		
Volume of Well, (Gals.)		

Sampling and Purging of Monitoring Wells

Purge Volume (Casings)	**Time**	**Depth to Water**	**Purge Rate**	**Temp**	**Spec C**	**DO**	**pH**	**ORP**	**Turb.**
Initial									
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									

Low Flow Sampling Method __ Purge & Bailer Method ___

GROUNDWATER ELEVATION CALCULATION SHEET
PELHAM BAY LANDFILL, BRONX, NEW YORK

Date _____ **Time** _____

Measurer _____

Well Number	Top of Well Elevation**	Depth to Groundwater (ft)	Water Table Elev.
MW – 104	19.132		
MW – 106	18.388		
MW – 109	23.952		
MW – 110	20.013		
MW – 113	14.442		
MW – 114	14.66		
MW – 115	24.807		
MW – 115B	24.876		
MW – 117 *	8.077		
MW – 117B *	Can't locate		
MW – 118	19.113		
MW – 119	20.421		
MW – 120	18.838		
MW – 120B	19.296		
MW – 121	15.621		
MW – 122	17.575		
MW – 124 *	Can't locate		
MW – 124B *	Can't locate		
MW – 126 (PZ-5)	Can't locate		
PZ-A	11.951		
PZ-B *	14.254		
PZ-C	11.374		
PZ-D *	12.411		
PZ-E	9.545		
PZ-F	9.645		

* MW -117, MW-117B, MW-124, MW-124B, PZ-B & PZ-D
are located outside landfill on Pelham park side

** Wells re-surveyed in July 2006

GROUNDWATER ELEVATION LOG
PELHAM BAY LANDFILL, BRONX, NEW YORK

Date _____ **Measurer** _____

GROUNDWATER ELEVATION			
Well Number	**Time**	**Elevation (ft) ***	**Comments**
MW – 104		19.132	
MW – 106		18.388	
MW – 109		23.952	
MW – 110		20.013	
MW – 113		14.442	
MW – 114		14.66	
MW – 115		24.807	
MW – 115B		24.876	
MW – 117		8.077	
MW – 117B		--	
MW – 118		19.113	
MW – 119		20.421	
MW – 120		18.838	
MW – 120B		19.296	
MW – 121		15.621	
MW – 122		17.575	
MW – 124		--	
MW – 124B		--	
MW – 126 (PZ-5)		--	
PZ-A		11.951	
PZ-B		14.254	
PZ-C		11.374	
PZ-D		12.411	
PZ-E		9.545	
PZ-F		9.645	

PZ-A, PZ-C, and PZ-E are piezometer wells upstream of slurry wall
PZ-B, PZ-D, and PZ-F are piezometer wells downstream of slurry wall

*** ALL ELEVATIONS REFER TO BRONX HIGHWAY DATUM, WHICH IS 2.608 FEET ABOVE MEAN SEA LEVEL AT SANDY HOOK, NEW JERSEY AS ESTABLISHED BY U.S. COAST AND GEODETIC SURVEY.**

ARCADIS

Appendix V

Groundwater Sample Collection
Protocol Modifications

APPENDIX V

GROUNDWATER SAMPLE COLLECTION PROTOCOL MODIFICATIONS

This document describes the modifications to the groundwater sample collection protocols provided in Volume III of the Operation, Maintenance and Monitoring (OM&M) Manual (see Appendix K of this SMP) to address the tidally-influenced nature of groundwater at the Site and deletion of the requirement to gauge for the presence of non-aqueous phase liquid (NAPL). Two groundwater sample collection protocols are provided as Appendix D (Groundwater Sample Collection Using Bailers) and Appendix E (Groundwater Sample Collection Using Low-Flow Rate Purging and Sampling Technique) in Volume III of the OM&M Manual. Additionally, Appendix C of Volume III of the OM&M Manual provides the Long-Term Monitoring Program Sampling and Analysis Plan, which provides general guidance for groundwater sample collection. The general modifications provided herein apply to both groundwater sample collection protocols and the protocol-specific modifications for each technique are described below.

General Groundwater Sample Collection Protocol Modifications

One of the primary objectives of the groundwater monitoring program is to obtain representative groundwater samples (i.e., to characterize groundwater quality during periods when the groundwater is not significantly mixed with surface water from Eastchester Bay). Since the groundwater at the Site is tidally-influenced (i.e., groundwater mixes with surface water from Eastchester Bay during flood [incoming] tide), groundwater samples collected during the incoming and high tides may result in lower concentrations of aqueous species in the groundwater due to dilution. Therefore, groundwater samples will be collected from the monitoring well network during ebb (i.e., outgoing) tide, but prior to low tide conditions (i.e., between approximately 3 to 5 hours following high tide). Collecting groundwater samples during this period should yield samples that are representative of groundwater quality and allow for a sufficient amount of water column to be present in the monitoring wells for well purging and sampling activities. Monitoring wells that generally have a smaller water column height, and therefore less groundwater available for purging and sampling, will be sampled during the earlier part of the ebb tide (i.e., between 3 to 4 hours following high tide). Monitoring wells that generally have a greater water column height will be sampled during the later part of the ebb tide (i.e., between 4 to 5 hours following high tide).

Based on historical NAPL gauging and groundwater quality data (i.e., NAPL has not been detected at the Site and concentrations of aqueous species in the groundwater are not indicative of the presence of NAPL), the monitoring well network will no longer be gauged for the presence of NAPL during the groundwater sampling events. Water-level measurements will be collected from the monitoring well network using an electronic water-level indicator. However, if NAPL is visually observed during purging activities, or if concentrations of aqueous species in the groundwater significantly increase, NAPL gauging will be conducted.

Low-Flow Rate Purging and Sampling Technique Modifications

1. The low-flow rate purging and sampling protocol indicates that dedicated gas-operated stainless steel and Teflon bladder pumps (equipped with Teflon or Teflon lined polyethylene tubing) will be used for well purging and sample collection. Bladder pumps will no longer be used during low-flow rate purging and sampling. Alternative well sampling pumps will be used including, but not limited to, submersible pumps (e.g., Grundfos Redi-Flo2, ProActive Monsoon) or peristaltic pumps. Polyethylene tubing will be used and will be dedicated to each monitoring well. The tubing will be replaced in each well as necessary. The submersible pump may be dedicated to the monitoring well or may be portable and used in different monitoring wells. A peristaltic pump will generally be used to purge and sample monitoring wells with a low yield. If a peristaltic pump is used, all sample parameters will be collected directly from the pump discharge with the exception of the volatile organic compound (VOC) sample. The VOC sample will be collected using a disposable polyethylene bailer after all other sample parameters have been collected.

2. The groundwater purging and sampling will be conducted in accordance with United States Environmental Protection Agency (EPA) low-flow (minimal drawdown) groundwater sampling procedures (see attached EPA April 1996 document).

3. Water-level measurements will be collected from the monitoring well and the total depth of the well will be measured (i.e., sounded) using a measuring tape before well purging and sampling activities begin.

4. Well purging flow rates will not exceed 500 milliliters per minute (mL/min) in order to minimize drawdown in the well. The flow rate will be adjusted (i.e., lowered) as necessary with the goal of not exceeding 0.3 feet of drawdown during purging. This goal may be difficult to achieve in some monitoring wells due to geologic heterogeneities within the screened interval (i.e., less transmissive formation). As discussed previously, peristaltic pumps may be used to sample monitoring wells with a low yield.

5. With respect to the monitoring of turbidity during well purging, the well is considered stabilized and ready for sample collection when the turbidity is 50 nephelometric turbidity units (NTUs) or less. The stabilization of turbidity is required along with the other field parameters that are to be monitored during well purging: pH, temperature, specific conductance, oxidation-reduction potential (ORP), and dissolved oxygen (DO).

6. The monitoring wells will be purged until the water quality indicator parameters have stabilized, as discussed in the low-flow rate purging and sampling protocol. However, if the stabilization criteria cannot be achieved after 1 hour of purging, then the groundwater sample will be collected following 1 hour of purging.

7. The polyethylene tubing will be disconnected from the flow-through cell prior to sample collection and the groundwater sample will be collected directly from the submersible pump discharge (i.e., prior to the flow-through cell). This will preclude the need to decontaminate

the flow-through cell between well locations. Groundwater samples will not be collected from the flow-through cell discharge.

8. If a submersible pump is dedicated to a monitoring well, then decontamination of the equipment will not be necessary. Non-dedicated equipment will be decontaminated as follows: Rinse equipment with Micro-90 low-phosphate detergent (or equivalent) and potable water solution and scrub with a brush. Rinse equipment with distilled/deionized rinse water.

Bailer Purging and Sampling Technique Modifications

1. The existing OM&M Manual procedures for bailer purging and sampling protocol indicates that a stainless steel or Teflon bailer will be used for well purging and sample collection. Additionally, a disposable polyethylene bailer will also be permitted for well purging and sample collection. A new or dedicated disposable polyethylene bailer will be used at each well where bailer purging and sampling techniques are being employed during each sampling event. Therefore, there will be no decontamination activities associated with bailer purging and sampling.

2. As discussed previously, NAPL has not been detected at the Site. Therefore, there is no need to initially lower the bailer partially into the water column and decant groundwater from the bailer into a glass container for observation of oil sheens.

3. The bailer purging and sampling protocol indicates that 5 well volumes will be purged prior to sample collection, assuming that the well has not been bailed dry. Alternatively, 3 well volumes will now be purged prior to sample collection.

4. The total depth of the well will be measured (i.e., sounded) using a measuring tape after well purging and sampling activities have been completed.

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/S-95/504 April 1996

EPA Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls[1] and Michael J. Barcelona[2]

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing units were identified and sampled in keeping with that objective. These were highly productive aquifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic *units*. With time it became apparent that conventional water supply generalizations of *homogeneity* did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

[1]National Risk Management Research Laboratory, U.S. EPA
[2]University of Michigan

Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aquifer heterogeneity and colloidal transport. Aquifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry, hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third *phase* as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria. These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling

objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

1) Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;

2) Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and

3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term *representativeness* applies to chemical and hydrogeologic data collected via wells, borings, piezometers, geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

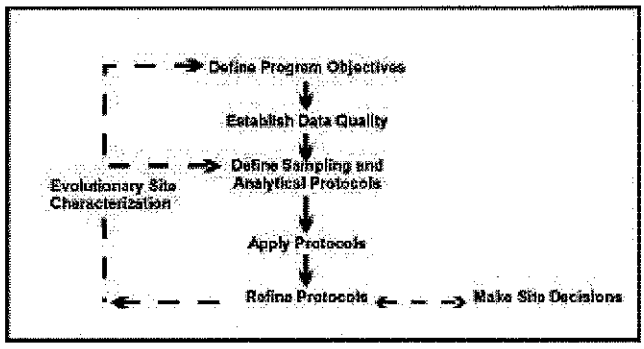


Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

1) Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-

flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the *mobile* load of contaminants present (dissolved and colloid-associated);
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water;
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- higher initial capital costs,
- greater set-up time in the field,
- need to transport additional equipment to and from the site,
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a *change in conditions* and trigger an *action.*

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). High-quality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and *fresh* screen waters during insertion of the sampling device or ground-water level measurement device; disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g. , pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- maximize tubing wall thickness, minimize tubing length;
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are ill-suited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a *fix* for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally *dissolved* [i.e., samples filtered with 0.45 µm filters]) concentrations of major ions and trace metals, 0.1 µm filters are recommended although 0.45 µm filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO_2 composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and non-disposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality

indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon™ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C.

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

(1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.

(2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.

(3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of

the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

a. "portable or non-dedicated mode" - Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.

b. "dedicated mode" - Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described herein as part of its in-house research program and under Contract No. 68-C4-0031 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

VIII. References

Backhus, D,A., J.N. Ryan, D.M. Groher, J.K. McFarlane, and P.M. Gschwend. 1993. Sampling Colloids and Colloid-Associated Contaminants in Ground Water. *Ground Water*, 31(3):466-479.

Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb. 1984. A laboratory evaluation of groundwater sampling mechanisms. *Ground Water Monitoring Review*, 4(2):32-41.

Barcelona, M.J. and J.A. Helfrich. 1986. Well construction and purging effects on ground-water samples. *Environ. Sci. Technol.*, 20(11):1179-1184.

Barcelona, M.J., H.A. Wehrmann, and M.D. Varljen. 1994. Reproducible well purging procedures and VOC stabilization criteria for ground-water sampling. *Ground Water*, 32(1):12-22.

Buddemeier, R.W. and J.R. Hunt. 1988. Transport of Colloidal Contaminants in Ground Water: Radionuclide Migration at the Nevada Test Site. *Applied Geochemistry*, 3: 535-548.

Danielsson, L.G. 1982. On the Use of Filters for Distinguishing Between Dissolved and Particulate Fractions in Natural Waters. *Water Research*, 16:179.

Enfield, C.G. and G. Bengtsson. 1988. Macromolecular Transport of Hydrophobic Contaminants in Aqueous Environments. *Ground Water*, 26(1): 64-70.

Gschwend, P.M. and M.D. Reynolds. 1987. Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Plume, *J. of Contaminant Hydrol.*, 1: 309-327.

Herzog, B., J. Pennino, and G. Nielsen. 1991. Ground-Water Sampling. In **Practical Handbook of Ground-Water Monitoring** (D.M. Nielsen, ed.). Lewis Publ., Chelsea, MI, pp. 449-499.

Horowitz, A.J., K.A. Elrick, and M.R. Colberg. 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations. *Water Res.*, 26(6):753-763.

Laxen, D.P.H. and I.M. Chandler. 1982. Comparison of Filtration Techniques for Size Distribution in Freshwaters. *Analytical Chemistry*, 54(8):1350.

McCarthy, J.F. and J.M. Zachara. 1989. Subsurface Transport of Contaminants, *Environ. Sci. Technol.*, 5(23):496-502.

McCarthy, J.F. and C. Degueldre. 1993. Sampling and Characterization of Colloids and Ground Water for Studying Their Role in Contaminant Transport. In: Environmental Particles (J. Buffle and H.P. van Leeuwen, eds.), Lewis Publ., Chelsea, MI, pp. 247-315.

Parker, L.V. 1994. The Effects of Ground Water Sampling Devices on Water Quality: A Literature Review. *Ground Water Monitoring and Remediation*, 14(2):130-141.

Penrose, W.R., W.L. Polzer, E.H. Essington, D.M. Nelson, and K.A. Orlandini. 1990. Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region, *Environ. Sci. Technol.*, 24:228-234.

Puls, R.W. and M.J. Barcelona. 1989. Filtration of Ground Water Samples for Metals Analyses. *Hazardous Waste and Hazardous Materials*, 6(4):385-393.

Puls, R.W., J.H. Eychaner, and R.M. Powell. 1990. Colloidal-Facilitated Transport of Inorganic Contaminants in Ground Water: Part I. Sampling Considerations. EPA/600/M-90/023, NTIS PB 91-168419.

Puls, R.W. 1990. Colloidal Considerations in Groundwater Sampling and Contaminant Transport Predictions. *Nuclear Safety*, 31(1):58-65.

Puls, R.W. and R.M. Powell. 1992. Acquisition of Representative Ground Water Quality Samples for Metals. *Ground Water Monitoring Review*, 12(3):167-176.

Puls, R.W., D.A. Clark, B.Bledsoe, R.M. Powell, and C.J. Paul. 1992. Metals in Ground Water: Sampling Artifacts and Reproducibility. *Hazardous Waste and Hazardous Materials*, 9(2): 149-162.

Puls, R.W. and C.J. Paul. 1995. Low-Flow Purging and Sampling of Ground-Water Monitoring Wells with Dedicated Systems. *Ground Water Monitoring and Remediation*, 15(1):116-123.

Ryan, J.N. and P.M. Gschwend. 1990. Colloid Mobilization in Two Atlantic Coastal Plain Aquifers. *Water Resour. Res.*, 26: 307-322.

Thurnblad, T. 1994. Ground Water Sampling Guidance: Development of Sampling Plans, Sampling Protocols, and Sampling Reports. Minnesota Pollution Control Agency.

U. S. EPA. 1992. RCRA Ground-Water Monitoring: Draft Technical Guidance. Office of Solid Waste, Washington, DC EPA/530/R-93/001, NTIS PB 93-139350.

U. S. EPA. 1995. Ground Water Sampling Workshop -- A Workshop Summary, Dallas, TX, November 30 - December 2, 1993. EPA/600/R-94/205, NTIS PB 95-193249, 126 pp.

U. S. EPA. 1982. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846. Office of Solid Waste and Emergency Response, Washington, D.C.

Figure 2. **Ground Water Sampling Log**

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

_____

Sampling Personnel _____

Time	pH	Temp	Cond.	Dis.O_2	Turb.	[ ]Conc			Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project _____ **Site** _____ **Well No.** _____ **Date** _____
Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____
Sampling Device _____ **Tubing type** _____ **Water Level** _____
Measuring Point _____ **Other Infor** _____

Sampling Personnel _____

Time	Pump Rate	Turbidity	Alkalinity	[ ] Conc	Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

ARCADIS

Appendix W

NYSDEC Groundwater Monitoring
Well Decommissioning Procedures

GROUNDWATER MONITORING WELL DECOMMISSIONING PROCEDURES

April 2003

New York State Department
of Environmental Conservation

Division of Environmental Remediation

DECOMMISSIONING PROCEDURES

NYS SUPERFUND STANDBY CONTRACT
WORK ASSIGNMENT D002852-10

NPL SITE MONITORING WELL DECOMMISSIONING

NEW YORK STATE DEPARTMENT
OF ENVIRONMENTAL CONSERVATION

MAY 1995
Revised October 1996

0266-317-002

TABLE OF CONTENTS

NYS SUPERFUND STANDBY CONTRACT
NPL SITE MONITORING WELL DECOMMISSIONING

TABLE OF CONTENTS (Continued)

LIST OF FIGURES/LOGS & PLATES

LIST OF APPENDICES

Appendix	Description
A	Health and Safety Plan
B	Equipment Decontamination SOPs
C	Construction Inspection Forms
D	Hydraulic Pressure Testing SOP

DISCLAIMER

October 21, 1996

RE: New York State Department of Environmental Conservation
Division of Environmental Remediation
Monitoring Well Decommissioning Procedures

Per your request, the enclosed referenced document is being made available to you for informational purposes. These procedures may be used as a guidance when decommissioning a monitoring well. Please note that this document does not address some site specific special situations that may be encountered in the field. These procedures have not been adopted by the Department of Environmental Conservation. Compliance with the procedures set forth in this document does not relieve any party of the obligation to successfully and satisfactorily decommission a well.

If you have any questions, please contact Ben Loredo, of my staff, at (518) 457-0927.

Sincerely,

Gerald J. Rider, Jr., P.E.
Chief, Operation, Maintenance and Support Section
Bureau of Hazardous Site Control
Division of Environmental Remediation
New York State Department of Environmental Conservation

Enclosure

INTRODUCTION

Malcolm Pirnie, Inc. has developed hazardous waste site monitoring well decommissioning procedures for the New York State Department of Environmental Conservation (NYSDEC) under the New York State Superfund Standby Contract, Work Assignment No. D002852-10. These procedures have been established as a guide for successful decommissioning of wells that are no longer used for monitoring at select National Priorities List (NPL) sites in New York State. A well is successfully decommissioned when:

- Migration of existing or future contaminants into an aquifer or between aquifers cannot occur.
- Migration of existing or future contaminants in the vadose zone cannot occur.
- The potential for vertical or horizontal migration of fluids in the well or adjacent to the well is minimized
- Aquifer yield and hydrostatic ahead are conserved.

