DEPARTMENT OF THE ARMY
WATERVLIET ARSENAL
WATERVLIET, NEW YORK 12189-4050

REPLY TO
ATTENTION OF:

Industrial Risk Management Division

March 15, 2002

Mr. Raymond Basso
U.S. Environmental Protection Agency
Chief – RCRA Programs Branch
290 Broadway, 22nd Floor
New York, New York 10007

Re: Draft Work Plan
Bedrock Chemical Oxidation Pilot Study
Siberia Area
Watervliet Arsenal, Watervliet, New York

Dear Mr. Basso:

Enclosed for your review please find one copy of the *Draft Work Plan - Bedrock Chemical Oxidation Pilot Study, Siberia Area, Watervliet Arsenal, Watervliet, New York.* Given the accelerated field schedule for this project, we would greatly appreciate an expedited review of this Work Plan and ask that you provide any comments by March 27, 2002.

Please contact Ms. JoAnn Kellogg at (518) 266-5286 or Mr. Stephen Wood at (410) 962-3506 if you have any questions concerning this submittal.

James J. Kardas

for JAMES J. KARDAS
Chief, Environmental Division

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SIBERIA AREA CHEMICAL OXIDATION PILOT STUDY WORK PLAN
Interim Corrective Measure Design and Installation
Siberia Area, Watervliet Arsenal, Watervliet, New York

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Appendix F	Nonconformance and Corrective Action Report
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Appendix H	Project Schedule
Appendix I	Monitoring Well Construction Details and Baseline Sampling Results

ACRONYMS AND ABBREVIATIONS

ASP	Analytical Services Protocol
CMS	Corrective Measures Study
CRQLs	Contract Required Quantitation Limits
DCA	Dichloroethane
DCE	Dichloroethene
DNAPLs	Dense Non-Aqueous Phase Liquids
DO	Dissolved oxygen
DOC	Dissolved Organic Carbon
DOT	U.S. Department of Transportation
FSP	Field Sampling Plan
GW	Groundwater
HASP	Site Specific Health and Safety Plan
IDL	Instrument Detection Limit
IDW	Investigation Derived Waste
LNAPL	Light Non-Aqueous Phase Liquid
MDL	Minimum Detection Limit
MMA	Main Manufacturing Area
MPI	Malcolm Pirnie, Inc.
MS	Matrix spikes
MSD	Matrix spike duplicate
NA	Natural attenuation
NBS	National Bureau of Standards
NCSS	National Cooperative Soil Survey
NPDES	National Pollutant Discharge Elimination System
NYSDEC	New York State Department of Environmental Conservation
OSWER	Office of Solid Waste and Emergency Response
PAHs	Polycyclic Aromatic Hydrocarbons
PARCCS	Precision, Accuracy, Representativeness, Completeness, Comparability, and Sensitivity
PCBs	Polychlorinated biphenyls
PCE	Perchloroethene (Tetrachloroethene)
RCRA	Resource Conservation and Recovery Act
RFA	RCRA Facility Assessment
RFI	RCRA Facility Investigation
PID	Photoionization Detector
PPE	Personal Protective Equipment
RFI	RCRA Facility Investigation
RPD	Relative Percent Difference
SA	Siberia Area
SOPs	Standard Operating Procedures

SVOCs	Semi-volatile organic compounds
SWMU	Solid Waste Management Unit
TAGM	Technical and Administrative Guidance Memorandum
TCA	Trichloroethane
TCE	Trichloroethene
TD	Technical Director
TDD	Technical Director Delegate
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
VC	Vinyl chloride
VOA	Volatile Organic Analysis
VOCs	Volatile Organic Compounds
WVA	Watervliet Arsenal
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
UIC	Underground Injection Control
USACE	US Army Corps of Engineers
USAMC	U.S. Army Materiel Command
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey

1.0 BACKGROUND AND PURPOSE OF DOCUMENT

1.1 INTRODUCTION

Malcolm Pirnie, Inc. (MPI) has been retained by the Baltimore District of the U.S. Army Corps of Engineers (USACE) to conduct a chemical oxidation pilot study at the Siberia Area (SA) of the Watervliet Arsenal (WVA). The purpose of the pilot study is to evaluate the effectiveness of potassium permanganate to reduce concentrations of chlorinated volatile organic compounds (VOCs) in the bedrock groundwater at a localized area within the North East Quadrant..