The decommissioning procedures are based on NYSDEC-approved methods originally developed by Malcolm Pirnie which entailed an extensive literature search and consultations withe industrial and NYSDEC officials. The literature search included sources from the National Ground Water Association, American Society for Testing and Materials (A.S.T.M.), State and EPA guidance documents, Malcolm Pirnie decommissioning procedures, and various other technical sources. A complete listing of sources is included at the end of these procedures. The industry officials consulted include drilling contractors, equipment suppliers and manufacturers, and A.S.T.M. members on Soil and Rock (D-18) and Water (D-19) committees.

These decommissioning procedures describe criteria for a satisfactorily decommissioning a monitoring well. Selection of a preferred decommissioning method will be dependent on site-specific and location-specified conditions such as the type of aquifer, the mature of the contamination, geological conditions and the type of well construction. Prior to initiating field work, the available site and location-specific data will be collected and

reviewed, and a pre-construction inspection of the monitoring well will be conducted to assist in determining the best-suited decommissioning method.

For maximum protection of human health and the environment, any material brought to the surface during the decommissioning process will be treated as a hazardous waste unless sample data indicates otherwise. The selection of disposal methods for these materials will depend on information reported in site investigation reports and analytical characterization of the retrieved materials for hazardous characteristics (see Sections 4.1.3 through 4.1.4). An appropriate procedure will be followed for the physical and hydrologic setting of the well that best protects the environment.

The following sections describe the procedures that will be implemented to properly decommission a well, including the procedure for selecting which decommissioning method will be used. There are eleven elements to be addressed in decommissioning a monitoring well at a hazardous waste site:

1) Reviewing Site Data
2) Selecting the Well Decommissioning Method
3) Preparing a Site-Specific Health and Safety Plan
4) Preparing a Materials Handling and Disposal Plan
5) Establishing Decontamination Procedures
6) Locating and Setting-Up on the Well
7) Removing the Protective Casing
8) Decommissioning of Screen and Riser
9) Selecting, Mixing, and Placing Grout
10) Backfilling and Site Restoration
11) Quality Assurance/Quality Control (QA/QC) Procedures

The proper well decommissioning methods and selection process are presented on the flow chart presented as Plate 1. For each decommissioning method, the specific procedures are determined by (1) geology, (2) contaminants, and (3) well design. For example, decommissioning a well that penetrates a confining layer may require a different approach than decommissioning an unconfined water table well.

1.0 REVIEWING SITE DATA

The first step in selecting the well decommissioning process consists of reviewing all pertinent site information; boring and well logs, field inspection sheets, and laboratory analytical results performed on site soil and groundwater samples. This site information will form the basis for decisions throughout the decommissioning process. Field inspection of the wells prior to decommissioning is also recommended to verify the characteristics and conditions of the wells. Special conditions such as access problems, well extensions through capped and covered landfills, and cap conditions due to seasonal weather patterns should be assessed. At well locations that have been extended, the burial of a previous concrete pad may require the excavation of soil to the top of the concrete pad to remove the well. Decommissioning work requiring the use of heavy vehicular equipment on RCRA landfill caps should be scheduled during dry weather if possible so as to minimize damage to the cover. If work must be performed during the Spring, Winter or inclement weather, special measures such as placement of plywood to reduce ruts should be employed to maintain the integrity of the completed landfill cover system. A sample Monitoring Well Field Inspection Log indicating the minimum information to be collected during field verification activities is included as Figure 1.

2.0 SELECTING THE WELL DECOMMISSIONING METHOD

The primary rationale for well decommissioning is to prevent contaminant migration along the disturbed construction zone created by the original well boring. This requires selection of a decommissioning procedure that takes into account factors such as:

- The hydrogeological conditions at the well site.
- The presence or absence of contamination in the groundwater.
- The original well construction details.

This section presents a summary of the well decommissioning methods and the selection process, which is illustrated in the flow chart presented as Plate 1. The primary well decommissioning procedures consist of:

- Casing pulling.
- Overdrilling.
- Grouting the casing in-place.
- Perforating the casing followed by grouting in-place.

A general discussion of each decommissioning procedure is presented in Sections 2.1 through 2.4.

2.1 CASING PULLING

In general, casing pulling is the preferred method for decommissioning wells where: no contamination is present; contamination is present but the well does not penetrate a confining layer; and when both contamination and a confining layer are present but the contamination cannot cross the confining layer. Additionally, the well construction materials and well depth must be such that pulling can be effected without breaking the riser.

Casing pulling involves removing the well casing by lifting. The procedure for removing the casing must allow grout to be added during pulling. The grout will fill the space once occupied by the material being withdrawn. Grout mixing and placement must be performed according to the procedures in Section 9.0.

An acceptable procedure to remove casing involves puncturing the bottom of the casing, flushing with water to remove sand (if necessary to mitigate lock-up of the casing during pulling), filling the casing with grout tremied from the bottom of the well, using jacks to free casing from the hole, and lifting the casing out by using a drill rig, backhoe, crane, or other suitable equipment. Additional grout must be added to the casing as it is withdrawn. In wells or wellpoints in which the bottom cannot be punctured, the casing or screened interval will be perforated prior to being filled with grout. This procedure should be followed for wells installed in collapsible formations or for highly contaminated wells. At site locations in which the borehole does not collapse it may not be necessary to perforate the well casing prior to pulling the well (i.e., grouting the borehole can be completed after the well materials have been removed). However, measurements of the borehole depth must

be taken before and after the well is pulled to ensure that no collapse of well construction or formation materials occurred.

In the event that the casing or well screen is severed during casing pulling or if borehole collapse occurs, the remaining materials can be removed by overdrilling using the conventional augering method described in Section 2.2. In situations where well materials such as PVC screens and risers are suspected to sever, and removal of all well materials is required (i.e., at wells that are contaminated or those that penetrate an aquiclude), the contractor should install rods inside the well so that the rods would serve as a steel guide pipe for advancing augers during overdrilling.

At sites in which well casings have been grouted into a rock socket the casing pulling procedure may not be feasible. An alternative procedure involving overdrilling into the bedrock, pulling the casing, and subsequently grouting the openhole interval may be employed. For uncontaminated wells or wells with low levels of contamination, overdrilling, grinding on the rock, and grouting inside and outside of the well should be acceptable if the casing cannot be pulled. When this procedure is not acceptable and the casing must be pulled from a contaminated well, a spin and flush drilling technique may be used to advance flushpoint casing equipped with a diamond cutting shoe to the bottom of the casing socket. Water used during the spin and flush casing advancement will be controlled by the use of oversized casing, a coupling and a drilling tee. Drilling water will be containerized and disposed of in accordance with the site specific Material Handling and Disposal Plan.

2.2 OVERDRILLING

Overdrilling is used where casing pulling is determined to be unfeasible, or where installation of a temporary casing is necessary to prevent cross-contamination, such as when a confining layer is present and contamination in the deeper aquifer could migrate to the upper aquifer as the well was pulled (see Section 2.5). The overdrilling method should:

- Follow the original well bore.
- Create a borehole of the same or greater diameter than the original boring.
- Remove all of the well construction materials.

Acceptable methods for overdrilling include the following:

- Using conventional augering (i.e., a hollow stem auger fitted with a plug). The plug cutter will grind the well construction materials, which will be brought to the well surface by the auger.

- Using a conventional cable tool rig to advance casing having a larger diameter than the original boring. The cable tool kit is advanced within the casing to grind the well construction materials and soils, which are periodically removed with large diameter bailer. This method is not applicable to bedrock wells.

- Using an over-reaming tool with a pilot bit nearly the same size as the inside diameter of the casing and a reaming bit slightly larger than the original borehole diameter. This method can be used for wells with steel casings.

- Using a hollow-stem auger with outward facing carbide cutting teeth having a diameter two to four inches larger than the casing. Outward-facing cutting teeth will prevent severing the casing and drifting off center.

- Using a hollow-stem auger with a steel guide pipe inside. The casing guides the cutter head and remains inside the auger. The guide pipe should be firmly attached to the inside of the casing by use of a packer or other type of expansion or friction device.

Prior to overdrilling, an expandable J-plug or other suitable well cap will be used to prevent the introduction of soil or cuttings into the well, thereby ensuring a continuous grout column for wells that are grouted in place.

In all cases above, overdrilling should advance through the original bore depth by a distance of 0.5 feet to ensure complete removal of the construction materials. When the overdrilling is complete, the casing and screen can be retrieved from the center of the auger (American Society for Testing and Materials, Standard D 5299-92, 1992), if one of the hollow stem auger methods described above is employed. Subsequent to overdrilling at flush mount well locations where it may be impractical to remove well materials from inside the augers, a 1-2 foot deep area should be excavated by hand around the flush-mount well to facilitate a conventional well removal while tremie-grouting inside the well. Alterna-

tively, the soil within the annular space may be removed by raising the augers to allow the soil to fall out and re-advance the augers to the original target depth. Grout should then be tremied within the annular space between the augers and well casings. The grout level in the borehole should be maintained as the drilling equipment and well materials are sequentially removed. After overdrilling is completed, the borehole must be grouted according to the procedures in Section 9.0 and the upper five feet of borehole must be restored according to the procedures in Section 10.0.

2.3 GROUTING IN-PLACE

Grouting in-place is the simplest decommissioning procedure, but offers the least long-term protection of all the methods. As discussed in Section 2.5, however, this method is preferred for the bedrock portion of bedrock wells, and is used for decommissioning cased wells in certain situations. For cased wells, the procedure involves filling the casing with grout to a level of five feet below the land surface, cutting the well casing at the five-foot depth, and removing the top portion of the casing and associated well materials from the ground. The casing must be grouted according to the procedures in Section 9.0. In addition, the upper five feet of the borehole is filled to land surface and restored according to the procedures described in Section 10.0.

For wells installed in bedrock, the procedure involves filling the casing (or open hole) with grout to the top of rock according to the procedures in Section 9.0. The grout mix, however, will vary according to the hydrogeological conditions as discussed in Section 2.5.

It should be noted that for wells located on landfills regulated under 6NYCRR Part 360, the screened interval of the well must be sealed separately and hydrostatically tested to ensure its adequacy before sealing the remaining borehole. The Standard Operating Procedure (SOP) for the hydrostatic test has been included under Appendix D.

2.4 CASING PERFORATION/GROUTING IN-PLACE

At this time, casing perforation is the preferred method for wells with four-inch or larger inside diameter which are designated to be grouted in-place in accordance with the selection flow chart. The procedure involves perforating the well casing and screen then grouting the well. A wide variety of commercial equipment is available for perforating casings and screens in wells with four-inch or larger inside diameters. Due to the diversity of application, experienced contractors must recommend a specific technique based on site-specific conditions. A minimum of four rows of perforations several inches long and a minimum of five perforations per linear foot of casing or screen is recommended (American Society for Testing and Materials, Standard D 5299-92, 1992).

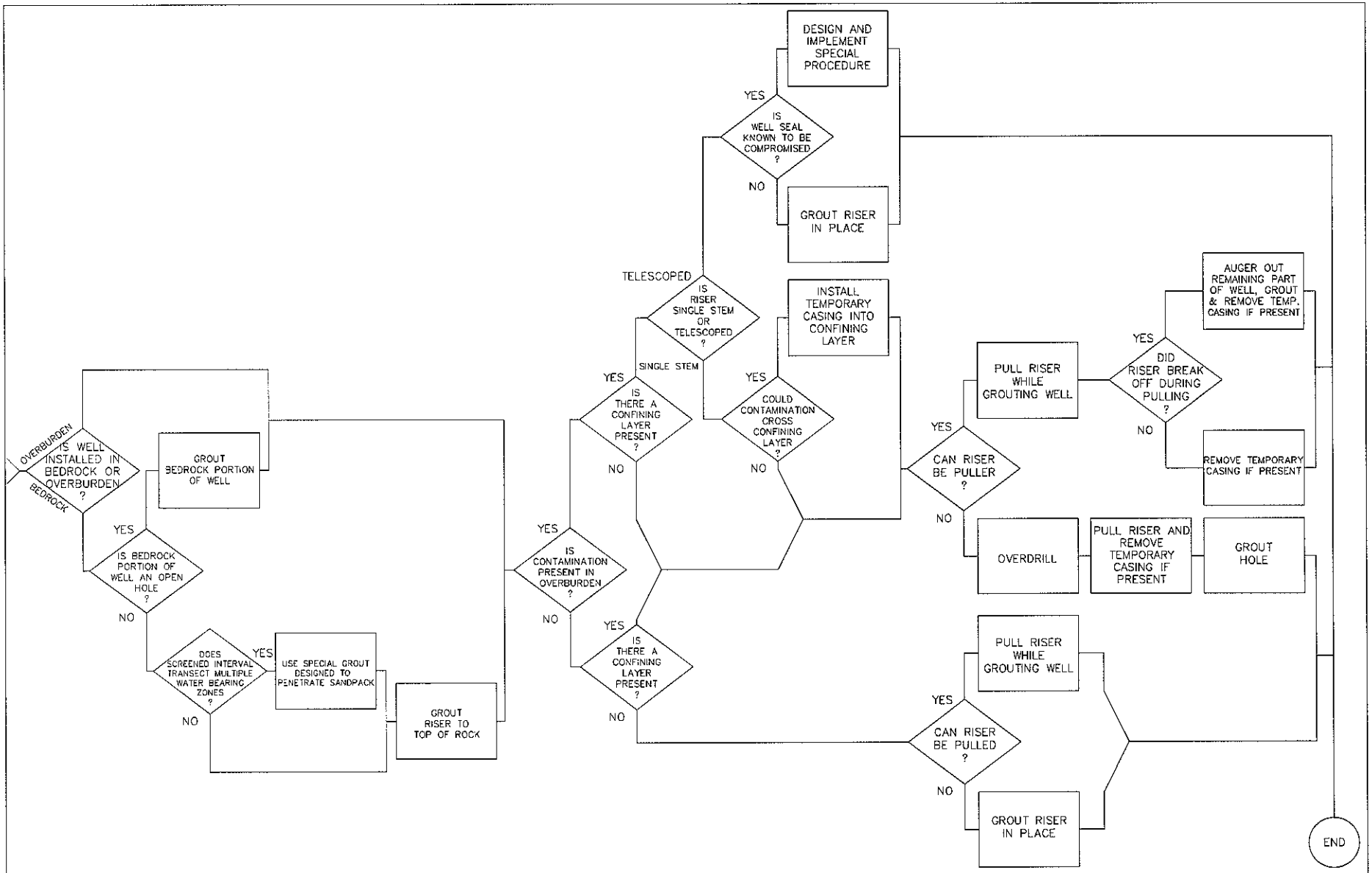
After perforating is complete, the borehole must be grouted according to the procedures in Section 9.0 and the upper five feet of borehole must be restored according to the procedures in Section 10.0.

2.5 SELECTION PROCESS AND IMPLEMENTATION

Selection of the decommissioning method is governed by the flow chart presented as Plate 1. A discussion of the selection criteria and decommissioning methodology is presented below.

2.5.1 Contaminated Monitoring Wells/Piezometers

For wells and piezometers suspected or known to be contaminated with NAPL or DNAPL product, measurement of the product volume will be determined using a weighted cotton string or by using an interface probe. Subsequent to calculation of the product volume, the NAPL/DNAPL product will be removed from inside the well. Removal of the contaminant product will be accomplished by bailing, pumping or installing an absorbent passive recovery system. Subsequent to product recovery, all contaminated materials will



Decommissioning Proceedure Selection

Source: Malcolm Pirnie for NYSDEC, March 1995, Plate 1

decom_flo2.dwg

be disposed of in accordance with the segregation and containment procedures described in Section 4.1.2.

2.5.2 Bedrock Wells

As illustrated on Plate 1,if the well is constructed within a bedrock formation, the screened or the open hole portion of the well is grouted to the top of the bedrock. Prior to initiating any grouting procedure, the depth of the well will be measured to determine if any silt or debris infilling has plugged the well. If plugging has occurred, the well will be flushed with an appropriately sized roller bit or drill rods to remove or suspend the obstruction in the water column. The borehole will then be tremie grouted from the bottom of the well to the top of bedrock to insure a continuous grout column. Note that if the bedrock well is cased, the screen should be perforated to the top of the rock if the inside diameter of the casing is 4-inches or larger. Furthermore, if the screened interval transects multiple water bearing zones the special grout mix discussed in Section 9.1.3 should be used to ensure penetration of the sand pack.

After the rock hole is grouted, the overburden portion of the well is decommissioned in accordance with the following sections. If the borehole extends to the surface, no further decommissioning procedures are required; however, the boring should only be filled to within 5-feet of the ground surface and site restoration should be completed in accordance with Section 10.0.

2.5.3 Uncontaminated Overburden Wells

For overburden wells and the overburden portion of bedrock wells, the first decision point in determining the decommissioning method considers whether the overburden portion of the well exhibits evidence of contamination, as determined through historical groundwater and/or soil sampling results. If the overburden portion of the well is uncontaminated, the next criteria considers whether the well penetrates a confining layer. In the case that the overburden portion of the well does not penetrate a confining layer, the casing should be pulled (and tremie-grouted) if possible. As a general rule, PVC wells greater than 25-feet deep should not be pulled unless site-specific conditions or other factors indicate that the

well can be pulled without breaking. If the well cannot be pulled, such as in the case that a bedrock portion of the well has already been grouted in place, or if the well materials and depth prohibit pulling or will likely result in breakage, the well should be grouted in-place as accordance with Section 2.3 (if the casing is less than 4-inch in diameter) or Section 2.4 (if the casing diameter is 4-inches or larger).

If the overburden portion of the well penetrates a confining layer, the casing should be removed by pulling (if possible) in accordance with Section 2.1. If the casing cannot be removed by pulling, the well should be removed by overdrilling. The overdrilling method used will depend on the site-specific conditions and requirements. If pulling is attempted and fails (i.e., a portion of the riser breaks) the remaining portion of the well should be removed by using the conventional augering procedure identified in Section 2.2. In all cases, after the well construction materials have been removed, the borehole will be grouted in accordance with Section 9.0 and the upper five feet will be restored in accordance with Section 10.0.

2.5.4 Contaminated Overburden Wells

If an overburden well or the overburden portion of a bedrock well is contaminated as evidenced by historical sampling results, the first decision point in selecting a decommissioning procedure is whether the well penetrates a confining layer. If the well does not penetrate a confining layer, the selection process follows the same pathway as for uncontaminated wells that penetrate a confining layer (i.e., the casing is pulled, if possible; otherwise the well is overdrilled - see Section 2.5.3). Plastic sheeting should be placed around the well surface to contain contaminated materials displaced during removal of the well.

For overburden wells that are contaminated and which penetrate a confining layer, the next selection criteria is whether the well riser is a single stem or is telescoped inside one or more outer casings. The procedures to be followed in determining the decommissioning method are presented for both situations below.

2.5.4.1 Single Stem Riser

If the riser is a single stem, the potential for cross-contamination between confining layers must be addressed. In particular, if the lower confining unit is contaminated, there is a potential that the contamination may be transferred to the upper unit as the well construction materials are removed to the ground surface. In this event, it will be necessary to install a temporary casing having a diameter larger than the original borehole into the top of the confining layer. This may be accomplished using a hollow stem auger or by employing a spin and flush technique to advance the casing. If the confining layer is less than 5 feet thick, the casing should be installed to the top of the confining layer. Otherwise, it is installed to a depth of 2 feet below the top of the confining layer. After the temporary casing has been set, the well can be removed and grouted through pulling (if possible) or through overdrilling if pulling is not feasible. Plastic sheeting should be placed around the well surface to contain contaminated materials displaced during removal of the well. As an alternative to installation of a temporary casing, the hollow-stem auger could serve the same purpose in that it would prevent the contamination from migrating to the upper unit. The hollow-stem auger would be advanced into the confining layer until the joint between the uppermost sections was nearly flush with the ground surface, and the sections would be disconnected to expose the riser prior to pulling or overdrilling.

After the casing and screen are removed and the well is grouted, the temporary casing (if used) is removed and the casing and/or hollow stem auger can be decontaminated for reuse. The upper 5 feet of the well surface should then be restored in accordance with Section 10.0.

2.5.4.2 Telescoped Riser

If the riser is telescoped in one or more outer casings, the decommissioning approach is dependent on the integrity of the well seal. For the purpose of the monitoring well decommissioning procedures, the well seal is defined as the bentonite seal above the sand pack. Although it is not possible to visually inspect or otherwise test the well seal to assess its condition, an indication of the well seal integrity may be obtained through review of the

boring logs and/or a comparison of groundwater elevations if the well is part of a cluster. Any problems noted on the boring logs pertaining to the well seal, such as bridging of bentonite pellets or running sands, or disparities between field notes (if available) and the well log would indicate the potential for a poor well seal. Alternatively, if the well is part of a cluster a comparison of groundwater elevations between the shallow and deep wells should also be performed. By observing trends at other clusters it may be possible to identify inconsistencies in groundwater elevations at the well slated for decommissioning, thereby indicating a poor well seal.

If there is no evidence that the well seal integrity is compromised, the riser should be grouted in-place in accordance with Section 2.3 or 2.4, depending on the diameter of the well casing, and the upper 5 feet of the well surface should be restored in accordance with Section 10.0. If indications are that the well seal is not competent, it will be necessary to design and implement a special procedure to remove the well construction materials, as the presence and configuration of the outer casing(s) will be specific in the individual wells and will be a key factor in the decommissioning approach. The special procedure should be designed to mitigate the potential for cross-contamination during removal of the well construction materials, and should be designed prior to initiating field work.

3.0 PREPARATION OF A SITE-SPECIFIC HEALTH AND SAFETY PLAN

Prior to initiating decommissioning activities at a site, it is necessary to prepare a site-specific health and safety plan (HASP) in accordance with the requirements of 29 CFR 1910.120. Accordingly, the HASP should include:

- The names of key personnel responsible for site health and safety, including an appointed site health and safety officer.
- A safety and health risk analysis for each site task and operation.
- Employee training requirements.
- Personal protective equipment (PPE) to be used by employees for each of the site tasks and operations being conducted.

- Medical surveillance requirements.
- Frequency and types of air monitoring, personnel monitoring and environmental sampling techniques and instrumentation to be used.
- Site control measures.
- Decontamination procedures.
- Site standard operating procedures.
- A contingency plan for responses to emergencies.
- Confined space entry procedures.

An example of a health and safety plan is attached as Appendix A. This document provides a general framework for preparing a HASP. Examples of site-specific information, such as names of responsible personnel, contaminant data, and other information which must be developed to meet the OSHA requirements discussed above are included in Appendix A but will need to be modified in the site-specific HASP.

4.0 PREPARATION OF A MATERIALS HANDLING AND DISPOSAL PLAN

Materials handling and disposal procedures for each of the wells slated for decommissioning should be identified in a site-specific materials handling and disposal plan. This plan will be used as a guideline to ensure safe and efficient control of contaminated materials, and will promote conformance with the applicable regulatory requirements for storage, characterization, labeling, transportation and disposal of materials prior to off-site transport.

4.1 MATERIALS HANDLING PROCEDURES

The materials anticipated to be generated during well decommissioning activities include decontamination fluids, disposable safety equipment (including personal protective

equipment), drill cuttings, groundwater, well construction materials (PVC and/or stainless steel casings, well screens, sand, bentonite/grout mixtures, etc.), and any spill-contaminated materials. Proper handling of these materials is effected through a series of steps, including: identification/pre-characterization of the waste materials; segregation/containment of the wastes including storage in proper containers; characterization of the waste materials through analytical testing to determine the absence/presence or nature of the contamination, and proper labeling in accordance with 49 CFR Part 172. Each of these steps is described in the following sections.

4.1.1 Identification/Pre-characterization

Prior to initiating well decommissioning activities at a site, the site history, most importantly historical analytical data from the monitoring wells, must be reviewed as well as the monitoring well construction details: number, type (overburden, bedrock), depth, diameter, and construction materials. This knowledge will aid in estimating the nature and quantities of waste materials which potentially may be generated as a result of decommissioning activities and will also assist in pre-determining the number of roll-off boxes, 55-gallon drums, and any other containers necessary to contain the wastes generated at each respective site.

4.1.2 Segregation and Containment

During well decommissioning activities, generated waste materials must be contained and segregated according to the nature of the suspected contamination. Well materials generated from decommissioning those wells with known contamination will be segregated from materials generated from those wells with little to no contamination (based on historical results). Contaminated materials will be further segregated according to contaminant type (e.g., well materials suspected of containing volatile organic contamination will be segregated from materials suspected of containing Polychlorinated Biphenyl (PCB) contamination).

For wells exhibiting contamination, all materials brought to the surface must either be decontaminated, disposed of at an appropriate Treatment, Storage and Disposal Facility

Fluids generated during the decommissioning program will generally be contained in 55-gallon drums unless extremely large volumes are expected; in this case 5,000-gallon tankers or other suitable temporary storage may be used. All drums will be initially labeled according to the wastewater source(s) and will be assumed to contain the same contaminants as the groundwater measured by the particular monitoring well being decommissioned. All 55-gallon drums containing fluids should be sealed and temporarily stored at the decontamination pad until final off-site disposal at an approved treatment facility.

4.1.3 Characterization

Hazardous waste characterization is necessary to determine the nature of the waste materials, to verify whether the materials are hazardous, and to determine proper disposition. Characterization of waste materials will be conducted at each of the sites to determine the appropriate disposal requirements. The decision as to the number, location and types of samples to be collected will be site specific and will depend on factors such as the quantity of waste generated and type of containers used, the nature of the waste, and the distribution of contaminant types across the site with respect to the origin of the waste materials. In general, the sample collection program will be designed to ensure that analytical data representative of all the materials to be disposed will be generated from the minimal number of samples. This may be accomplished by means such as:

- collection of composite samples for contaminants such as metals and PCBs (compositing is not typically acceptable for volatile organic compound analyses).
- collection of grab samples from select drums/containers suspected of elevated contaminant concentrations based on visual observation (e.g., soil staining, liquid sheen or non-aqueous product) or PID screening

Sample analysis will be based on site history and the requirements of the disposal facility. At a minimum, the samples should be analyzed for the parameters of concern indicated by past monitoring well analytical results, as well as the hazardous waste

(TSDF), or properly containerized in a secure area for disposal by others. For all uncontaminated wells, the materials (except the casings) can be left at the surface near the former well unless the surrounding land use prohibits this disposal (e.g., if the well is located in an area where people could be exposed to the materials left on the surface; or if recovered decommissioning materials would not be consistent with the intended use of the land). In this case, the materials must be disposed of in a 6NYCRR Part 360 landfill. For contaminated wells, PVC and/or steel casing materials may be decontaminated for disposal in a Part 360 landfill, provided that the decontamination effort is thorough and cost effective. Requirements for characterization and disposal of contaminated materials are discussed in Sections 4.1.3 through 4.1.5.

Containment methods will be based on the estimated quantity of materials anticipated to be generated at each respective site. Solid waste materials (i.e., well construction materials, soils, drill cuttings, PPE), will typically be contained in roll-off boxes or 55-gallon drums. Since federal DOT regulations (49 CFR Part 177) generally limit the combined truck and cargo weight to 80,000 lbs, most hazardous waste transporters will limit the roll-off box capacity to 20 tons of hazardous waste per shipment. Thus, if the materials are to be transported off-site to a treatment, storage and disposal facility (TSDF) that accepts bulk waste, and if the anticipated quantity of waste will be large (greater than 5 tons), water-tight roll-off containers may be more practical and cost-effective for temporarily containing and transporting the waste in lieu or in combination with 55-gallon drums (e.g., 55-gallon drums may still be used for personal protective equipment or other articles not directly derived from the abandoned well). The roll-off containers should be lined with disposable HDPE liners to prevent contact with the container, and will be initially labeled according to the source(s) of the contained waste materials. Likewise, if drums are used they will be lined with a protective plastic sleeve, filled and the drum initially labeled according to the source of the contaminated materials. After the contents of the roll-offs and drums have been characterized, they should be labeled in accordance with 49 CFR Part 172. Roll-off containers will be covered with polyethylene covers and tarps with bows during temporary storage and transportation, and all drums will be sealed.

characteristic parameters: toxicity by TCLP; ignitability; reactivity; and corrosivity in accordance with 40 CFR Part 261.

4.1.4 Labeling

Depending on the nature of the materials, proper labeling of the storage containers (roll-offs and/or drums) must be completed according to 49 CFR Part 172.

4.1.5 Disposal

Disposal of waste materials will depend on whether the waste has been characterized as hazardous or non-hazardous. Non-hazardous waste will be disposed of on-site in accordance with NYSDEC TAGM #4032 with the prior consent of the owner and the Department, or may be landfilled at a permitted 6NYCRR Part 360 facility.

For wastes that exhibit contamination, the requirements for disposal or treatment will be dependent on the waste characteristics. To determine these requirements the following procedure should be followed upon receipt of the waste characterization results:

1) Determine if the waste is characteristically hazardous (by failure of any of the criteria for toxicity, corrosivity, reactivity, or ignitability) or if it is a listed hazardous waste per the classifications identified in 40 CFR Part 261.

2) Determine the EPA hazardous waste code(s) for the applicable waste classification(s) listed in 40 CFR Part 261.

3) Determine any treatment standards for the hazardous waste code(s) per 40 CFR Part 268. Depending on the waste classification, treatment standards may be based on final concentration in the waste/waste extract or may require a specific treatment technology (e.g., incineration).

4) If the hazardous waste contains other constituents that are not listed in the treatment standards, and if landfilling is a disposal option, it should be determined if the waste is a California List waste per the criteria in 40 CFR Part 268.32 (e.g., under these regulations, nonliquid wastes must not contain total halogenated organics at or in excess of 1,000 ppm).

5) If the hazardous waste meets all treatment standards including the California List Standards (if applicable), it may be disposed of at a permitted hazardous

waste land disposal facility. For each shipment the generator is required to provide the following manifest information:

- Hazardous Waste Code(s)
- Corresponding concentration-based or technology-based treatment standards.
- Manifest number.
- Waste analysis data.
- Certification Statement per 40 CFR 268.7(a)(2)(D)(ii).

In addition, the generator is required to maintain the records specified in 40 CFR Part 268.7(a)(7) for a minimum of 5 years.

6) If the waste fails to meet any of the treatment standards listed in 40 CFR Part 268, it must be sent to a treatment, storage, or recycling facility. If the waste's treatment standard is technology-based, it must be treated in accordance with the specified method. Land disposal is not allowable unless the waste is eligible for a National Capacity Variance (40 CFR Subpart C) and meets the California List standards. In all cases, the notification and recordkeeping requirements identified above must be fulfilled by the generator.

The hazardous waste will be transported in accordance with DOT regulations (49 CFR Parts 172-173) to either a secure hazardous waste landfill or TSDF, as appropriate. The contractor will be responsible for arranging for proper transportation and the disposal of the wastes. The Engineer will sign a hazardous waste manifest, as an agent of the Owner.

5.0 EQUIPMENT DECONTAMINATION REQUIREMENTS

Since the monitoring well decommissioning will involve multiple wells, there is a possibility of contamination from one well location to another. To avoid cross-contamination, procedures have been established for decontamination after operations at each well location is complete. The procedures for decontamination of personnel at the site will be specified in the site-specific Health and Safety Plan. Decontamination of equipment will

follow established equipment cleaning protocols which are written in accordance with the Engineer's corporate policies and OSHA regulations.

The drilling and excavation equipment (i.e., drill rigs, cutting bits, and associated equipment) will be cleaned at a constructed decontamination facility. In general, the decontamination facility (i.e., decon pad or wash pad) will consist of plywood placed over a heavy synthetic liner. The pad will slope down to a sump that will collect all liquids. A detailed description and drawing of the decontamination facility that will be constructed is included in Appendix B as Item 1.

The drilling and excavation equipment will be prepared before it is brought to the decontamination facility and then cleaned at the facility. The preceding preparation includes removing gross soil/rock from the equipment to minimize losses during movement to the decon pad. At the decontamination facility, the equipment will be rinsed with low-volume water or steam, washed with phosphate-free detergent, and rinsed again with pressurized low-volume water or steam. The equipment will be inspected by the Engineer's field representative after cleaning. The detailed cleaning procedures are included in Appendix B as Item 2.

In the event that sampling equipment must be used, the decontamination guidelines included in Appendix B as Item 3 will be followed. In general, these guidelines describe cleaning with non-phosphate detergent, then performing rinsing cycles with water and acid. After the equipment is air-dried, it must be wrapped in aluminum foil to avoid accidental contamination after cleaning.

After all equipment is decontaminated, the solutions produced must be properly containerized and disposed of. All other disposable contaminated supplies/equipment such as disposable safety and sampling equipment will also need to be properly disposed of. Unless characterization of the decon fluids and disposable equipment is performed in accordance with Section 4.0, these materials will be handled in the same manner as the drill cuttings/fluids from the well locations. All materials must be temporarily stored in a secure area such as the fenced decon pad.

If sampling is necessary, the Engineer's personnel will be responsible for the decontamination of the sampling equipment. The decontamination of drilling and excavation

equipment is the responsibility of the Contractor(s). The Engineer's field representative will make daily inspections to insure that decontamination procedures are being followed.

6.0 LOCATING AND SETTING-UP ON THE WELL

The following tasks shall be performed to locate the well to be decommissioned:

- Notify property owner and/or other interested parties including the governing regulatory agency prior to site mobilization whenever possible.
- Review information about the well contained in the site file. This information may include one or more of the following: the site map, well boring log, well construction diagram, field inspection log, well photograph, and proposed well decommissioning procedure.
- Verify the well location and identification by locating the identifying marker.
- Verify the depth of the well in the well construction log by sounding with a weighted tape.

After the well has been located, the decommissioning procedure should be selected in accordance with Section 2.0 based on the available boring and sampling data. The rig must be set up prior to initiating drilling to ensure proper alignment with the well (i.e., the drill string must be aligned with the monitoring well).

7.0 REMOVING THE PROTECTIVE CASING

7.1 GENERAL

Removal of the protective casing of a well must not interfere with or compromise the integrity of decommissioning activities performed at the well.

The procedure for removing the protective casing of a well depends upon the decommissioning method used. When a well is decommissioned by the overdrilling or casing pulling method, the protective casing may be removed either before or after the casing is removed. When the decommissioning procedure requires casing perforation or grouting

in-place, the protective casing should be removed after grout is added to the well. The protective casing handling and disposal must be consistent with the methods used for the well materials, unless an alternate disposal method can be employed (e.g., steam cleaning followed by disposal as nonhazardous waste).

7.2 PRIOR TO SEALING THE WELL BORE

When overdrilling, the protective casing must be removed first, unless the drilling tools have an inside diameter larger than the protective casing. The variety of protective casings available preclude developing a specific removal procedure. In all cases, however, the specific procedure used must minimize the risk of:

- breaking the well casing off below ground and
- allowing foreign material to enter the well casing.

If the decommissioning method used is casing pulling, the decision of when to remove the protective casing is not critical.

An acceptable protective casing removal method involves breaking up the concrete seal surrounding the casing and jacking or hoisting the casing out of the ground. A check should be made during pulling to insure that the inner well casing is not being hoisted with the protective casing. If this occurs, the well casing should be cut off after the base of the protective casing is lifted above the land surface.

7.3 AFTER SEALING THE WELL

If the decommissioning method used allows well casing to remain in the ground, the protective casing should be removed after the well has been properly filled with grout. This will insure that the well is properly sealed regardless of problems with protective casing removal. During grouting in-place, the well casing must be removed to a depth of five feet below the land surface. The upper five feet of casing and the protective casing can be removed in one operation if a casing cutter is used. If the height of the protective casing

makes working conditions at the well awkward, the casing can be cut off at a lower level. However, the inner well casing must remain aboveground and cannot be damaged in any way that prevents the well from being filled with grout.

8.0 DECOMMISSIONING OF SCREEN AND RISER

After setting up on the well and removing the protective casing (if necessary), the well screen and riser are decommissioned in accordance with the appropriate procedure and methodology as discussed in Section 2.0 (i.e., if the wells are overdrilled or pulled, the casing and riser are removed. Otherwise, they are perforated and/or grouted in-place). During the decommissioning activities the requirements of the site-specific health and safety plan, materials handling and disposal plan and equipment decontamination plan will be followed to ensure maximum protection of human health and the environment.

9.0 SELECTING, MIXING, AND PLACING GROUT

9.1 SELECTING GROUT MIXTURE

There are two types of grout mixes that may be used to seal wells: a standard mix and a special mix. Both mixes use Type 1 Portland cement and four percent bentonite by weight. However, the special mix uses a smaller volume of water and is used in situations where excessive loss of the standard grout mix is possible (e.g. highly-fractured bedrock or coarse gravels).

9.1.1 Standard Grout Mixture

For most boreholes, the following standard mixture will be used:

- One 94-pound bag Type I Portland cement
- 3.9 pounds powdered bentonite
- 7.8 gallons potable water

This mixture results in a grout with a bentonite content of four percent by weight, and will be used in all cases except in boreholes where excessive use of grout is anticipated. In these cases a special mixture will be used (see Section 9.1.2).

See Section 9.2 for grout mixing procedures.

9.1.2 Special Mixture

In cases where excessive use of grout is anticipated, such as high permeability formations and highly fractured or cavernous bedrock formations, the following special mixture will be used:

- One 94-pound bag type I Portland cement
- 3.9 pounds powdered bentonite
- 1 pound calcium chloride
- 6.0-7.8 gallons potable water (depending on desired thickness)

The special mixture results in a grout with a bentonite content of four percent by weight. It is thicker than the standard mixture because it contains less water. This grout is expected to set faster than the Standard Grout Mixture. The least amount of water that can be added for the mixture to be readily pumpable is six gallons per 94-pound bag of cement.

See Section 9.2 for grout mixing procedures.

9.1.3 Alternate Special Grout

In cases where the penetration of the sandpack is critical, such as bedrock wells with screens that transect multiple water-bearing zones, the following alternate mixture will be used:

- One 94 pound bag Type III Portland Cement.
- 3.9 pounds powdered bentonite.
- 7.8 gallons potable water.

Refer to Section 9.2 for grout mixing procedures. It should be noted that this grout is expected to set faster than the standard grout mixture.

9.2 GROUT MIXING PROCEDURE

To begin the grout-mixing procedure, calculate the volume of grout required to fill the borehole. If possible, the mixing basin should be large enough to hold all of the grout necessary for the borehole. Tall cylindrical and long shallow basins should not be used as it is difficult to obtain a homogeneous mixture in these types of basins.

Mix grout until a smooth, homogeneous mixture is achieved. No lumps or dry clots should be present. Grout can be mixed manually or with a mechanized mixer. One acceptable type of mixer is a vertical paddle grout mixer. Colloidal mixers should not be used as they tend to excessively decrease the thickness of the grout for the above recipes.

9.3 GROUT PLACEMENT

Grout will be placed in the borehole from the bottom to the top using a tremie pipe of not less than 1-inch diameter. Grout will then be pumped into the borehole until the grout appears at the land surface (when grouting open holes in bedrock, the grout level only needs to reach above the bedrock surface). Any groundwater displaced during grout placement will be pumped via suction lift to a 55-gallon drum for proper disposal.