The goals of the Work Plan are to:

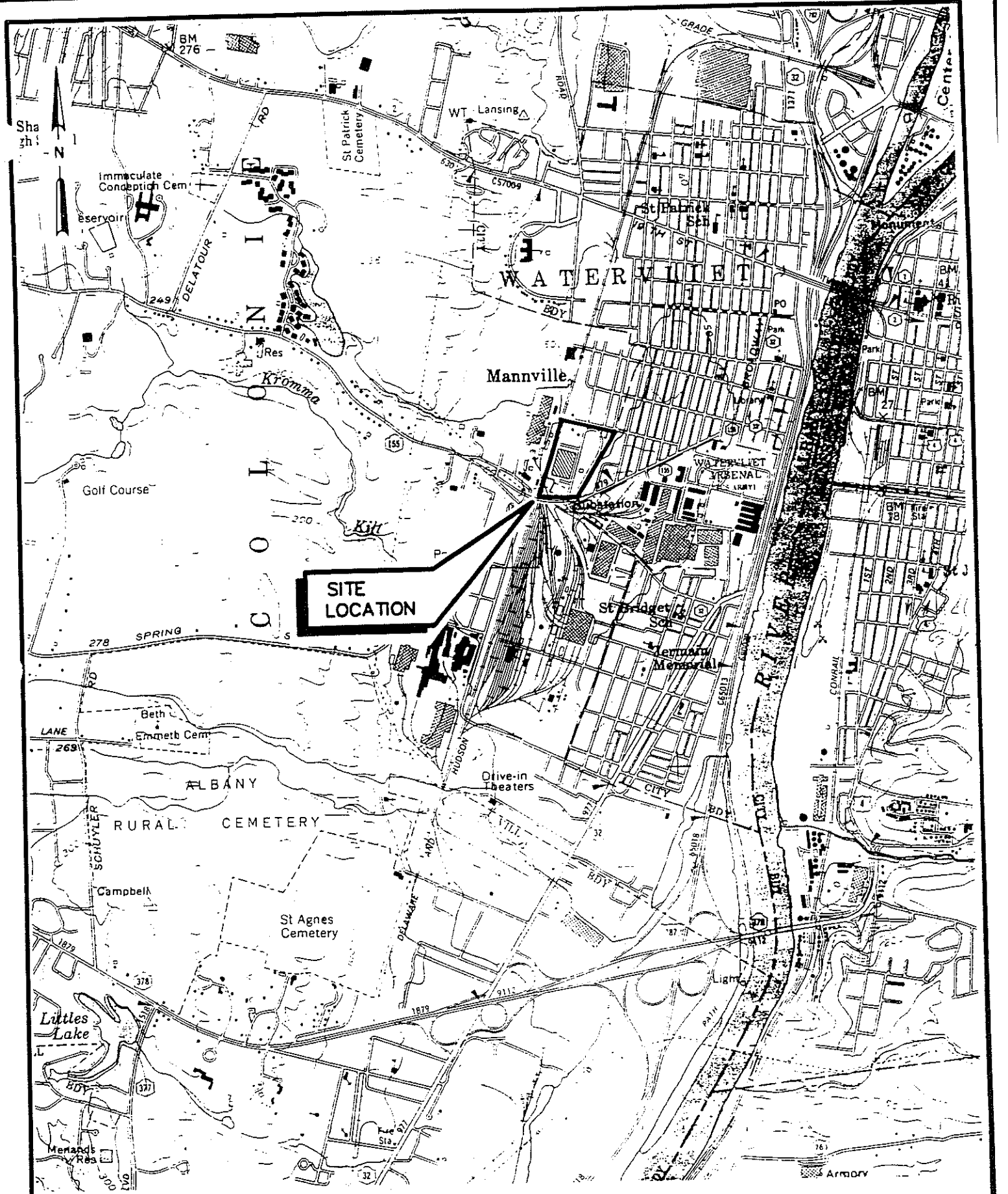
- Present an overview of the contamination at the SA
- Present the pilot study design with technology selection rationale
- Present methodology for monitoring the pilot study to quantify contaminant reduction