At this time the rate of settling should be observed. When the grout level stabilizes, casing or augers will be removed from the hole. As each section is removed, grout will be added to keep the level between 0-feet and 5-feet below land surface. If the grout level drops below the land surface to an excessive degree, an alternate grouting method must be used. One possibility is to grout in stages; i.e., the first batch of grout is allowed to partially cure before a second batch of grout is added.

Upon completion of grouting, insure that the final grout level is approximately five feet below land surface. A ferrous metal marker will be embedded in the top of the grout to indicate the location of the former monitoring well.

10.0 BACKFILLING AND SITE RESTORATION

The uppermost five feet of the borehole at the land surface will be filled with a material appropriate to the intended use of the land. The materials will be physically similar to the natural soils. No materials will be used that limit the use of the property in any way. The surface of the borehole will be restored to the condition of the area surrounding the borehole. For example, concrete or asphalt will be patched with concrete or asphalt of the same type and thickness, grassed areas will be seeded, and topsoil will be used in other areas. All solid waste materials generated during the decommissioning process will be disposed of properly.

11.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES

This section describes the quality control/quality assurance (QA/QC) procedures necessary for monitoring and ensuring the Contractor's adherence to the Monitoring Well Decommissioning Project procedures, plans and specifications, prepared by the Engineer. This section will discuss the minimum inspection and documentation requirements necessary to facilitate proper well decommissioning procedures and also will:

- Review the general requirements specified in the Contract Documents.
- Define roles and responsibilities of all parties.
- Establish the key tasks to be monitored by the on-site construction inspector and the appropriate inspector forms and logs to be used for recording the Contractor's activities.
- Establish procedures for communicating change orders, field modifications and variations from the Contract Documents to the Owner.
- Establish scheduled meetings and briefings during the construction phase.

The overall goal of the project QA/QC program is to ensure that proper well decommissioning techniques and procedures are used in accordance with the requirements

of the Contract Documents. The QA/QC procedures herein should be followed by QA personnel including: Construction Contractor personnel, the Contractor's subcontracted laboratory and field personnel, and the Engineer's on-site construction inspector.

11.1 RESPONSIBILITY AND AUTHORITY

The principal organizations involved in developing, designing and conducting well decommissioning activities are the Owner, Engineer, and the Construction Contractor.

11.1.1 Owner

The Owner will be responsible for reviewing the well decommissioning procedures to determine whether the documents meet their requirements, and to obtain approval of the procedures from the appropriate regulatory agencies. The Owner will have the responsibility and authority to review and accept or reject any design or procedural revisions or requests. The Owner also has the responsibility and authority to review and approve the Construction Monitoring Report and all QA documentation collected during well decommissioning activities.

11.1.2 Engineer

The Engineer will be responsible for reviewing and approving any engineering design changes, construction monitoring and quality assurance in accordance with this QA Plan. The Engineer will inform all parties involved with construction of their responsibilities, lines of communication, lines of authority, and QA/QC procedures. The Engineer's construction inspector (QA Engineer) will monitor decommissioning activities and will be assigned specific responsibilities and tasks. Most of the waste sample collection and testing will be conducted by the contractor at a frequency and manner specified in the site specific Materials Handling and Disposal Plan.

The person filling the construction inspector (QA Engineer) position will be trained and certified to operate an HNu organic vapor photoionization detector (PID), will be OSHA 40-hour Hazardous Waste Worker trained and will have a working knowledge of documents

pertaining to well decommissioning activities, including this plan. The Engineer's field personnel will be instructed to contact the construction inspector (QA Engineer) in the event well decommissioning requirements are not being met, QA procedures are not being implemented, or construction problems have been encountered.

11.1.3 Construction Contractor

In addition to performing the monitoring well decommissioning in accordance with the design documents, the Contractor will be required to obtain the services of a qualified testing laboratory to perform the analytical testing of the waste materials and will also be responsible for procuring transportation and disposal/treatment services.

11.2 PROJECT MEETINGS

The Engineer's management of the monitoring well decommissioning project will include conducting periodic project meetings as described below:

11.2.1 Pre-construction Meeting

The Engineer will schedule and attend one (1) pre-construction meeting for the purpose of discussing the project approach and answering contractor questions. The Engineer will also prepare and distribute meeting minutes. The meeting will also:

- Provide each party (organization) with relevant QA documents and supporting information.
- Familiarize each organization with the QA Plan and its role relative to the well decommissioning criteria and construction documents.
- Review the responsibilities of each organization and review the lines of authority and communication for each organization.
- Discuss the established procedures for observations and tests including waste sampling.

- Discuss the established procedures for handling construction deficiencies, repairs, and/or retesting.
- Review methods for documenting and reporting inspection data.

11.2.2 Monthly Progress Meetings

Monthly project meetings will be held during the course of the work to discuss the project schedule and work performed to date, and to address and resolve any existing or anticipated problems.

A special meeting will be held when and if a major QA problem or deficiency is present or likely to occur. At a minimum, the meeting shall be attended by the Construction Contractor and the Engineer's on-site inspector (QA Engineer). The purpose of the meeting will be to define and resolve the problem(s) or deficiencies encountered. The meeting minutes will be documented by the Engineer.

11.3 KEY TASKS

The key tasks that the Engineer will conduct during the well decommissioning project are briefly summarized below.

11.3.1 Review of Contractor Submissions

Prior to well decommissioning activities, all written submissions required by the contract documents will be evaluated and forwarded to the Owner, together with written submissions regarding their suitability. The Engineer will also obtain and review all necessary shop drawings, material tests and as-built drawings submitted throughout the construction and will make recommendations for acceptance/rejection to the Owner. The contractor's progress will be continuously monitored during the construction period, and Owner will be informed of the schedule and any corrective measures planned or implemented.

Throughout the project, payment requests by the contractor will be reviewed for accuracy and completeness prior to making recommendations relative to payment. Review

will involve comparing actual notes of field personnel to items contained in the payment request. Discrepancies will be discussed with the contractor and will be amended if necessary.

11.3.2 Construction Inspection

The Engineer will provide full-time inspection of the contractor during all critical well decommissioning activities at each of the sites. This will be accomplished by providing an experienced on-site inspector(s) to document the contractor's adherence to the contract specifications and monitoring the contractor's progress. The Engineer will notify the Owner in the event that the contractor fails to perform the decommissioning work as specified in the contract and recommend to the Owner the acceptance, conditional approval/disapproval or rejection of the contractor's work. The Engineer will issue instructions, field orders, interpretations and clarification of contract language to the contractor as required. In the event that a change order is necessary, the Engineer will submit the change order with a detailed cost estimate to the Owner. The Engineer will also document, evaluate and recommend a course of action for all disputes and claims with the contractor.

In addition, the Engineer will inspect, evaluate and document the monitoring well condition after the well has been removed.

11.4 DOCUMENTATION

The Engineer's on-site construction inspector will document all monitoring well decommissioning activities. Such documentation will include, at a minimum, daily reports of construction activities, photographs, and sketches as necessary. Field investigation reports will be completed by the construction inspector when major questions arise at the site. Forms to be used for this purpose are presented in Appendix C.

The Engineer will maintain complete and detailed records associated with all construction and related activities during the duration of the project. These records will be maintained at the Engineer's office(s) and will include but not be limited to the following:

- Daily work completed and important conversations.
- Contractor's daily use of personnel, material and equipment.
- Records documenting the contractor's deviation from work as specified in the contract documents, and any instructions issued regarding deviations.
- Unusual circumstances (weather conditions, labor disputes, environmental problems, health and safety hazards encountered, etc.).
- General files including correspondence and other documentation related to the project.
- Job meeting minutes with documentation on resolution of issues raised.
- Records of contractor's submittals including shop drawings, modifications/change orders, soil tests, material tests and action taken (e.g.,Owner approval/disapproval, further information needed).
- Construction photos.
- Telephone conversation

In addition, the Engineer will submit monthly Project Summary Reports to the Owner. These reports will identify the work which has been accomplished and will document the status of each monitoring well at each site where decommissioning work has occurred.

Upon substantial completion of the decommissioning activities at each site, the Engineer will prepare a detailed list of any work remaining unfinished. The Engineer will then prepare and submit a written notice to the Owner which will include a determination as to whether the completed work meets the requirements of the contract documents. Following satisfactory completion of the work, the Engineer will perform a final inspection of the site and submit a notice to the Owner that decommissioning activities were performed in accordance with the contract documents as revised by any approved change orders or modifications to the scope of work.

Documentation on the condition of the removed wells with respect to the impacts of hazardous waste, minerals and other pertinent environmental factors, or discernable through

direct observation, will be presented to Owner along with any recommendations for future well installation techniques and materials.

12.0 REFERENCES

Adaska, Wayne. Personal Communication, A.S.T.M. Grouting Subcommittee. 1993

Aller, Linda, and others. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. National Ground Water Association, Dublin, Ohio, 1989

American Society for Testing and Materials, A.S.T.M. D 5299-92, Standard Guide for the Decommissioning of Ground Water Wells, Vadose Zone Monitoring Devices, Boreholes, and Other Devices for Environmental Activities, A.S.T.M., Philadelphia, 1992

American Water Works Association. Abandonment of Test Holes, Partially Completed Wells, and Completed Wells. 1984

Angevine, Mary. Personal Communication, Marcor of New York, Inc. 1993

Blas, Stanley. Personal Communication, SJB Services, Inc. 1993

Edil, Tuncer B. and others. Sealing Characteristics of Selected Grouts for Water Wells. GROUNDWATER, Vol. 30, No.3, 1992

Ellingsworth, Michael. Personal Communication, Parratt-Wolff, Inc. 1993

Gaber, M.S., and Fisher, B., Michigan Water Well Grouting Manual. Michigan Department of Public Health, Lansing, MI. 1988

Hansen, M., Personal Communication, Chem-Grout, Inc., 1993.

Johnson Division of UOP, Inc., Ground Water and Wells. Johnson Division of UOP, Inc., Saint Paul, Minnesota. 1975

Malcolm Pirnie, Inc., Decommissioning Procedures. Prepared for New York State Department of Environmental Conservation, Division of Hazardous Waste Remediation. April 1993.

Malcolm Pirnie, Inc., Recommended Field Practices/Guidelines. Unpublished, 1990

Morgan, Robert. Personal Communication, A.S.T.M. Soil Committee D-18. 1993

New York State Department of Environmental Conservation, Division of Hazardous Waste Remediation, Final Division Technical and Administrative Guidance Memorandum - Disposal of Drill Cuttings. 1989

New York State Department of Environmental Conservation, Division of Solid Waste, 6 NYCRR Part 360 Solid Waste Management Facilities, 1988

New York State Department of Environmental Conservation, Division of Solid and Hazardous Waste, Guidelines for Exploratory Boring, Monitoring Well Installation, and Documentation of These Activities, undated

New York State Department of Environmental Conservation, Region I - Water Unit, Specifications for Abandoning Wells and Boreholes in Unconsolidated Materials, undated

Thew, Jeffrey. Personal Communication, North Star Drilling Co. 1993

U.S. Department of the Interior. Ground Water Manual, United States Government Printing Office, Washington D.C. 1977

United States Environmental Protection Agency, Manual of Water Well Construction Practices, EPA 570/9-75-001

United States Environmental Protection Agency, The Handbook of Suggested Practices for the Design and Installation of Groundwater Monitoring Wells, EPA 600/4-89/034.

Walker, Brian. Personal Communication, Global Drilling Suppliers, Inc. 1992

EXAMPLE

APPENDIX A

HEALTH AND SAFETY PLAN

EXAMPLE

HEALTH AND SAFETY PLAN FOR MULTIPLE NPL SITES MONITORING WELL DECOMMISSIONING

NEW YORK STATE DEPT. OF ENVIRONMENTAL CONSERVATION DIVISION OF HAZARDOUS WASTE REMEDIATION

AUGUST 1994
REVISED NOVEMBER 1994
REVISED MARCH 1995

Site Health and Safety Officer

Project Manager

Corporate Health & Safety Manager

EXAMPLE

We, the undersigned, being employed by Consultant, have read in full and understand this Health and Safety Plan:

Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date
Signature	Print	Date

EXAMPLE

HEALTH AND SAFETY PLAN
FOR
MULTIPLE NPL SITES MONITORING WELL DECOMMISSIONING

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF ATTACHMENTS

1.0 INTRODUCTION

1.1 GENERAL

In accordance with Consultant corporate policies and OSHA regulations, this Health and Safety Plan (HASP) describes specific health and safety practices and procedures to be used during Monitoring Well Decommissioning activities at the _____ Site, located in-_____, New York. The HASP covers Consultant employees and activities, and is not intended to cover the activities of other employers on the site. This general Health and Safety Plan will be modified for each monitoring well-decommissioning assignment with site-specific data including site-specific contaminant and emergency response information, identification of hazards associated with the individual contaminants or categories of contaminants known to be present at the site, a hospital route, and identification of task-specific personal protective equipment (PPE). Consultant accepts no responsibility for the Health and Safety of subcontractor personnel. This HASP presents information on known site health and safety hazards and includes the equipment, materials and procedures that will be used to eliminate or control these hazards and is based on an assessment of potential health and safety hazards at the site using available historical information. Environmental monitoring will be performed during the course of field activities to provide real-time data for an on-going assessment of potential physical and chemical hazards. Personal detector tubes will be utilized in conjunction with an HNu photoionization detector to determine the extent of exposure to chemical hazards.

All Consultant personnel involved with site inspection, environmental sampling, and other monitoring well decommissioning activities will be required to comply with this Health and Safety Plan. Tasks on this site will be completed using methods that meet the requirements set forth in the OSHA Health and Safety regulations contained in 29 CFR 1910 and 1926. Construction subcontractor(s) conducting drilling and excavating operations are required to provide their own Health and Safety Plans.

1.2 ORGANIZATION

The Consultant Project Manager, the Health and Safety Officer and the Site Health and Safety Coordinator (or his designee) identified below will determine and enforce compliance.

- PROJECT MANAGER

  Name:
  Telephone: Office:
  Home:

- CORPORATE HEALTH AND SAFETY MANAGER:

  Name:
  Telephone: Office:
  Home:

- SITE HEALTH AND SAFETY OFFICER

  Name:
  Telephone: Office:
  Home:

- SITE HEALTH AND SAFETY COORDINATOR

  Name:
  Telephone: Office:
  Home:

The following roles have been identified for consultant project personnel:

Project Manager - The Project Manager has full responsibility for implementing and executing an effective program of employee protection and accident prevention. He may delegate authority to expedite and facilitate any application of the program.

Health and Safety Manager - The Health and Safety Manager serves as the administrator of the corporation's health and safety program. He is responsible for ensuring that consultant field personnel are properly trained, that they have obtained medical clearance to wear respiratory protection (per 29 CFR Part 1910.134(b)(10)), and that they are properly trained in the selection, use and maintenance of personal protective equipment, including qualitative respirator fit testing.

The Health and Safety Manager will also serve as scientific advisor for the duration of the project, providing guidance on data interpretation and the determination of appropriate levels of worker protection.

Site Health and Safety Officer - The Site Health and Safety Officer is knowledgeable in safety and worker protection techniques as they relate to the project. Responsibilities include the development of the specific provisions of this HASP, including the level of personnel protection to be employed, identification of emergency procedures, and personnel/equipment decontamination procedures. This individual will provide technical assistance to project management on problems relating to industrial hygiene and work site safety.

Any health and safety briefings required during the course of the project will be conducted by the Site Health and Safety Officer. Examples of briefings might include accident prevention, respirator refresher courses or current issues. The frequency of safety briefings will be based upon the potential hazards specific to the designated work tasks and any new information relative to such hazards which are discovered during the project.

Site Health and Safety Coordinator - Consultant's Site Health and Safety Coordinator or his/her designee will be responsible for enforcement of this HASP for consultant employees at the site and for monitoring the personal exposures of employees to hazardous substances contained in air, soil or water. This will consist of spot checking workplace air sampling performed by the Subcontractor such as organic vapor monitoring and the documentation of such data. Consultant's Site Health and Safety Coordinator or his/her designee will communicate directly with consultant's Site Health and Safety Officer on a regular basis to advise him/her of monitoring results and any unexpected conditions found at the site. As data are received and evaluated, the Site Health and Safety Officer will adapt this Health and Safety Plan to fit the current consultant employee protection needs at the site. All affected consultant employees and the Subcontractor's designated Site Health and Safety Officer will be informed of the air sampling results.

When unsafe work conditions are identified, the Site Health and Safety Coordinator or his/her designee is authorized to order consultant personnel to stop work. Resolution of all on-site health and safety problems will be coordinated through the Project Manager with assistance from the Health and Safety Manager and Site Health and Safety Officer as well as the Subcontractor's designated Health and Safety personnel.

2.0 HAZARD EVALUATION

2.1 SUMMARY OF PROJECTED RISKS

Due to the variety of potential contaminants at the site, the possibility exists that workers will be exposed to hazardous substances during field activities (see Table 2-1). The principal points of exposure would be through direct contact with contaminated fill/soils and groundwater, through the inhalation of contaminated particles or vapors. In addition, the use of drill rigs and backhoes on-site will present conditions for potential physical injury to workers. Further, since work will be performed during summer/winter time periods, the potential exists for heat/cold stress to impact workers especially those wearing protective equipment and clothing. The specific tasks involved in well decommissioning have been delineated in the July 1994 Work Plan for Multiple NPL Sites Monitoring Well Decommissioning, and in the February 1995 NPL Site Monitoring Well Decommissioning Procedures prepared by Consultant.

Although no work can be considered completely risk-free, logical and reasonable precautions will be implemented to provide an adequate level of protection for workers. The integration of medical evaluations, worker training relative to chemical hazards, safe work practices, proper personal protection, environmental monitoring, work zones and site control, appropriate decontamination procedures and contingency planning into the project approach will minimize the chance of unnecessary exposures and physical injuries.

2.2 PHYSICAL HAZARDS

Well decommissioning and sampling activities at the _____ Site may present the following physical hazards:

- The potential for physical injury during heavy construction equipment use, such as drill rigs and backhoes.
- The potential for heat/cold stress to employees during the summer/winter months (see Section 8.0).
- The potential for slip-and-fall injuries due to rough, uneven terrain.

- The potential for injury due to fire/explosion if methane gas is released during drilling operations and/or excavations (see Sections 5.0 and 11.0).

2.3 BIOLOGICAL HAZARDS

- **Poison Ivy (Rhus Radicans)**

Poison ivy may be found at the site. It is highly recommended that all personnel entering into an area with poison wear a minimum of a paper Tyvek to avoid skin contact.

Contact with poisonous plants:

Characteristic Reactions:

The majority of skin reactions following contact with offending plants are allergic in nature and characterized by:

- general symptoms of headache and fever
- itching
- redness
- a rash

Some of the most common and most severe allergic reactions result from contact with plants of the poison ivy group, including poison oak and poison sumac. Such plants produce severe rash characterized by redness, blisters, swelling, and intense burning and itching. The victim may develop a high fever and feel very ill. Ordinarily, the rash begins within a few hours after exposure, but may be delayed 24 to 48 hours.

Distinguishing Features of Poison Ivy Group Plants:

The most distinctive features of poison ivy and poison oak are their leaves, which are composed of three leaflets each. Both plants have greenish-white flowers and berries that grow in clusters.

First Aid:

a. Remove contaminated clothing; wash all exposed areas thoroughly with soap and water, followed by rubbing alcohol.

b. Apply calamine or other soothing lotion if rash is mild.

c. Seek medical advice if a severe reaction occurs, or if there is a known history of previous sensitivity.

- **Ticks**

Heavily vegetated areas of a site may have ticks. it is highly recommended that all personnel walking through such areas wear a minimum of a paper Tyvek and latex boot covers. The ticks will stand out against the light colors. A tick repellent or insect repellent containing DEET is also suggested.

Ticks can transmit several diseases, including Rocky Mountain spotted fever, a disease that occurs in the eastern portion of the United States as well as the western portion, and Lyme disease. Ticks adhere tenaciously to the skin or scalp. there is some evidence that the longer an infected tick remains attached, the greater is the chance that it will transmit disease.

First Aid:

a. Cover the tick with heavy oil (mineral, salad, or machine) to close its breathing pores. The tick may disengage at once; if not, allow oil to remain in place for a half hour. Carefully (slowly and gently) remove the tick with tweezers, taking care that all parts are removed.

b. With soap and water, thoroughly, but gently, scrub the area from which the tick has been removed, because disease germs may be present on the skin; also wipe the bite area with an antiseptic. Although use of tweezers for the removal of the tick and application of heat to the tick's body often have been attempted, these methods may leave tick parts in the wound or may injure the skin.

c. If you have been bitten, place the tick in a jar labeled with the date, location of the bite, and the location acquired. If any symptom appears, such as an expanding red rash, contact a physician immediately.

- **Lyme Disease**

Lyme disease may cause a number of medical conditions, including arthritis, that can be treated if you recognize the symptoms early and see your doctor. Early signs may include a flu-like illness, an expanding skin rash, and joint pain. If left untreated, Lyme disease can cause serious nerve and heart problems as well as a disabling type of arthritis.

You are more likely to spot early signs of Lyme disease rather than see the tick or its bite. This is because the tick is so small (about the size of the head of a common pin or a period on this page and a little larger after they fill with blood), you may miss it or signs of a bite. However, it is also easy to miss the early symptoms of Lyme disease.

In its early stage, Lyme disease may be a mild illness with symptoms like the flu. It can include a stiff neck, chills, fever, sore throat, headache, fatigue, and joint

pain. But this flu-like illness is usually out of season, commonly happening between May and October when ticks bite.

Most people develop a large, expanding skin rash around the area of the bite. Some people may get more than one rash. The rash may feel hot to the touch and may be painful. Rashes vary in size, shape, and color, but often look like a red ring with a clear center. The outer edges expand in size. It's easy to miss the rash and the connection between the rash and the tick bite. The rash develops from three days to as long as a month after the tick bite. Almost one-third of those with Lyme disease never get the rash.

Joint or muscle pain may be another early sign of Lyme disease. These aches and pains maya be easy to confuse with the pain that comes from other types of arthritis. However, unlike many other types of arthritis, this pain seems to move or travel from joint to joint.

In later stages, lyme disease may be confused with other medical problems. These problems can develop months to years after the first tick bite.

Early treatment of Lyme disease symptoms with antibiotics can prevent the more serious medical problems of later sages. If you suspect that you have symptoms of Lyme disease, contact your doctor.

Lyme disease can cause problems with the nervous system that look like diseases. These include symptoms of stiff neck, severe headache, and fatigue usually linked to meningitis. They may also include pain and drooping of the muscles on the face, called Bell's Palsy. Lyme disease can also mimic symptoms of multiple sclerosis or other types of paralysis.

Lyme disease can also cause serious but reversible heart problems, such as irregular heart beat. Finally, Lyme disease can result in a disabling, chronic type of arthritis that most often affects the knees. Treatment is more difficult and less successful in later stages. Researchers think these more serious problems may be linked to how the body's defense or immune system responds to the infection.

2.4 NOISE

Hearing protection is required for workers operating or working near heavy equipment where the noise level is greater than 85 dBA (TWA). The SSHO will determine the need for and appropriate testing procedures; i.e., sound level meter and/or dosimeter for noise measurement.

2.5 CHEMICAL HAZARDS

This section presents an example of a chemical Hazards Summary for a site characterized by trichloroethylene (TCE) contamination. Similar information will need to be provided on a site-by-site basis for all chemicals that may be encountered during the well decommissioning work.

Table 2-1 presents the potential chemicals that may be encountered during well decommissioning work at the _____ Site. The information presented in Table 2-1 is based on the available analytical data for the wells to be decommissioned. A summary of the exposure hazards for these chemicals is presented below.

- **Trichloroethylene (TCE)** is a common industrial solvent used primarily in dry cleaning and metal degreasing. Trichloroethylene exposure at vapor levels of 200 ppm has been associated with mild behavioral and psychomotor effects, including vertigo, fatigue, and headache. TCE is a suspected human carcinogen. The principal routes of potential personnel exposure to TCE are through inhalation of volatilized TCE and direct skin contact.

3.0 MEDICAL SURVEILLANCE

Medical monitoring, including initial employment, annual and employment termination examinations will be provided to Consultant employees whose work may result in potential chemical exposure or present unusual physical demands. Medical evaluations will be performed by an occupational physician designated by Consultant. The medical evaluations will be conducted according to the Consultant Medical Monitoring Program and include an evaluation of the workers' ability to use respirator protective equipment (as per 29 CFR 1910). The examination will include:

- Occupational history;
- Medical history;
- Medical review;
- Medical surveillance examination with emphasis on organ systems potentially affected by toxic substances identified in the work environment;
- Medical certification of physical requirements (sight, hearing, musculoskeletal, cardiovascular) for safe job performance; and
- Laboratory testing to include a complete blood count, white cell differential count, serum multiphasic screening and urinalysis.

The purposes of the medical evaluation are to: (1) determine fitness for duty on hazardous waste sites (such an evaluation is based upon the employee's occupational and medical history, a comprehensive physical examination and an evaluation of the ability to work while wearing protective equipment); and (2) establish baseline medical data.

Supplemental examinations may be performed whenever there is an actual or suspected excessive exposure to chemical contaminants or upon experience of exposure symptoms, or following injuries or temperature stresses.

In conformance with OSHA regulations, Consultant will maintain and preserve medical records for a period of 30 years following termination of employment. Employees have access to the results of medical testing and to full medical records and analyses.

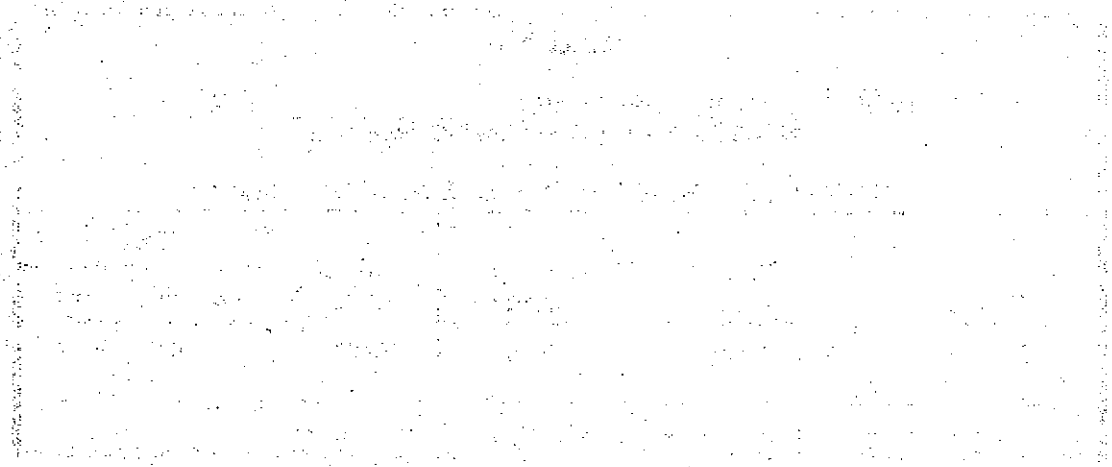
TABLE 2-1

HEALTH AND SAFETY PLAN FOR _____ SITE
MONITORING WELL DECOMMISSIONING

POTENTIAL CONTAMINANTS AND CONCENTRATIONS

Chemical	Affected Media	Maximum Concentration	Location of Max.	TWA[1]	
				mg/m³	ppm
Trichloroethylene (TCE)	Groundwater	1,500 ug/l	MW-1	269	50

Note (1): *Time-weighted average per 1994 ACGIH Threshold Limit Values.*



4.0 EMPLOYEE TRAINING PROGRAM

All employees who may be exposed to hazardous substances, health hazards, or safety hazards shall be adequately trained prior to engaging in any on-site work activities. At a minimum, such training shall include an initial 40-hour Hazardous Waste Site Worker Protection Course, an 8-hour Annual Refresher Course subsequent to the initial 40-hour training, and 3 days of actual field experience under the direct supervision of a trained, experienced supervisor (i.e., the Health and Safety Coordinator or his/her designee). This training shall be conducted by a qualified instructor and shall be specifically designed to meet the requirements of OSHA Standard 29 CFR 1910.120(e)(2). At a minimum, the initial 40-hour training course will include the following:

TOPICS

- OSHA/SARA/EPA/RCRA/HCS Requirements
- Decontamination of Personnel & Equipment
- Fire, Explosion & Accident Prevention
- Respiratory Protection Selection & Use
- Preparation of Health & Safety Plans
- Emergency Preparedness & Escape
- Protective Clothing Use & Selection
- Air Monitoring & Surveillance
- Work Practices to Minimize Risk
- Waste Site Safety
- Hazard Recognition
- Medical Surveillance
- Cold & Heat Stress
- Site Entry & Set-Up
- Permissible Exposure Limits
- Site Control & Work Zones
- Chemical & Physical Hazards
- Confined Space Entry

WORKSHOPS/EXERCISES

- Self-Contained Breathing Apparatus
- Air Monitoring Equipment Workshop
- Air Purifying Respirator Workshop
- Decontamination
- Qualitative/Quantitative Fit Test
- Level A/B Field Exercise
- Level B/C Field Exercise
- Air Tank Refilling Workshop

Records and certifications received from the course instructor documenting each employee's successful completion of the training identified above will be maintained on file in Consultant's

corporate headquarters offices. Subcontractor(s) will be required to provide similar documentation of training for all their personnel who will be involved in on-site work activities.

Any employee who has not received adequate training and has been so certified shall be prohibited from engaging in on-site work activities that may involve exposure to hazardous substances, health hazards or safety hazards. All individuals functioning in a supervisory capacity shall have had a minimum of 8 hours of Hazardous Waste Site Supervisor Training.

Prior to commencing work at a hazardous waste site, all Consultant employees will participate in an initial health and safety briefing conducted by the Site Health and Safety Officer to discuss site-specific hazards, PPE requirements, and emergency response procedures. In addition, periodic health and safety briefings will be conducted by Consultant's Site Health and Safety Officer for Consultant employees on an as-needed basis. Problems relative to respiratory protection, inclement weather, heat/cold stress or the interpretation of newly-available environmental monitoring data are examples of topics which might be covered during these briefings.

5.0 SAFE WORK PRACTICES

All Consultant employees shall obey the following safety rules during on-site work activities conducted within the exclusion and support zones:

General:

- Eating, drinking, chewing gum or tobacco, smoking, or any practice which increases the probability of hand-to-mouth transfer of contaminated material is strictly prohibited;
- The hands and face must be thoroughly washed upon leaving the work area and prior to engaging in any activity indicated above.
- Any required respiratory protective equipment and clothing must be worn by all personnel going on-site. Excessive facial hair (i.e., beards, long mustaches or sideburns), which interferes with the satisfactory respirator-to-face seal is prohibited;
- Contact with surfaces/materials either suspected or known to be contaminated will be avoided to minimize the potential for transfer to personnel, crosscontamination and need for decontamination;
- Medicine and alcohol can potentiate the effects of exposure to toxic chemicals. Due to possible contraindications, use of prescribed drugs should be reviewed with the consultant occupational physician. Alcoholic beverage and illegal drug intake are strictly forbidden during site work activities;
- All personnel shall be familiar with standard operating safety procedures and additional instructions contained in this Health and Safety Plan;
- On-site personnel shall use the "buddy" system. No one may work alone, i.e., out of earshot or visual contact with other workers in the exclusion zone;
- Personnel and equipment in the contaminated area shall be minimized, consistent with effective site operations;
- All employees have the obligation to correct or report unsafe work conditions;
- Use of contact lenses on-site will not be permitted. Spectacle kits for insertion into full-face respirators will be provided for Consultant employees, as required.

The recommended general safety practices for working around the drilling Contractor's and/or backhoe operator's equipment (i.e. drill rigs and backhoes) are as follows:

Contractor's Duties:

- The drilling Contractor is responsible for the condition of his equipment and its safe operation on the site. Consultant personnel are responsible for their own safety when working around this equipment. The inspector will include a check for obvious structural damage, loose nuts and bolts, loose or missing guards, cable guides or protective covers, fluid leaks, damaged hoses, cables, pressure gauges or pressure relief valves, and damaged drilling tools and equipment. The equipment should also have a fire extinguisher. The project manager will notify all subcontractors that they are expected to conduct daily inspections of their equipment and report any potential problems to the Consultant Site Health and Safety Coordinator or his/her designee. If the condition of the equipment is considered to be unsafe based on the Contractor's inspection, and/or the Consultant Site Health and Safety Coordinator's inspection, have the Contractor make the necessary repairs prior to beginning construction. If the Contractor refuses to fix the equipment or is not operating the equipment safely, the job site will be closed down and the Project Manager contacted for additional instructions.

- Drilling/excavation will not be initiated without first clearing underground services such as; gas, water, telephone, sewer, hydrogen, steam, and cable T.V.

- Drill rigs and backhoes should not be operated within 20 feet of overhead wires. This distance may be increased if windy conditions are anticipated. The site should also be clear to ensure the project staff can move around the heavy machinery safely.

- Slippage is one of the most common causes of accidents around drill rigs and test pits. Drainage should be provided to divert mud and water away from the construction site.

- The Contractor should keep the construction site tidy. This will prevent personnel from tripping and will allow for fast emergency exit from the site.

- A drill rig must not be moved from site to site with the drill mast in the raised position.

- Proper lighting will be provided if drilling/excavating at night.

- Drilling/excavation will be discontinued during an electrical storm.

Consultant's Duties:

- Hard hats and safety boots must be worn at all times in the vicinity of the drill rig and/or backhoe. Hearing protection is also recommended. Safety glasses are necessary.
- The presence of combustible gases should be checked before igniting any open flame (e.g., during welding).
- Consultant personnel shall stand upwind of any drilling/excavating operation when not immediately involved in sampling/logging activities.
- Consultant personnel will not enter trenches unless the trenches are shored or back sloped according to OSHA 29CFR 1926.652.
- Consultant personnel will not approach the edge of an unsecured trench closer than 2 feet.

6.0 PERSONAL PROTECTIVE EQUIPMENT

This section presents an example of personal protective equipment requirements for an unspecified site. Similar information will need to be provided on a site-by-site basis for all tasks that will be undertaken as part of the well decommissioning work.

6.1 PROTECTION LEVELS

Personnel must wear protective equipment when work activities involve known or suspected atmospheric contamination; when vapors, gases, or particulates may be generated; or when direct contact with dermal-active substances may occur. Full-face respirators will be used to protect the lungs, the gastrointestinal tract, and the eyes against air toxicants. Chemical-resistant clothing will be used to protect the skin from contact with skin-destructive and skin-absorbable chemicals. All personal protective equipment shall be maintained and stored as specified by the manufacturers. Good personal hygiene and safe work practices, as identified in Section 5.0, are also necessary to limit or prevent the ingestion of potentially harmful substances.

Based upon current information regarding both the contaminants suspected to be present at the _____ Site and the various tasks that are included in the well decommissioning program, the minimum required levels of protection shall be as identified in Table 6-1. The Site Health and Safety office will monitor the use of PPE during extreme temperature conditions.

EXAMPLE

TABLE 6-1

HEALTH AND SAFETY PLAN FOR _____ SITE
MONITORING WELL DECOMMISSIONING

REQUIRED LEVELS OF PROTECTION

Activity	Respiratory*	Clothing[2]	Gloves	Boots	Other Modifications[3]
Field Reconnaissance	D/C	T	–	L	Safety Glasses
Well Decommissioning Inspection	D/C	T	L/N	L	Hard Hat, Safety Glasses

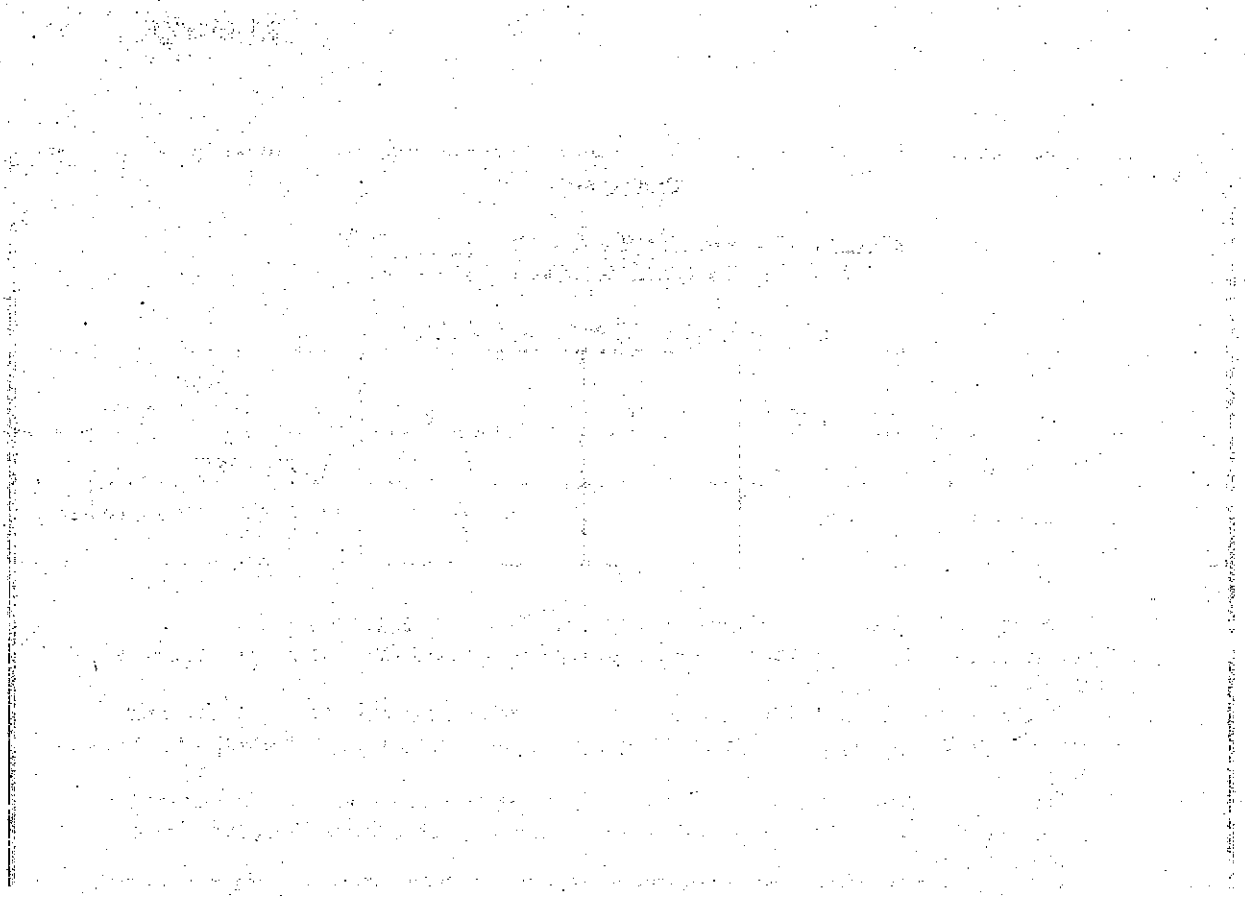
Notes:

(1) T = Tyvek; L/N = Latex Inner Glove, Nitrile Outer Glove; L = Latex Outer Boot

(2) Tyvek uniforms will be worn when Level C conditions are present (mandatory) or when Level D conditions are present (optional).