This Work Plan includes:

- Summary of the contamination present at the SA
- Pilot Study Design
- Field sampling plan (FSP)
- Quality Assurance Project Plan (QAPP)
- Site Specific Health and Safety Plan (HASP)

1.2 SITE DESCRIPTION

The WVA, a 140-acre government-owned installation under the command of the U.S. Army Materiel Command (USAMC), is located in the City of Watervliet, New York (Figure 1-1). The WVA consists of two primary areas: the Main Manufacturing Area (MMA), encompassing approximately 125 acres, where manufacturing and administrative operations occur, and the Siberia Area (SA), primarily used for the storage of raw and hazardous materials, finished goods, and supplies brought from the MMA (Figure 1-2). To the east of WVA, Broadway Street (Route 32) and a six-lane interstate highway (I-787) separate the WVA from the Hudson River. Residential/light commercial properties are located along the northern and southern site boundaries.



SOURCE: TROY SOUTH 7.5 MIN. QUAD. 1983 EDITION

SCALE: 1"=2000'

US Army Corps of Engineers

SIBERIA AREA

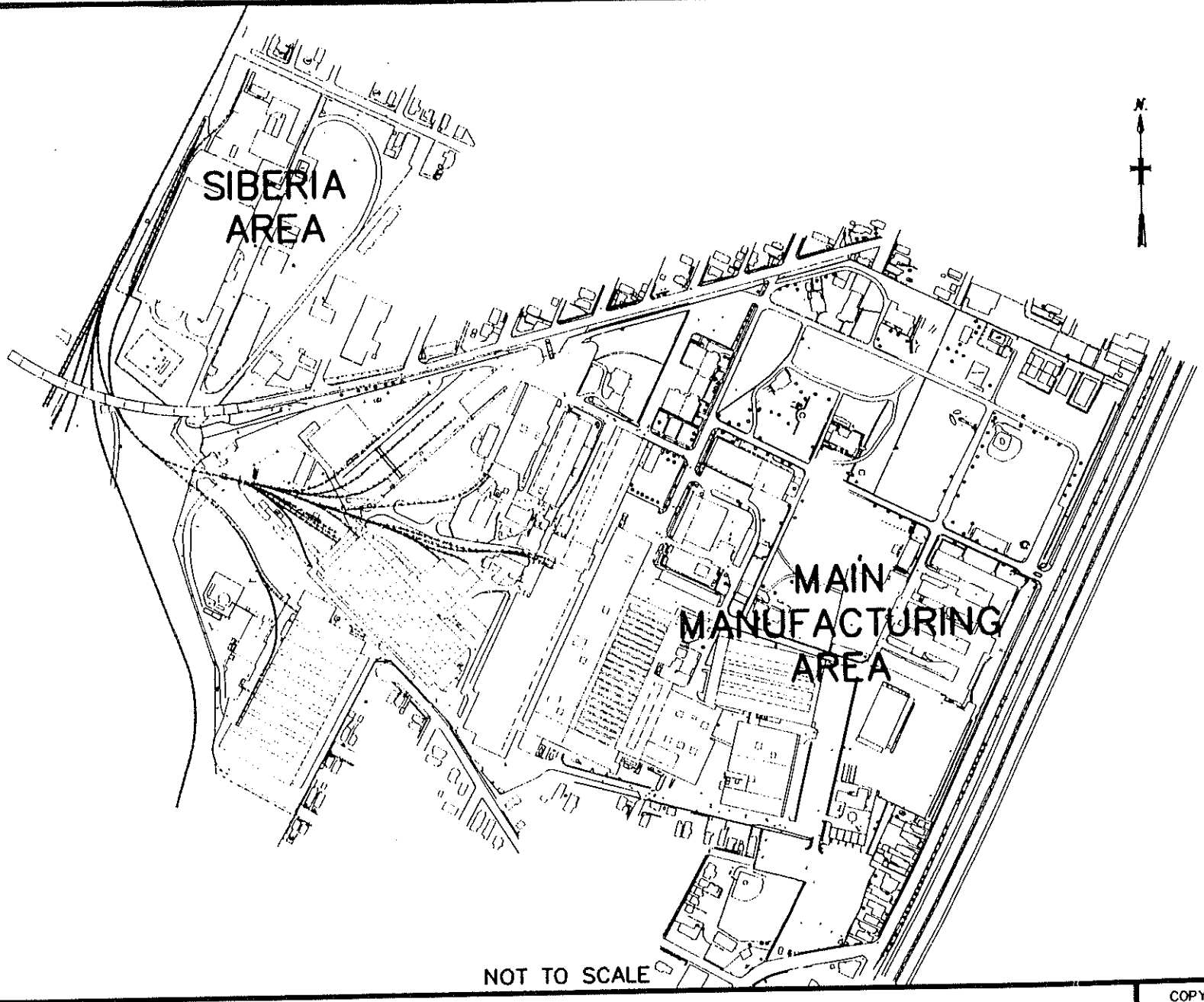
SITE LOCATION MAP

WATERVLIET ARSENAL

USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 1-1



NOT TO SCALE

US Army Corps

SITE PLAN

WATERVLIET ARSENAL

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FIGURE 1-2

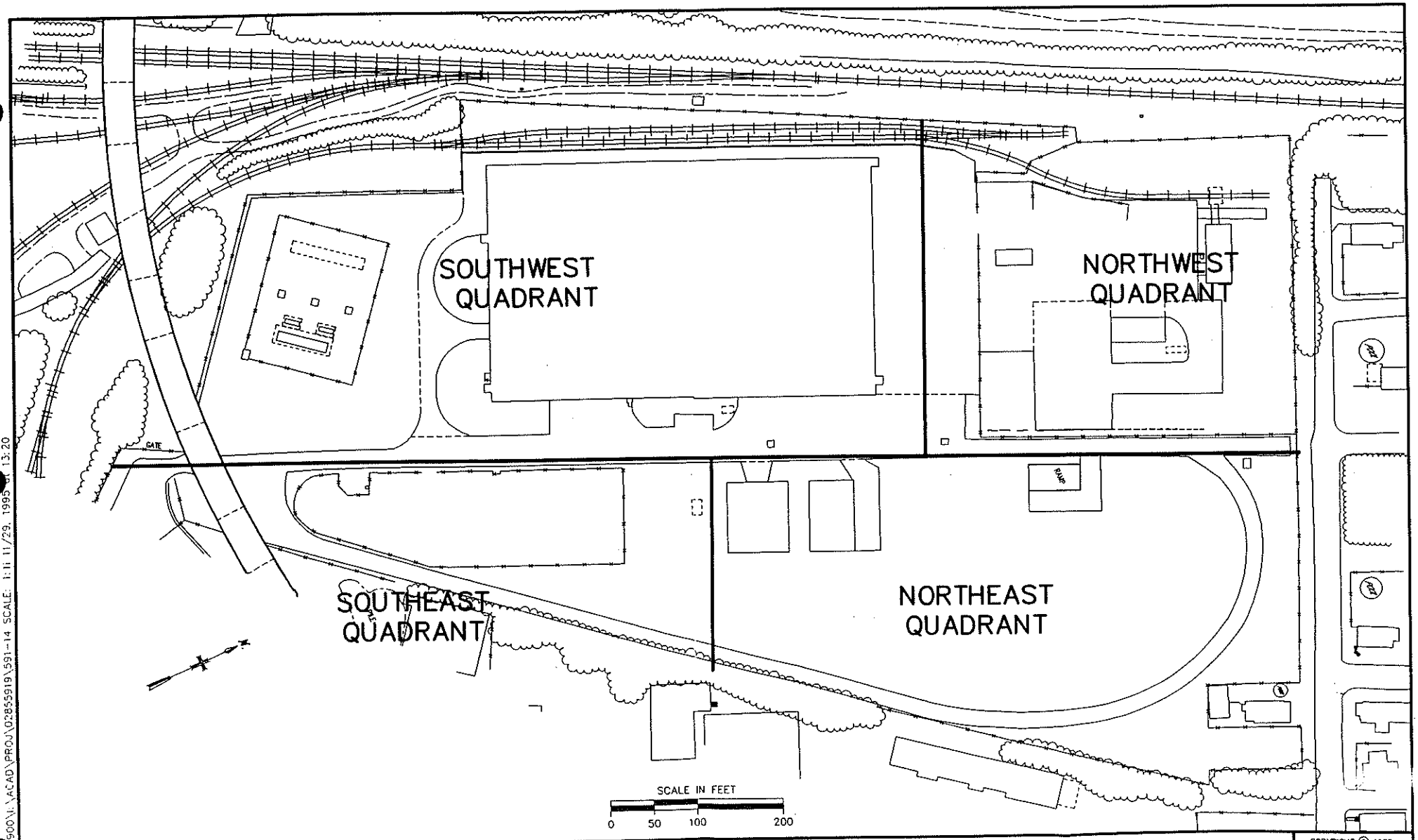
The Siberia Area is located within a light industrial area and is bounded by residential properties to the north and northeast, light industrial/commercial properties to the east (Perfection Plating, Shaker Tire Company), light industrial properties to the south (former Delaware & Hudson railroad yard), and heavier industries located further to the west (Adirondack Steel).

To assist in the descriptions of locations within the Siberia Area, the Area has been divided into four quadrants: southwest (SW), southeast (SE), northeast (NE) and northwest (NW) (see Figure 1-3). The Main Substation and Building 145 are located in the SW Quadrant; a lumber yard is located in the SE Quadrant; former burn pit and Buildings 148 and 151 are located in the NE Quadrant; and the Chip Handling Facility is located in the NW Quadrant. The pilot study will be located in the NE Quadrant.

1.3 SITE HISTORY

The WVA is a national registered historic landmark established in 1813 with the purchase of 12 acres of land by the U.S. War Department. Its original purpose was to distribute supplies (i.e., ammunition, harnesses, and gun cartridges) to troops along the northern and western frontiers. Over the years, the main function of the WVA changed from the production of small arms ammunition, cannon cartridges, and leather goods, to the production of the nation's first 16-inch gun. The WVA also played a major role in the research and development of cannons, mortars, and recoilless rifles. From 1950 to 1970, the WVA built anti-aircraft weapons; the 90 mm gun for the medium tank, the 152 mm gun launcher, the lightweight 60 mm mortar, and a new 8-inch gun/howitzer for use in the Korean and Vietnam Wars. Currently the WVA manufactures cannons. Benet Laboratories, a tenant organization located at WVA, conducts research and development at WVA.

The NE Quadrant of the Siberia Area was historically used for burning of waste (Figure 1-4). According to a RCRA Facility Assessment (RFA) report completed by the NYSDEC in 1992, an open storage area located near Building 149 (a guard shack near the north fence) and the refuse loading ramp was used for empty drum storage (500 to 1500 drums) awaiting recycling or sale. Currently, the area is used for storage of scrap lumber, empty drums, and cannon barrels. The refuse loading ramp is used for loading concrete, scrap metal and other refuse into containers that are hauled away regularly by contractors. A 1,000 gallon waste oil UST is located adjacent to the ramp,