(3) At the discretion of the Site Health and Safety Officer, respirators will be donned whenever potentially contaminated airborne particulate (i.e., dust) are generated in significant amounts in the breathing zone.

* Respiratory protection shall correspond to guidelines presented in Section 7.2. The Level C requirement is an air-purifying cartridge respirator equipped with Organic Compound/Acid Gases/Dust cartridges.



7.0 ENVIRONMENTAL MONITORING

7.1 GENERAL APPROACH

7.1.1 On-Site Monitoring

Modifications to the level of protection established for consultant employees for each task will be based upon measurements of the contaminants present in the work environment. Tasks and activities proposed for each site along with the estimated potential of exposure to contaminants known to be present in the groundwater and soil at each site will be used to determine the minimum required levels of personal protection and will be described in the Site-Specific Health and Safety Plans. Based upon the existing data base, a release of organic vapors is anticipated during both intrusive investigations and sampling activities. Ambient breathing zone concentrations may, at times, exceed the permissible exposure limits (PEL) established by OSHA for the individual compounds (see Table ____). Respiratory and dermal protection may be modified (upgraded or downgraded) based upon real-time field monitoring data.

Contaminated soil and groundwater are most likely to be encountered during over drilling, excavation, sampling and other monitoring well decommissioning activities. The air monitoring program to be implemented by Consultant will monitor volatile contaminants as well as the presence of respirable dust when the soil is physically disturbed by drilling equipment and backhoes. A combustible gas meter and total organic vapor analyzer (HNu) shall be utilized by Consultant personnel to verify field conditions during drilling/excavating operations. Real time monitoring will be performed by consultant personnel on a periodic basis during other on-site activities such as sample collection and reconnaissance surveys. Drager detector-type tubes will be used to measure chemical specific concentrations in air. The level of respiratory and dermal protection in use will be based upon an evaluation of general and chemical specific air monitoring data.

Monitoring instruments will be protected from surface contamination during use to allow for easy decontamination. When not in use, the monitoring instruments will be placed on plastic sheeting to avoid surface contact. Additional monitoring instruments may be required if the situations or conditions change.

During drilling/excavating and soil examination operations, the work area surrounding the borehole will be monitored at regular intervals using an HNu photoionization detector, (or similar organic vapor monitoring device) as well as an explosimeter and a particulate meter. Observed values will then be recorded and maintained as part of the permanent field record. Breathing zone monitoring with an HNu will be performed at two-hour intervals during drilling and continuously during test pit work. The actual frequency of breathing zone monitoring will be dependent primarily upon values generated by screening the cuttings and the proximity of the worker's breathing zones to the source of contamination. Contaminant values which are in excess of established action levels appropriate for the prescribed level of protection will be immediately addressed.

Any split-spoon samples which are collected will be surveyed with the HNu, or similar equipment as each sample is retrieved. These values will be recorded with the respective sample number and will assist in the determination of the adequacy of employee protective equipment. In addition, to minimize dermal contact with potentially contaminated fill/soils, long-handled spoons and knives shall be used during split-spoon sampling and examination of the soil-core sample by the hydrogeologist.

7.2 MONITORING ACTION LEVELS

7.2.1 On-Site Levels

The HNu or other appropriate instrument(s) will be used by either Consultant personnel or the Contractor to monitor organic vapor concentrations as specified in this plan and in the Contractor's Health and Safety Plan. Methane gas will be monitored with the "combustible gas" option on the explosimeter/tritector or other appropriate instrument(s) in accordance with the drilling Contractor's Health and Safety Plan. In addition, fugitive dust/particulate concentrations will be monitored using a real-time particulate monitor, as specified in this plan and in the Contractor's Health and Safety Plan. Readings obtained in the breathing zone may be interpreted (with regard to other site conditions) as follows for on-site Consultant personnel:

- Total atmospheric concentrations of unidentified vapors or gases ranging from 0 to background on the Hnu - Continue Operations Under Level D (see Attachment 1).

- Total atmospheric concentrations of unidentified vapors or gases yielding sustained readings above background to 5 ppm on the Hnu (vapors not suspected of containing high levels of chemicals toxic to the skin) - Continue Operations Under Level C (see Attachment 1).

- Total atmospheric concentrations of unidentified vapors or gases yielding sustained readings of 5 to 50 ppm above background on the Hnu - continue operations under Level B (see Attachment 1), re-evaluate and alter (if possible) Work Plan to achieve lower vapor concentrations.

- Total atmospheric concentrations of unidentified vapors or gases above 50 ppm on the Hnu - discontinue engineering operations and exit the work zone immediately.

The explosimeter will be used to monitor levels of both combustible gases and oxygen during site activities. Action levels based on the instrument readings shall be as follows:

- Less than 10% LEL - Continue engineering operations with caution;

- 10-25% LEL - Continuous monitoring with extreme caution, determine source/cause of elevated reading;

- Greater than 25% LEL - Explosion hazard, evaluate source and leave the Work Zone;

- Less than 19.5% oxygen - leave Work Zone immediately;

- 19.5-25% oxygen - Continue engineering operations with caution; and

- Greater than 25% oxygen - Fire hazard potential, leave Work Zone immediately.

The particulate monitor will be used to monitor respirable dust concentrations during all intrusive activities. Action levels based on the instrument readings shall be as follows:

- Less than 150 ug/m^3 - Continue field operations

- Greater than 150 ug/m^3- Don dust/particulate mask or equivalent. Initiate engineering controls (viz. wetting of excavated soils or tools at discretion of Site Health and Safety Officer).

Readings with the explosimeter, particulate monitor and organic vapor analyzer will be recorded and documented in the Health and Safety logbook. All instruments will be maintained

according to the manufacturer's specifications and calibrated before use and the procedure will be documented in the Health and Safety logbook.

7.2.2 Community Air Monitoring

Real-time air monitoring for volatile compounds and particulate levels will be performed at the perimeter of the work area. Volatile compounds will be measured using an HNu or similar device. Drager detector-type tubes which are compound-specific will be used to monitor the perimeter of the work area. For purposes of this monitoring activity the perimeter of the work areas are determined to be 50 feet from the outside edge of the excavation or boring. Air monitoring will occur as follows:

- Volatile organic compounds will be monitored at the downwind perimeter of the work area daily at 2-hour intervals. If total organic vapor levels exceed 5 ppm above background, work activities must be halted and monitoring continued under the provisions of a Vapor Emission Response Plan. Readings will be recorded and be available for State (DEC and DOH) personnel to review.

- Particulates should be continuously monitored upwind, downwind, and within the work area at temporary particulate monitoring stations. If the downwind particulate level is 150 ug/m^3 greater than the upwind particulate level, then dust suppression techniques must be employed. Readings will be recorded and be available for State (DEC and DOH) personnel to review.

7.2.2.1 Vapor Emission Response Plan

If the ambient air concentration of organic vapors exceeds 5 ppm above background at the perimeter of the work area, activities will be halted and monitoring continued. The exclusion zone shall be extended to include the area in which the organic vapors exceed 5 ppm above the background. If the organic vapor level decreases below 5 ppm above background, work activities can resume but more frequent intervals of monitoring, as directed by the Safety Officer, must be conducted. If the organic vapor levels are greater than 5 ppm over background, but less than 25 ppm over background at the perimeter of the work area, activities can resume, provided:

- the organic vapor level 200 feet downwind of the work area or half the distance to the nearest residential or commercial structure, whichever is less, is below 5 ppm over background, and

- more frequent intervals of monitoring, as directed by the Safety Officer, are conducted.

If the organic vapor level is above 25 ppm at the perimeter of the work area, activities must be shut down. When work shutdown occurs, downwind air monitoring as directed by the Safety officer will be implemented to ensure that vapor emission does not impact the nearest residential or commercial structure at levels exceeding those specified in the Major Vapor Emission section.

7.2.2.2 Major Vapor Emission

If any organic levels greater than 5 ppm over background are identified 200 feet downwind from the work area or half the distance to the nearest residential or commercial property, whichever is less, all work activities must be halted.

If, following the cessation of the work activities or as the result of an emergency, organic levels persist for more than 30 minutes above 5 ppm above background 200 feet downwind or half the distance to the nearest residential or commercial property from the work area, then the air quality must be monitored within 20 feet of the perimeter of the nearest residential or commercial structure (20-Foot Zone).

If efforts to abate the emission source are unsuccessful and if any of the following levels persist for more than 30 minutes in the 20-Foot Zone, then the Major Vapor Emission Response Plan shall automatically be placed into effect if organic vapor levels are approaching 5 ppm above background. However, the Major Vapor Emission Response Plan shall be immediately placed into effect if organic vapor levels are greater than 10 ppm above background.

7.2.2.3 Major Vapor Emission Response Plan

Upon activation, the following activities will be undertaken:

1. All Emergency Response Contacts as listed in the Health and Safety Plan of the Work Plan will go into effect.

2. The local police authorities will immediately be contacted by the Safety Officer and advised of the situation.

3. Frequent air monitoring will be conducted at 30-minute intervals within the 20-Foot Zone. If two successive readings below action levels are measured, air monitoring may be halted or modified by the Safety Officer.

8.0 HEAT/COLD STRESS MONITORING

Since some of the work activities at the Monitoring Well Decommissioning Sites will be scheduled for both the summer and winter months, measures will be taken to minimize heat/cold stress to Consultant employees. Consultant's Site Health and Safety Coordinator or his/her designee will be responsible for monitoring Consultant employees for symptoms of heat/cold stress.

8.1 HEAT STRESS MONITORING

Personal protective equipment may place an employee at risk of developing heat stress, probably one of the most common (and potentially serious) illnesses encountered at hazardous waste disposal sites. The potential for heat stress is dependent on a number of factors, including environmental conditions, clothing, workload, physical conditioning and age. Personal protective equipment may severely reduce the body's normal ability to maintain equilibrium (via evaporation, convection and radiation), and by its bulk and weight increases energy expenditure.

The signs and symptoms of heat stress are as follows:

- Heat rash may result from continuous exposure to heat or humid air.
- Heat cramps are caused by heavy sweating with inadequate electrolyte replacement. Signs and symptoms include:
  - muscle spasms
  - pain in the hands, feet and abdomen
- Heat exhaustion occurs from increased stress on various body organs including inadequate blood circulation due to cardiovascular insufficiency or dehydration. Signs and symptoms include:
  - pale, cool, moist skin
  - heavy sweating
  - dizziness
  - nausea
  - fainting
- Heat stroke is the most serious form of heat stress. Temperature regulation fails and the body temperature rises to critical levels. Immediate action must be taken

to cool the body before serious injury and death occur. Competent medical help must be obtained. Signs and symptoms are:

- red, hot, usually dry skin
- lack of or reduced perspiration
- nausea
- dizziness and confusion
- strong, rapid pulse
- coma

The monitoring of personnel wearing protective clothing should commence when the ambient temperature is 70 degrees Fahrenheit or above. For monitoring the body's recuperative ability to excess heat, one or more of the following techniques should be used as a screening mechanism.

- Heart rate may be measured by the radial pulse for 30 seconds as early as possible in the resting period. The rate at the beginning of the rest period should not exceed 110 beats per minute. If the rate is higher, the next work period should be shortened by 10 minutes (or 33%), while the length of the rest period stays the same. If the pulse rate is 100 beats per minute at the beginning of the next rest period, the following work cycle should be further shortened by 33%.

- Body temperature may be measured orally with a clinical thermometer as early as possible in the resting period. Oral temperature at the beginning of the rest period should not exceed 99.6 degrees Fahrenheit. If it does, the next work period should be shortened by 10 minutes (or 33%), while the length of the rest period stays the same. However, if the oral temperature exceeds 99.6 degrees Fahrenheit at the beginning of the next period, the following work cycle may be further shortened by 33%. Oral temperature should be measured again at the end of the rest period to make sure that it has dropped below 99.6 degrees Fahrenheit. No consultant employee will be permitted to continue wearing semipermeable or impermeable garments when his/her oral temperature exceeds 100.6° Fahrenheit.

8.1 COLD STRESS MONITORING

Exposure to cold conditions may result in frostbite or hypothermia, each of which progresses in stages as shown below.

- **Frostbite** occurs when body tissue (usually on the extremities) begins to freeze. The three states of frostbite are:

  1) **Frostnip**- This is the first stage of the freezing process. It is characterized by a whitened area of skin, along with a slight burning or painful sensation.

Treatment consists of removing the victim from the cold conditions, removal of boots and gloves, soaking the injured part in warm water (102-108°F) and drinking a warm beverage.

2) **Superficial Frostbite** - This is the second stage of the freezing process. It is characterized by a whitish-grey area of tissue which will be firm to the touch but will yield little pain. Treatment is identical to that for Frostnip.

3) **Deep Frostbite** - In this final stage of the freezing process the affected tissue will be cold, numb and hard, and will yield little to no pain. Treatment is identical to that for Frostnip.

- **Hypothermia** occurs when the body loses heat faster than it can produce it. The stages of hypothermia (which may not be clearly defined or visible at first) are the following:

1) Shivering
2) Apathy (a change to a disagreeable mood)
3) Unconsciousness
4) Bodily freezing
5) Death (if untreated)

Treatment of hypothermia is given below:

- Remove the victim from the cold environment and remove wet or frozen clothing. (Do this carefully as frostbite may have started.)

- Perform active re-warming with hot liquids for drinking (Note: do not give the victim any liquid containing alcohol or caffeine in this case) and a warm water bath (102-108°F)

- Perform passive re-warming with a blanket or jacket wrapped around the victim.

In any potential cold stress situation, it is the responsibility of the Site Health and Safety Officer to encourage the following:

- Workers should dress warmly, with more layers of thin clothing as opposed to one thick layer.

- Personnel should remain active and keep moving.

- Personnel should be allowed to take shelter in a heated area, as necessary.

- Personnel should drink warm liquids (no caffeine or alcohol if frostbite has set in).

9.0 WORK ZONES AND SITE CONTROL

Work zones around the areas designated for drilling, test pit excavation, sample collection, and monitoring well installation will be established by the Contractor on a daily basis and communicated to all employees and other site users by the Contractor's Site Health and Safety Officer. It shall be the Contractor's Site Health and Safety Officer's responsibility to ensure that all site workers are aware of the work zone boundaries and to enforce proper procedures in each area. The zones will include:

- **Exclusion Zone ("Hot Zone")** - the area where contaminated materials may be exposed, excavated or handled and all areas where contaminated equipment or personnel may travel. The zone will be delineated by flagging tape. All personnel entering the Exclusion Zone must wear the prescribed level of personal protective equipment identified in Section 7.0;

- **Contamination Reduction Zone** - the zone where decontamination of personnel and equipment takes place. Any potentially contaminated clothing, equipment and samples must remain in the Contamination Reduction Zone until decontaminated;

- **Support Zone** - the part of the site which is considered non-contaminated or "clean". Support equipment will be located in this zone, and personnel may wear normal work clothes within this zone.

During drilling operations, Consultant personnel will establish a second exclusion zone immediately upwind of the borehole. Split-spoons shall be brought into this zone to Consultant personnel by the Contractor(s). Sample collection and logging of soil-core samples will be completed in this zone.

Access of non-essential personnel to the Exclusion and Contamination Reduction Zones will be strictly controlled by the Contractor. Only personnel who are essential to the completion of the task will be allowed access to these areas and only if they are wearing the prescribed level of protection. Entrance of all personnel must be approved by the Contractor's Site Health and Safety Officer.

A log containing the names of workers and their level of protection will be maintained by the Contractor(s).

The zone boundaries may be changed by the Site Health and Safety Officer as environmental conditions warrant, and to respond to the necessary changes in work locations on-site.

10.0 DECONTAMINATION PROCEDURES

10.1 PERSONAL DECONTAMINATION FOR MPI EMPLOYEES

The degree of decontamination required is a function of both a particular task and the physical environment within which it takes place. The following decontamination procedure, although somewhat specific to the tasks described herein, will remain flexible, thereby allowing the decontamination crew to respond appropriately to the changing environmental conditions which may arise at the site. The procedure shall be followed by all Consultant personnel who are on the site.

Station 1:	Equipment Drop	1. Deposit Equipment used on-site (tools, containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths. Segregation at the drop reduces the probability of cross contamination.
Station 2:	Boots and Gloves Wash and Rinse	2. Scrub outer boots and outer gloves with decon solution or detergent water. Rinse off using copious amounts of water.
Station 3:	Tape, Outer Boot and Glove Removal	3. Remove tape, outer boots and gloves. Deposit tape and gloves in container provided by Contractor.
Station 4:	Canister or Mask Change	4. If worker leaves exclusive zone to change canister (or mask), this is the last step in the decontamination procedure. Worker's canister is exchanged, new outer gloves and boot covers donned, and worker returns to duty.
Station 5:	Outer Garment Removal	5. Protective suit removed and deposited in separate container provided by Contractor(s).
Station 6:	Face Piece, Hard Hat, Safety Goggles Removal	6. Face piece or safety glasses removed (if used). Avoid touching face with fingers. Facepiece and/or safety glasses deposited on plastic sheet. Hard hat removed and placed on plastic sheet.

Station 7: Inner Glove Removal	7. Inner gloves are the last personal protective equipment to be removed. Avoid touching the outside of the gloves with bare fingers. Dispose of these gloves in container provided by Contractor.

10.2 DECONTAMINATION FOR MEDICAL EMERGENCIES

In the event of a minor, non-life threatening injury, personnel should follow the decontamination procedures as defined, and then administer first-aid.

In the event of a major injury or other serious medical concern (i.e., heat stroke), immediate first-aid is to be administered and the victim transported to the hospital in lieu of further decontamination efforts unless exposure to a site contaminant would be considered "Immediately Dangerous to Life or Health."

10.3 DECONTAMINATION OF FIELD EQUIPMENT

Decontamination of heavy equipment will be conducted by the Contractor(s) in accordance with his approved Health and Safety Plan in the Contamination Reduction Zone. Heavy equipment and tools utilized during drilling/excavating and monitoring well decommissioning activities will be placed on a decontamination pad and cleaned with high-pressure water followed by steam. Decontamination water will be prevented from moving outside the decontamination pad and will be transferred to a holding tank. The Contractor(s) Health and Safety Officer will make daily inspections to determine that this procedure is being followed. All hazardous chemicals (eg., decon fluids) brought to the site will be properly labeled and their Material Safety Data Sheets will be maintained on-site in accordance with the requirements of 29 CFR 1910-1200.

Decontamination of all tools used for sample collection purposes will be conducted by Consultant personnel. Decontamination fluids will remain within the confines of the deco pad area. Spend fluids will be containerized and prepared for proper off-site disposal. Decontamination of all bailers, split-spoons, spatula knives, and other tools used for multi-media environmental sampling and examination shall be as follows:

- disassemble the equipment;
- water wash to remove all visible foreign matter;
- wash with detergent;

- rinse all parts with distilled-deionized water;
- allow to air dry; and
- wrap all parts in aluminum foil or polyethylene to prevent contamination of clean equipment.