US Army Corps of Engineers

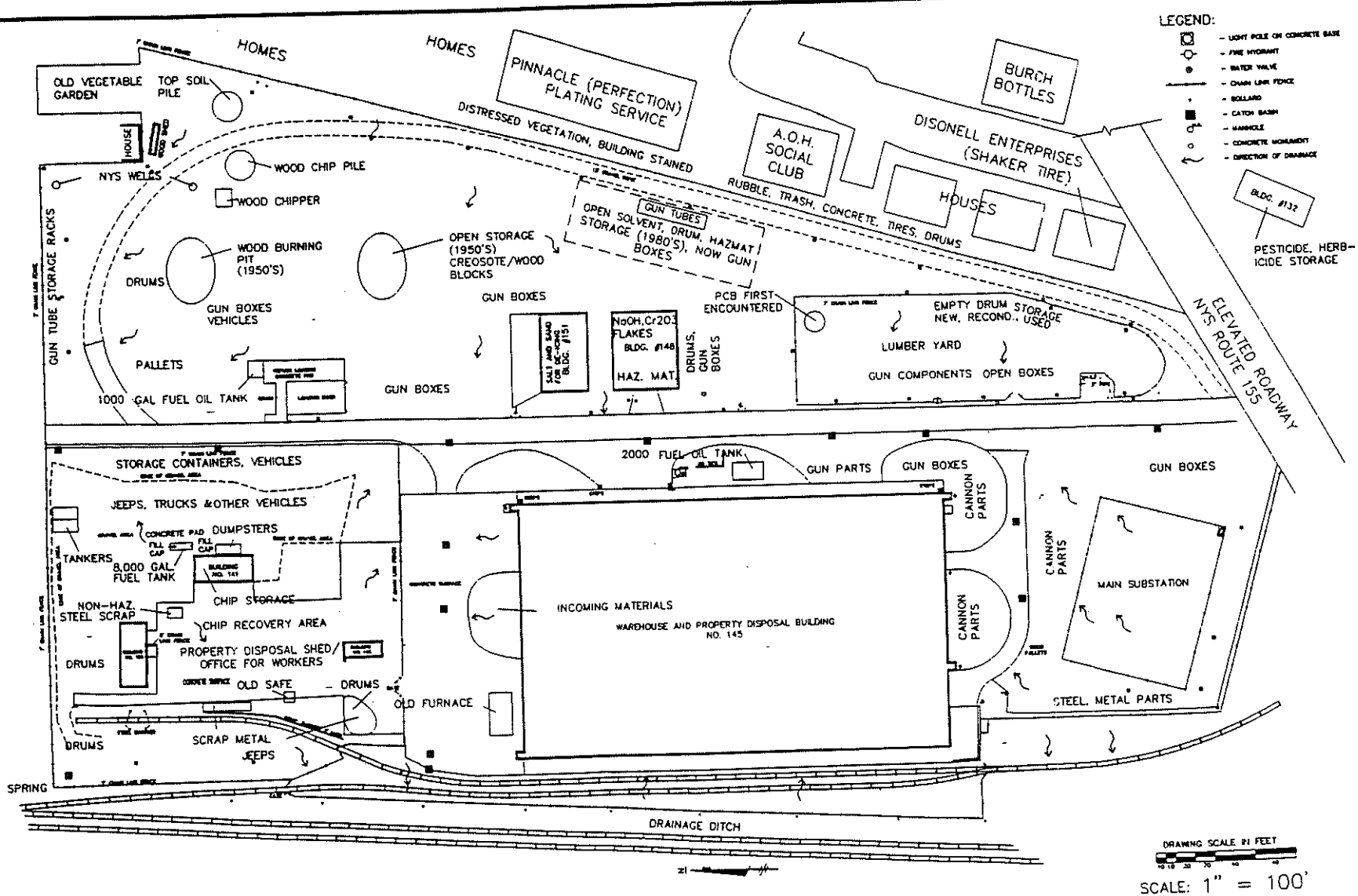
SIBERIA AREA
APPROXIMATE QUADRANT BOUNDRIES

WATERVLIET ARSENAL
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FIGURE 1-3

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SOURCE: IMS R.F.I. WORKPLAN, 1994.

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SIBERIA AREA
LAND USE AND SITE CONDITIONS

WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

FIGURE 1-4

near its northern edge. The UST is used to collect any waste oil or solvents that drain out of the refuse lying in containers.

1.4 PILOT STUDY GOALS

The goals of the Siberia Area Chemical Oxidation Pilot Study are:

- Demonstrate that potassium permanganate solution can be efficiently delivered and distributed through the contaminated zone.
- Estimate the rate of diffusion of potassium permanganate from fractures into matrix blocks between fractures both in the laboratory and in the field.
- Achieve a significant degree of remediation of the contaminated zone by reducing contaminant mass in the test area

2.0 PREVIOUS SITE INVESTIGATIONS

Several environmental studies have been conducted at the SA of the WVA. The most comprehensive investigation, a Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI), was conducted by Malcolm Pirnie from 1994 to 1995 (MPI, 1997). Additional investigations were completed as part of a Corrective Measures Study (CMS) completed by Malcolm Pirnie in 1998. Previous investigations are listed below and are summarized in the RFI:

- William F. Cosulich Associates, P.C. Report – 1980
- CT Male Associates, 1986
- Environmental Science and Engineering, Inc. – 1987
- Groundwater Technology, Inc Report – 1987
- EA Science and Technology, Inc. – 1988
- Environmental Science and Engineering, Inc. – 1991

2.1 SUMMARY OF RFI GROUNDWATER INVESTIGATION ACTIVITIES

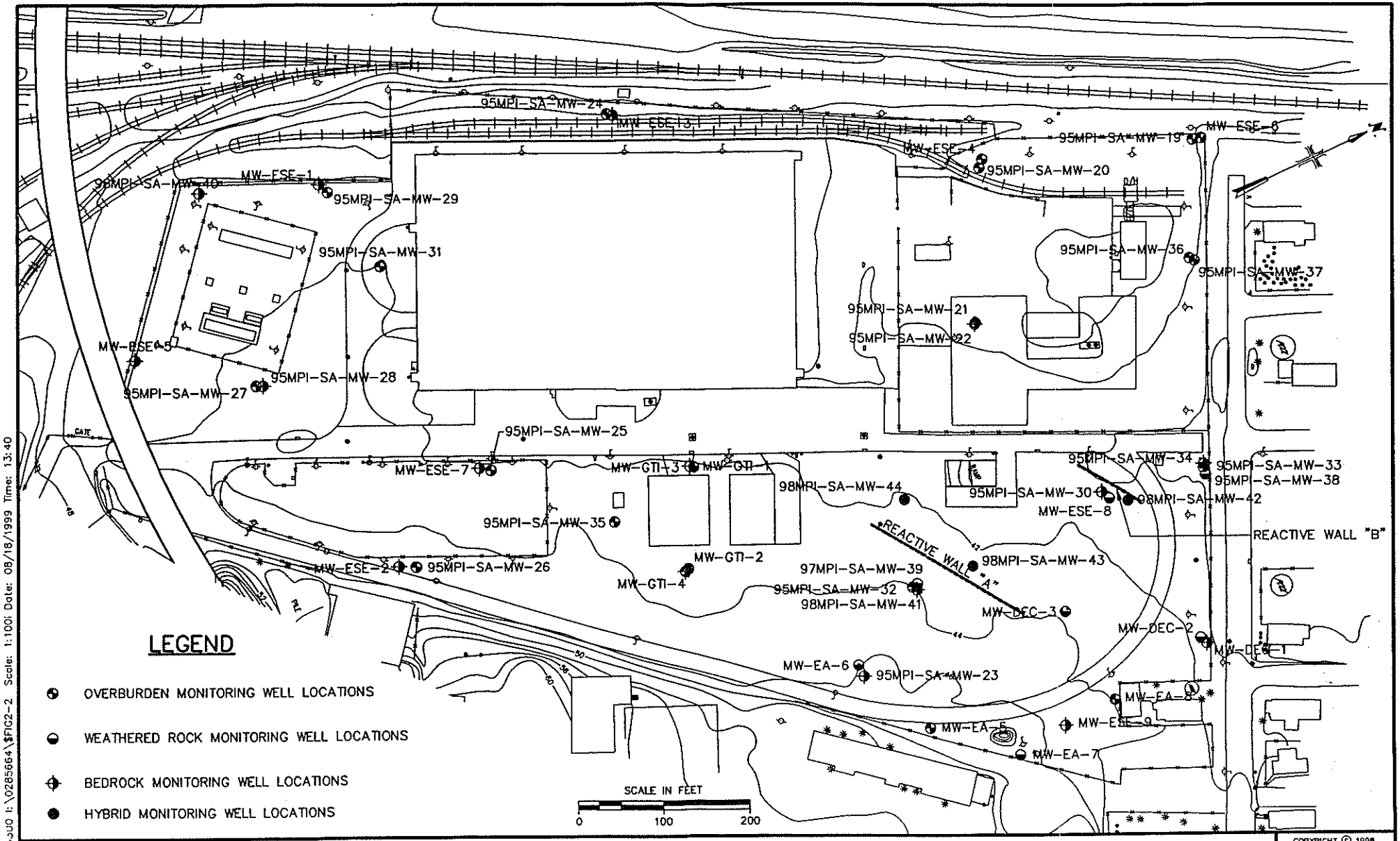
In December 1994, a groundwater field screening survey was conducted at the Siberia Area. A direct push rig was used to collect sixty-nine groundwater samples that were analyzed on site. Based on the results from the field screening, twenty monitoring wells were installed at the Siberia Area in 1995 as part of the RFI groundwater investigation. Groundwater sampling was performed in July 1995 and in April 1996. The results of the screening and monitoring well sampling indicated that groundwater contamination is generally limited to the NE Quadrant of the Siberia Area. The organic contamination in the NE Quadrant consists of chlorinated volatile organic compounds primarily in the overburden. In the SW quadrant, petroleum hydrocarbon contamination was detected during the groundwater field screening survey. Chromium (total and hexavalent) concentrations in the groundwater collected in the NE Quadrant were elevated compared to the rest of the site. Samples containing chromium concentrations exceeding NYSDEC Class GA Standards in the NE Quadrant were collected from all stratigraphic units (overburden, weathered burden, and bedrock).