11.0 FIRE PREVENTION AND PROTECTION

11.1 GENERAL APPROACH

Recommended practices and standards of the National Fire Protection Association (NFPA) and other applicable regulations will be followed in the development and application of Project Fire Protection Programs. When required by regulatory (DEC) authorities, the Contractor will prepare and submit a Fire Protection Plan for the approval of the contracting officers, authorized representative or other designated official. Essential considerations for the Fire Protection Plan will include:

- Proper site preparation and safe storage of combustible and flammable materials;
- Availability of coordination with private and public fire authorities;
- Adequate job-site fire protection and inspections for fire prevention; and
- Adequate indoctrination and training of employees.

11.2 EQUIPMENT AND REQUIREMENTS

- Fire extinguishers will be provided by the Contractor(s);
- Fire extinguishers will be inspected, serviced, and maintained in accordance with the manufacturer's instructions. As a minimum, all extinguishers shall be checked monthly and weighed semi-annually, and recharged if necessary; and
- Immediately after each use, fire extinguishers will be either recharged or replaced.

11.3 FLAMMABLE AND COMBUSTIBLE SUBSTANCES

- All storage, handling or use of flammable and combustible substances will be under the supervision of qualified persons; and
- All tanks, containers and pumping equipment, whether portable or stationary, which are used for the storage and handling of flammable and combustible liquids, will meet the recommendations of the National Fire Protection Association.
- If the LEL exceeds 10% for any compound, fans will be used to dissipate volatile/ combustible gases and to minimize the explosion hazard during drilling/excavation activities. In addition, % O_2/explosive gas monitoring will be conducted throughout the drilling/excavation operations.

ATTACHMENT 1

PROTECTION ENSEMBLES

ATTACHMENT 1

PROTECTION ENSEMBLES

Equipment designed to protect the body against contact with known or anticipated chemical hazards have been divided into four categories according to the degree of protection afforded:

- Level A: Should be selected when the highest level of respiratory, skin and eye protection is needed.

- Level B: Should be selected when the highest level of respiratory protection is needed, but a lesser level of skin protection is required; Level B protection is the minimum level recommended on initial site entries until the hazards have been further defined by on-site studies.

- Level C: Should be selected when the types of airborne substances are known, the concentrations have been measured and the criteria for using air-purifying respirators are met. In atmospheres where no airborne contaminants are present, Level C provides dermal protection only.

- Level D: Should not be worn on any site with respiratory or skin hazards. This is primarily a work uniform providing minimal protection.

The level of protection selected is based primarily on:

- Types and measured concentrations of the chemical substances in the ambient atmosphere and their associated toxicity; and

- Potential or measured exposure to substances in air, splashes of liquids or other indirect contact with material due to the task being performed.

In situations where the types of chemicals, concentrations, and possibilities of contact are not known, the appropriate level of protection must be selected based on professional experience and judgement until the hazards may be further characterized. The individual components of clothing and equipment must be assembled into a full protective ensemble to protect the worker from site-specific hazards, while at the same time minimizing hazards and drawbacks of the personal protective gear itself. Ensemble components based on the widely used USEPA Levels of Protection are detailed below for levels B, C, and D protection.

Level B Protection Ensemble

Recommended

- Pressure-demand, full-facepiece self-contained breathing apparatus (MSHA/NIOSH approved) or pressure-demand supplied-air respirator with escape SCBA;
- Saranex chemical-resistant clothing (overalls and long-sleeved jacket; hooded one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit); disposable chemical-resistant one-piece suit);
- Inner and outer chemical resistant gloves (silver shell);
- Chemical-resistant latex safety boots/shoes; and
- Hard hat.

Optional

- Coveralls.
- Disposable boot covers.
- Face shield.
- Long cotton underwear.

Meeting any one of the following criteria warrant the use of Level B protection:

The types and atmospheric concentrations of toxic substances have been identified and require the highest level of respiratory protection, but a lower level of skin and eye protection. These would be atmospheres:

- with concentrations Immediately Dangerous to Life and Health (IDLH)
- exceeding limits of protection afforded by a full-face air-purifying mask;
- containing substances for which air-purifying canisters do not exist or have low removal efficiency;
- containing substances requiring air-supplied equipment, but substances and/or concentrations do not represent a serious skin hazard;
- containing less than 19.5% oxygen; or

- with evidence of incompletely identified vapors or gases as indicated by direct reading organic vapor detection instrument, but those vapors and gases are not suspected of containing high levels of chemicals harmful to skin or capable of being absorbed through the intact skin.

Level B equipment provides a high level of protection to the respiratory tract, but a somewhat lower level of protection to skin. The chemical-resistant clothing required in Level B is available in a wide variety of styles, materials, construction detail and permeability. These factors all affect the degree of protection afforded. Therefore, a specialist should select the most effective, chemical-resistant clothing based on the known or anticipated hazards and task. Level B skin protection is selected by:

- Comparing the concentrations of identified substances in the air with skin toxicity data;
- Assessing the effect of the substance (at its measured air concentrations or splash potential) on the small area of the head and neck unprotected by chemical-resistant clothing.

Level C Protection Ensemble

Recommended

- Full-facepiece, air-purifying respirator equipped with MSHA and NIOSH approved organic vapor/acid gas/dust/mist combination cartridges or as designated by the Health and Safety Manager;
- Chemical-resistant clothing (polycoated Tyvek overalls and long-sleeved jacket, hooded, one- or two-piece chemical splash suit or disposable chemical-resistant one-piece suit);
- Inner and outer chemical-resistant gloves (butyl/nitrile);
- Chemical-resistant latex safety boots/shoes; and
- Hardhat.

Optional

- Coveralls;
- Disposal boot covers;
- Face shield;
- Escape mask;
- Long cotton underwear.

The use of Level C protection is permissible upon satisfaction of these criteria:

- Measured air concentrations of identified substances will be reduced by the respirator to below the substance's permissible exposure limit (PEL), threshold limit value (TLV), and/or the concentration is within the service limit of the cartridge;
- Atmospheric contaminant concentrations do not exceed IDLH levels; and
- Atmospheric contaminants, liquid splashes or other direct contact will not adversely affect the small area of skin left unprotected by chemical-resistant clothing.

Level C protection is distinguished from Level B by the equipment used to protect the respiratory system, assuming the same type of chemical-resistant clothing is used. The main selection criterion for Level C is that conditions permit wearing an air-purifying device. The device (when required) must be an air purifying respirator (MSHA/NIOSH approved) equipped with filter cartridges. Cartridges must be able to remove the substances encountered. Respiratory protection will be used only with proper fitting, training and the approval of a qualified individual. In addition, an air-purifying respirator can be used only if:

- Oxygen content of the atmosphere is at least 19.5% in volume;
- Substances are identified and concentrations measured;
- Substances have adequate warning properties;
- Individual passes a qualitative fit-test for the mask; and
- Appropriate cartridge/canister is used, and its service limit concentration is not exceeded.

An air monitoring program is part of all response operations when atmospheric contamination is known or suspected. It is particularly important that the air be monitored thoroughly when personnel are wearing air-purifying respirators. Continual surveillance using direct-reading instruments is needed to detect any changes in air quality necessitating a higher level of respiratory protection.

Level D Protection Ensemble

Recommended

- Tyvek coveralls;
- Safety boots/shoes;
- Safety glasses or chemical splash goggles;

- Hardhat;
- Latex gloves.

Optional

- Gloves;
- Escape mask;
- Face shield.

The use of Level D protection is permissible upon satisfaction of these criteria:

- No hazardous air pollutants have been measured; and
- Work functions preclude splashes, immersion or the potential for unexpected inhalation of any chemicals; and
- Atmospheric contains at least 19.5% oxygen.

Level D protection is primarily a work uniform. It can be worn in areas where only boots can be contaminated, or where there are no inhalable toxic substances.

ATTACHMENT 2

CONTINGENCY PLAN AND HOSPITAL ROUTE

(to be developed on a site-specific basis)

ATTACHMENT 2

This attachment presents an example of an emergency response plan for a site in the Love Canal, NY area. A similar plan will need to be developed for each site where well decommissioning activities are to be performed.

Personnel Exposure

- Skin contact: Use copious amounts of soap and water. Wash/rinse affected area for at least 15 minutes. Decontaminate and provide medical attention. Eyewash stations will be provided on site. If necessary, transport to Niagara Falls Memorial Hospital.

- Inhalation: Move to fresh air and, if necessary, transport to Niagara Falls Memorial Hospital.

- Ingestion: Decontaminate and transport to Niagara Falls Memorial Hospital.

Personal Injury

Minor first-aid will be applied on-site as deemed necessary. In the event of a life threatening injury, the individual should be transported to Niagara Falls Memorial Hospital via ambulance. The Consultant and Subcontractor Health and Safety Officers will supply available chemical-specific information to appropriate medical personnel as requested.

The consultant or subcontractor first aid kits will conform to Red Cross and other applicable good health standards, and shall consist of a weatherproof container with individually-sealed packages for each type of item. First aid kits will be fully equipped before being sent out on each job and will be checked weekly by the On-Site Health and Safety Coordinator to ensure that the expended items are replaced.

Communications

Internal emergency communication systems are used to alert workers to danger, convey safety information, and maintain site control. Any effective system can be employed. Hand signals and air-horn blasts are also commonly used. It shall be the responsibility of the Subcontractor's Site Health and Safety Officer to ensure that an adequate method of internal communication is understood by all personnel entering the site. Unless all personnel are otherwise informed, the following signals shall be used.

1) Emergency signals by portable air horn, siren, or whistle: two short blasts, personal injury; continuous blast, emergency requiring site excavation.

2) Visual signals: hand gripping throat, out of air/cannot breathe; hands on top of head, need assistance; thumbs up, affirmative/ everything is OK; thumbs down, no/negative; grip partner's wrist or waist, leave area immediately.

Evacuation

In the event that an area must be evacuated due to an emergency, such as a chemical spill or a fire, workers shall exit upwind, if possible. Since work conditions and work zones within the site may be changing on daily basis, it shall be the responsibility of the Subcontractor's Site Health and Safety Officer to review evacuation routes and procedures as necessary and to inform all site workers of any charges.

Adverse Weather Conditions

In the event of adverse weather conditions, the Consultant's Site Health and Safety Coordinator in conjunction with the Consultant's Health and Safety Officer will determine if engineering operations can continue without sacrificing the health and safety of the Consultants employees. Some of the items to be considered prior to determining if work should continue are:

- Potential for heat/cold stress;
- Inclement weather - related working conditions;
- Limited visibility; and
- Potential for electrical storms.

Emergency Telephone Numbers

PROJECT MANAGER:

CORPORATE HEALTH AND SAFETY MANAGER:

SITE HEALTH AND SAFETY OFFICER:

SITE HEALTH AND SAFETY COORDINATOR:

NIAGARA FALLS MEMORIAL HOSPITAL:	(716) 278-4000
FIRE	911 (Local) 285-1234
AMBULANCE	911 or 285-3663
POLICE	911 (Local) 286-4711
ON-SITE CELLULAR TELEPHONE	(716) 866-4367

The site location is:
Love Canal Site
Military Road
Niagara Falls, New York

Nearest Trauma Center:
Children's Hospital of Buffalo
219 Bryant Street
Buffalo, New York
Dr. James Allen (716) 878-7953

Directions to Hospital

The following directions describe the most efficient route to Niagara Falls Memorial Hospital (see Figure A-1):

(1) From the Site, turn right onto Military Rd. and proceed north to Pine Ave.

(2) Turn left (west) onto Pine Avenue and proceed to 10th Street.

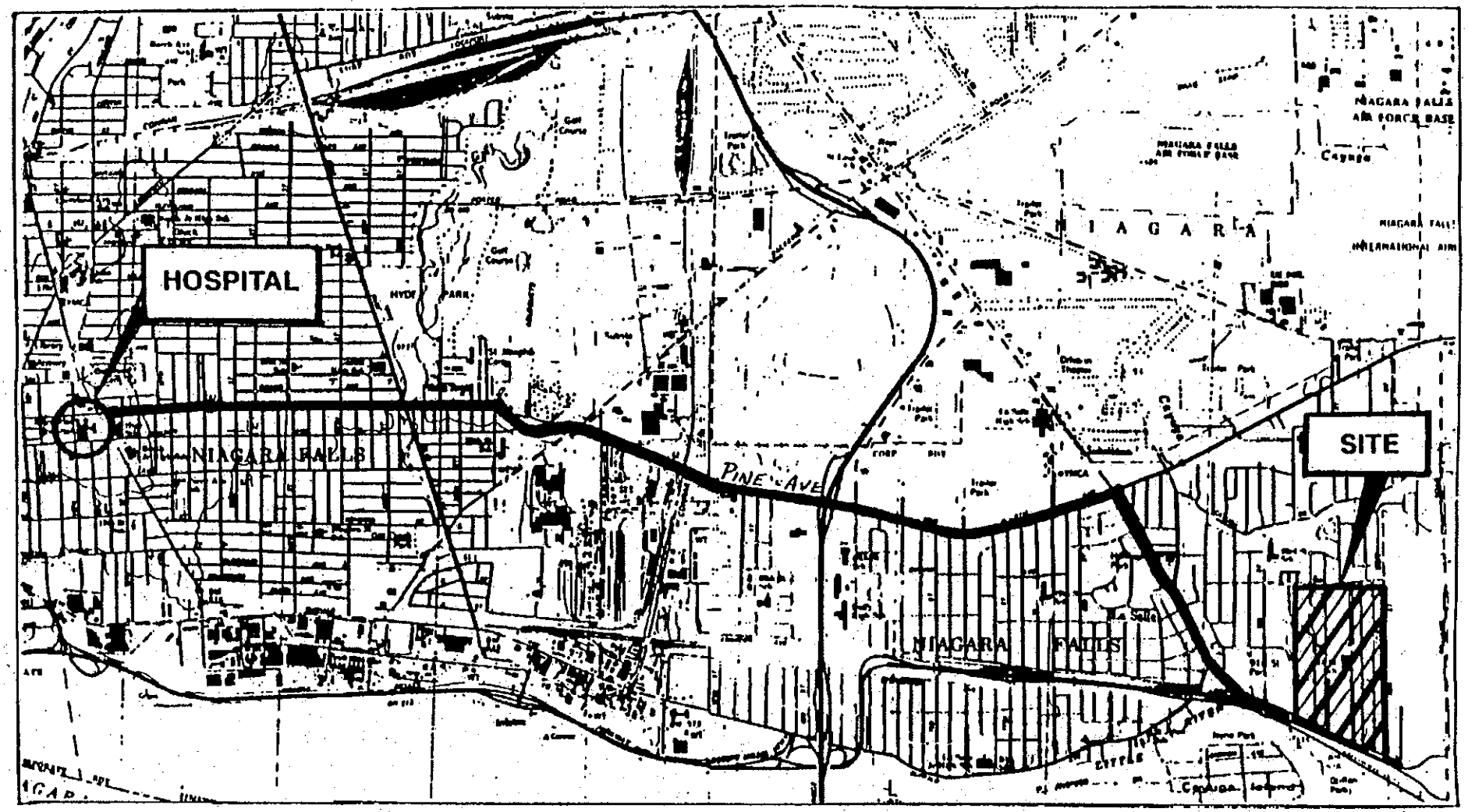
(3) Turn left (south) onto 10th St. and proceed for approximately one-tenth (1/10) mile.

(4) Hospital is on the left side of road (601 10th St.)

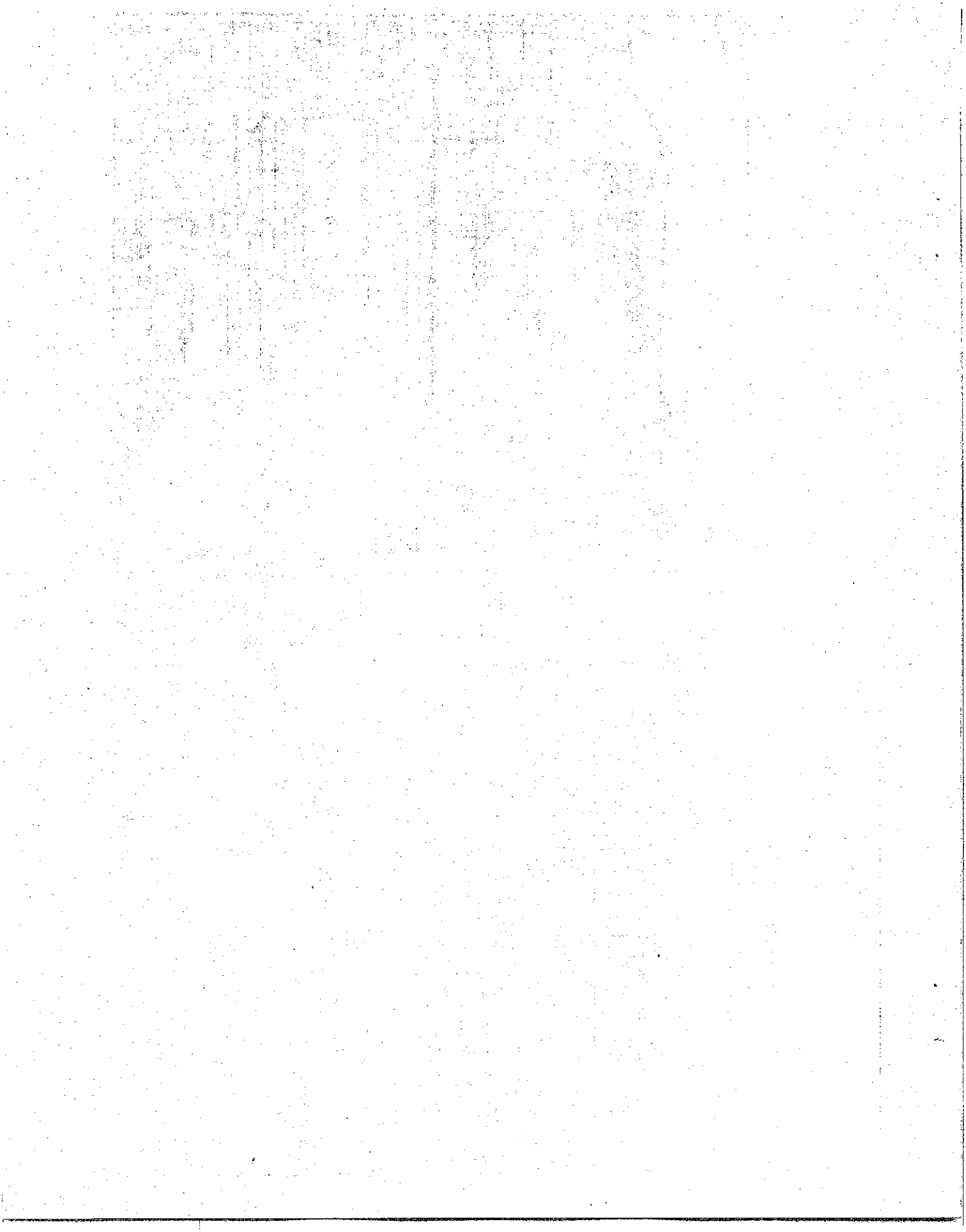
Records and Reporting

It shall be the responsibility of each employer to establish and assure adequate records of all:

- Occupational injuries and illnesses;
- Accident investigations;
- Reports to insurance carrier or State compensation agencies;
- Reports required by client;
- Records and reports required by local, state, federal and/or international agencies;
- Property or equipment damage;
- Third party injury or damage claims;
- Environmental testing logs;
- Explosive and hazardous substances inventories and records;



HOSPITAL ROUTE



APPENDIX B

EQUIPMENT DECONTAMINATION SOPs

Appendix B : Item 1 - DECONTAMINATION FACILITY CONSTRUCTION

Applicability: GENERAL Revision No.: ____ Date: _____

Prepared By: NWT Date: 02/02/90 Approved By: GHF Date: 02/02/90

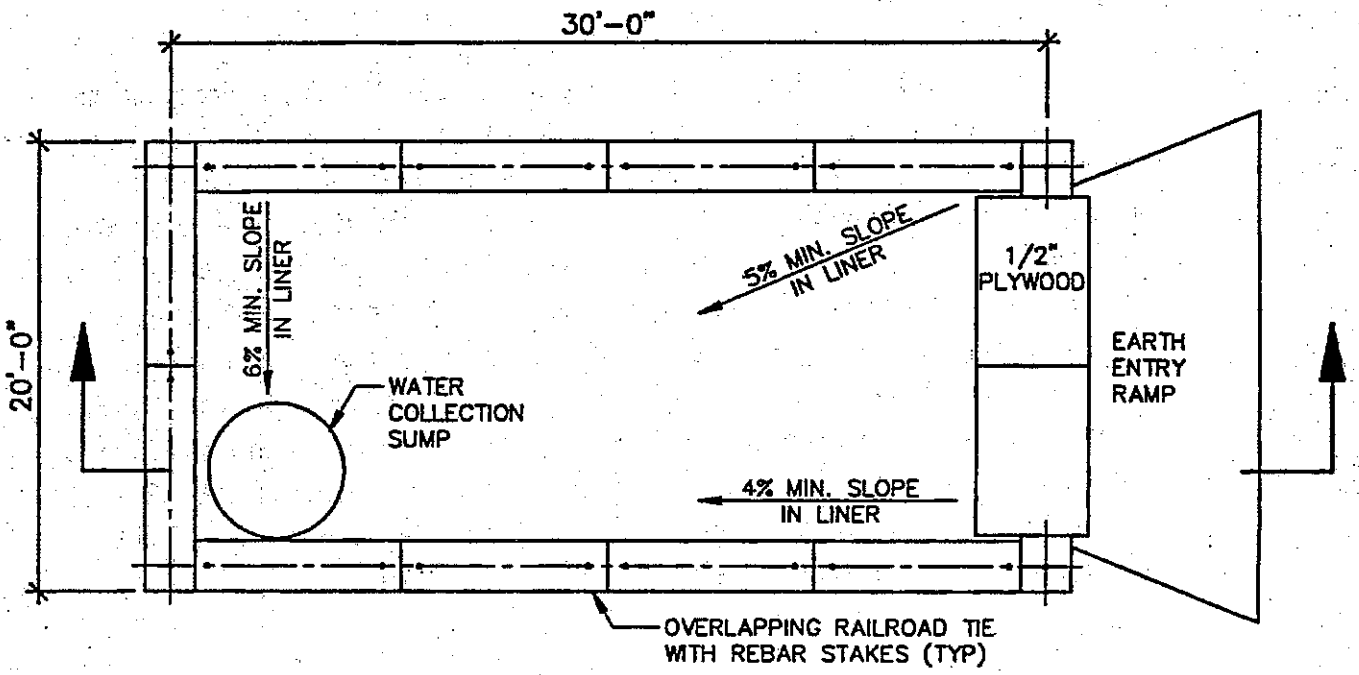
1.0 INTRODUCTION

This guideline presents the construction details for a decontamination facility (i.e., decon pad or wash pad) to be used for the decontamination of drilling and excavation equipment (i.e., drill rigs, backhoes, augers, cutting bits, drill steel, buckets, and associated equipment). A synthetic liner will be installed under the pad for leak and spill protection. In addition, the pad will be constructed with an integral sump to allow for removal of collected liquids. The surface of the liner will be sloped to direct gravity drainage towards a sump. Liquids collected in the sump will be pumped out as necessary and stored in containers until final disposition according to State and Federal regulations. In addition, the decon pad will be covered by a tarp to preclude the collection of precipitation in the sump.

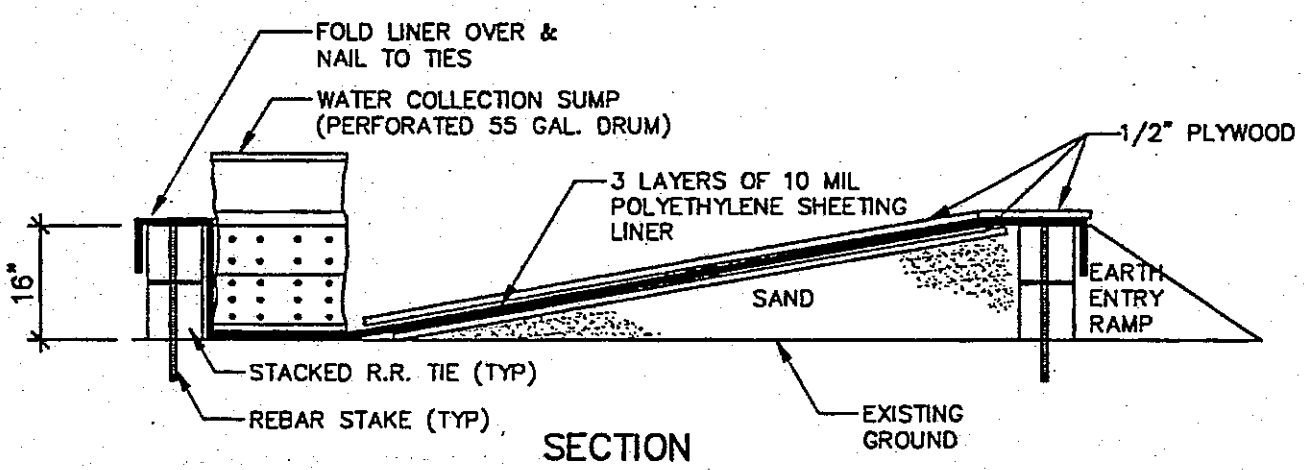
APPENDIX B : ITEM 1 – DECONTAMINATION FACILITY CONSTRUCTION

APPLICABILITY: GENERAL REVISION NO.: DATE:

PREPARED BY: DATE: APPROVED BY: DATE:



PLAN VIEW
NOT TO SCALE



SECTION
NOT TO SCALE

Appendix B : Item 2 - DRILLING/EXCAVATION EQUIPMENT DECONTAMINATION PROTOCOLS

Applicability: GENERAL Revision No.: 1 Date: 10/8/90

Prepared By: NWT Date: 12/20/89 Approved By: GHF Date: 02/02/90

1.0 INTRODUCTION

This guideline presents a method for the decontamination of drilling and excavation equipment (i.e., drill rigs, backhoes, augers, cutting bits, drill steel, buckets, and associated equipment) used during a subsurface investigation. Equipment will be decontaminated at an established and clearly demarcated decontamination facility (see appropriate guideline) prior to initiating surface penetration of each boring/excavation (drill equipment cleaning is not required between wells of the same nest). This will prevent cross-contamination from the previous drilling/excavation location.

2.0 METHODOLOGY

1. Remove all soil/rock material from the equipment at the survey site.
2. Wrap augers, tools, plywood, and other reusable items with a plastic cover prior to transport from the survey site to the decontamination facility.
3. Transport equipment to the decontamination facility.
4. Wash equipment thoroughly with pressurized low-volume water or steam (power washer or steam jenny) using a wire brush to remove visible soils/etc. adhering to the equipment.
5. Use phosphate-free detergent (e.g., Alconox) to remove any oils, grease, and/or hydraulic fluids adhering to the equipment.
6. Rinse with pressurized low-volume water or steam.

7. Allow equipment to air dry.

8. Wrap with clean plastic or aluminum foil, if appropriate, to prevent contamination if equipment is going to be stored or transported.

9. Fluids used for decontamination will not be recycled. Store all wash water, rinse water, and decontamination fluids in containers until final disposal requirements are determined.

10. Following final rinse, inspect openings to verify they are fee of soil/etc. particulates which may contribute to possible cross-contamination.

3.0 REFERENCES

(a) USEPA Region IV Engineering Support Branch. 1986. Standard Operating Procedures and Quality Assurance Manual.

072

Appendix B : Item 3 - SAMPLING EQUIPMENT DECONTAMINATION PROTOCOLS

Applicability: NYSDEC-SPECIFICATION Revision No.: 3 Date: 10/9/90

Prepared By: AJM Date: 10/31/89 Approved By: KLB Date: 12/12/89

1.0 INTRODUCTION

This guideline presents a method for the decontamination of sampling equipment used in the collection of environmental samples.

2.0 HEALTH AND SAFETY

Nitric acid is a strong oxidizing agent as well as being extremely corrosive to the skin and eyes. Solvents such as acetone, methanol, hexane, and isopropanol are flammable liquids. Limited contact with skin can cause irritation, while prolonged contact may result in dermatitis. Eye contact with the solvents may cause irritation or temporary corneal damage. Safety glasses with protective side shields, neoprene or nitrile gloves, and long-sleeve protective clothing must be worn whenever acids and solvents are being used.

3.0 METHODOLOGY

1. All equipment used in sampling must be clean and free from residue of any previous samples. To accomplish this, the following procedures are to be followed:

   a. wash equipment thoroughly with non-phosphate detergent and tap water[1] using a brush to remove any particulate matter or surface film;

   b. rinse with tap water[1];

   c. rinse with a 10% HNO_3 solution[2];

d. rinse with tap water[1];

e. rinse with deionized water (demonstrated-analyte-free)[3];

f. air dry; and

g. wrap in aluminum foil (shiny side out)

2. Well evacuation equipment, such as submersible pumps and bailers, which are put into the borehole must be decontaminated following the procedures listed above. All evacuation tubing must be dedicated to individual wells, (i.e., tubing cannot be reused).

3. Bailer cord must be cleaned with non-phosphate detergent and demonstrated analyte-free deionized water before use. Cord can be reused; it is not necessary to dedicate it to individual wells. If a ten (10) foot or greater length leader is being used, only the leader need be cleaned (assumes bailer cord is not allowed to contact water).

4. All unused sample bottles and sampling equipment must be maintained in such a manner that there is no possibility of casual contamination.

4.0 EQUIPMENT REQUIREMENTS

- personal protective garment and gear
- brush, buckets, and wash basins
- squirt bottles
- supply of solvents and water
- aluminum foil

5.0 REFERENCES

New York State Department of Environmental Conservation, Division of Hazardous Substances Regulation, August 1989, RCRA Quality Assurance Project Plan Guidance.

Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual, April 1, 1986. USEPA Region IV.

NOTES

(1) Tap water may be used from any municipal water treatment system. The use of an untreated potable water supply is not an acceptable substitute.

(2) Omit this step if metals are not being analyzed. For carbon steel split spoon samplers, a 1% rather than 10% HNO_3 solution should be used.

(3) Deionized water must be demonstrated to be analyte-free water. The criteria for analyte-free water are the Method Detection Limits (MDLs) for the analytes. Specifically for the common laboratory contaminants listed below, the allowable limits are set at three times the respective MDLs determined by the most sensitive analytical method:

1. Methylene Chloride
2. Acetone
3. Toluene
4. 2-Butanone
5. Phthalates

APPENDIX C

CONSTRUCTION INSPECTION FORMS

Inspector's Daily Report

CONTRACTOR:
ADDRESS:

TELEPHONE:
LOCATION _____ FROM _____ TO _____
WEATHER _____ TEMP _____ A.M. _____ P.M. _____ DATE _____

CONTRACTOR'S WORK FORCE AND EQUIPMENT											
DESCRIPTION	*H*	*#*	*DESCRIPTION*	*H*	*#*	*DESCRIPTION*	*H*	*#*	*DESCRIPTION*	*H*	*#*
Field Engineer						Equipment			Front Loader Ton		
Superintendent			Ironworker			Generators			Bulldozer		
						Welding Equip.					
Laborer-Foreman			Carpenter								
Laborer									Backhoe		
Operating Engineer			Concrete Finisher								
Carpenter						Paving Equip. & Roller					
						Air Compressor					

SEE REVERSE SIDE FOR SKETCH ☐YES ☐NO
WORK PERFORMED:

PAY ITEMS:

CONTRACT		STA		DESCRIPTION	QUANTITY	REMARKS
NO.	ITEM	FROM	TO			

TEST PERFORMED:
PICTURES TAKEN:
VISITORS:

QA PERSONNEL
SIGNATURE
REPORT NO.
SHEET _____ of _____

MEETINGS HELD & RESULTS:

REMARKS:

REFERENCES TO OTHER FORMS:

SKETCHES

SAMPLE LOG

SAMPLE NUMBER:

APPROXIMATE LOCATION OF STOCKPILE:

NUMBER OF STOCKPILE:

DATE OF COLLECTION:

CLIMATOLOGIC CONDITIONS:

FIELD OBSERVATION:

PROBLEM IDENTIFICATION REPORT

FORM H

DATE _____

DAY | S | M | T | W | T H | F | S |

Project _____ Job No. _____

Contractor _____

Subject _____

WEATHER
TEMP.
WIND
HUMIDITY

Partly Sunny	Clear	Overcast	Rain	Snow
To 32	33 64	65 76	70 85	85 up
Still	Moderate	Strong	Approx. Avg.	
Dry	Moderate	Humid		

PROBLEM DESCRIPTION (Reference Daily Report No.): _____

PROBLEM LOCATION - REFERENCE TEST RESULTS AND LOCATION (Note: Use sketches on back of form as appropriate): _____

PROBABLE CAUSES: _____

SUGGESTED CORRECTIVE MEASURES: _____

APPROVALS:

QA ENGINEER: _____

PROJECT MANAGER: _____

DISTRIBUTION: 1. Proj. Mgr.
2. Field Office
3. File
4. Owner

QA Personnel Signature _____

Wiley-Fisk Form 8-3

CORRECTIVE MEASURES REPORT

FORM I

DATE _____

DAY | S | M | T | W | TH | F | S |

Project _____ Job No. _____

Contractor _____

Subject _____

WEATHER

TEMP.

WIND

HUMIDITY

CORRECTIVE MEASURES UNDERTAKEN (Reference Problem Identification Report No.): _____

RETESTING LOCATION: _____

SUGGESTED METHOD OF MINIMIZING RE-OCCURRENCE: _____

APPROVALS:

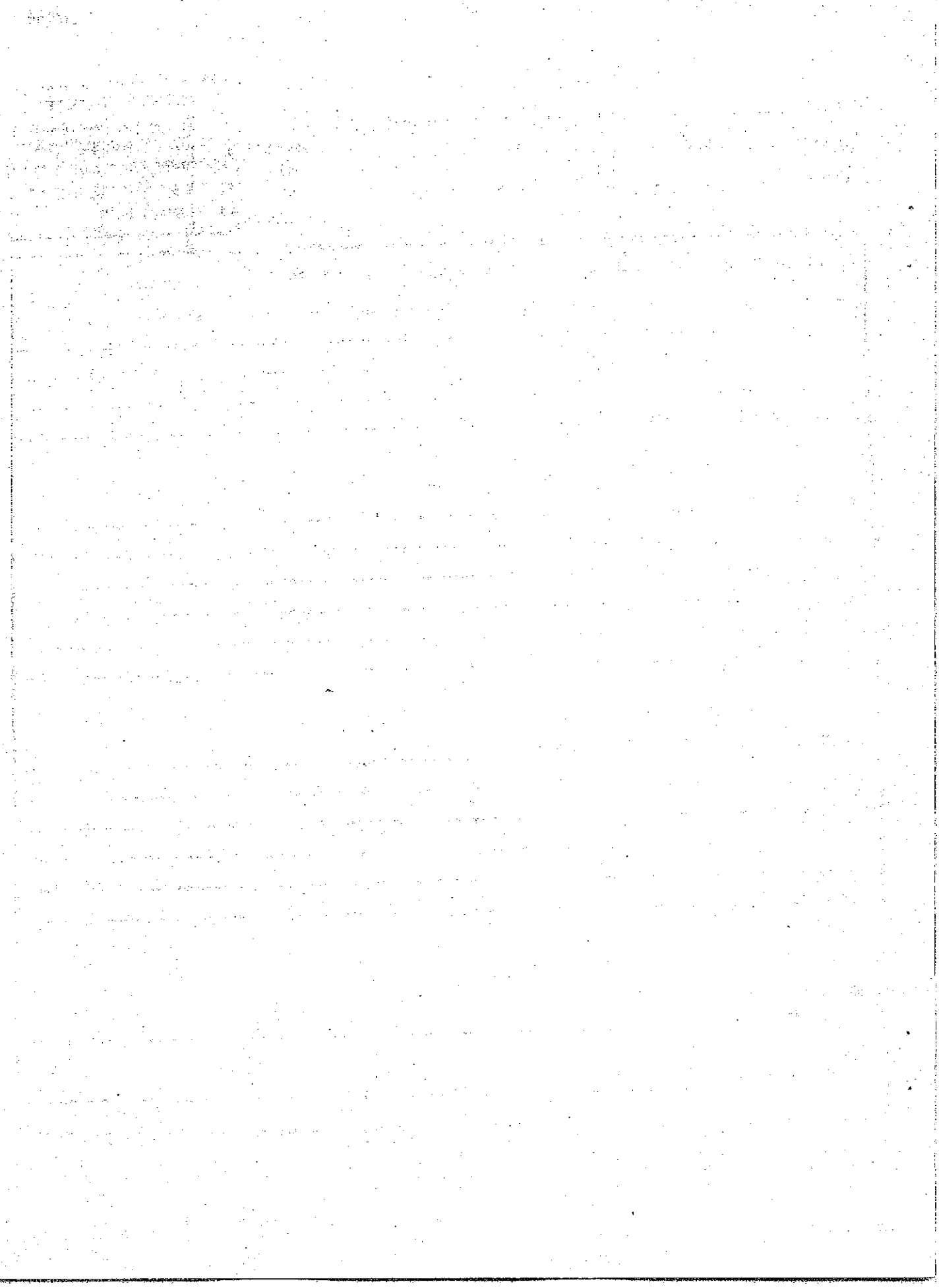
QA ENGINEER: _____

PROJECT MANAGER: _____

DISTRIBUTION: 1. Proj. Mgr.
2. Field Office
3. File
4. Owner

QA Personnel
Signature _____

Wiley-Fisk Form 8-3



APPENDIX D

HYDRAULIC PRESSURE TESTING SOP

Appendix D : Item 1 - HYDRAULIC PRESSURE TESTING OF SCREENED INTERVAL

Applicability: HAZARDOUS WASTE Revision No.: ____ Date: _____

Prepared By: BGP Date: 4/28/95 Approved By: ___ Date: _____

1.0 INTRODUCTION

This guideline presents a method for evaluating the integrity of a grout seal in the screened interval of a well being decommissioned by grouting in place.

2.0 METHODOLOGY

1. Grout the screened interval of the well using a tremie pipe, up to a level of one to two feet above the screened section.

2. Allow the grout to set for a period of not less than 24 hours and not greater than 72 hours before pressure testing of the grouted interval is begun.

3. Place a pneumatic packer at a maximum of four and one half feet above the top of the screened section of the well casing.

4. Apply an inflation pressure to the packer, not exceeding the pressure rating of the well casing material. If the interval between the top of the grout and the bottom of the packer is not saturated, use potable water to fill the interval.

5. Apply a gauge pressure of 5 psig at the well head to the interval for a period of 5 minutes to allow for temperature stabilization. After 5 minutes maintain the pressure at 5 psig for 30 minutes.

6. The grout seal shall be considered acceptable if the total loss of water to the seal does not exceed 0.5 gallons over a 30-minute period.

7. If the grout seal is determined to be unacceptable, an additional 5 feet of grout will be added to the well casing with a tremie pipe. The interval will be retested as described above.

110