2.2 SUMMARY OF CMS GROUNDWATER INVESTIGATION ACTIVITIES

During the finalization of the RFI, the USEPA and NYSDEC generated several comments on the nature and extent of contamination in the soils and groundwater at the Siberia Area. As a result of these concerns, additional investigations were completed in 1998 as part of a Corrective Measures Study (CMS). During the CMS investigation in 1998, two new monitoring wells were installed to further define the vertical extent of volatile organic compound (VOC) contaminated groundwater in the NE Quadrant of the SA. The new monitoring wells, 97-MPI-SA-MW39 (MW-39), and 98-MPI-SA-MW41 (MW-41) were installed adjacent to monitoring well 95-MPI-SA-MW32 (see Figure 2-1), where contaminated groundwater was previously identified in the overburden. MW-39 was screened in weathered bedrock at a depth of 14 feet below ground surface (bgs). MW-41 was drilled to a depth of 94 feet bgs into competent bedrock. MW-41 was constructed with 4-inch PVC casing from ground surface to approximately 74 feet bgs and an open hole from 74 feet bgs to 94 feet bgs.

Groundwater samples collected from MW-39 contained 3,966 µg/L of total VOCs. Groundwater samples collected at continuous depth intervals during the installation of MW-41 confirmed the presence of contaminated groundwater. Concentrations of VOCs at MW-41 steadily decreased with depth from 4,704 µg/L at 14 to 34 feet bgs, 2,710 µg/L at 34 to 54 feet bgs, 64 µg/L from 54 to 74 feet bgs, and 51 µg/L from 74 to 94 feet bgs. Compounds detected at the highest concentrations included vinyl choride (VC), tetrachloroethene (PCE), cis-1,2-dichloroethene (cis-DCE), trichloroethene (TCE), and chloroform. Based on these chemical analytical data, it is reasonable to assume that the vertical depth of chlorinated organic compound contamination in the bedrock has been established at MW-41.

The areal extent of contamination in the bedrock can be estimated by the analytical results obtained in bedrock wells installed up-gradient, side-gradient, and down-gradient of MW-41. Analytical data from bedrock wells MW-22 (20–30 feet bgs), MW-23 (14-29 feet bgs), MW-30 (35-45 feet bgs), MW-34 (12-27.5 feet bgs), ESE-9 (11-16 feet bgs) and DEC-1 (43.75-53.75 feet bgs) were assessed during the CMS study to estimate the lateral extent of contamination in bedrock. Chlorinated organic compounds above the NYSDEC Class GA standard were not detected in any of these wells (downgradient, cross-gradient, and upgradient from MW-41). Although these wells were not completed to the same depth below grade as MW-41, they are open to the same bedrock



MONITORING WELL LOCATIONS

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US Army Corps of Engineers

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FIGURE 2-1

83 0285664.000 I:\0285664\SFIG2-2 Scale: 1:100i Date: 08/18/1999 Time: 13:40

intervals where the highest detections of contaminants were found in MW-41 (i.e., 14-34 feet bgs and 34-54 feet bgs). In addition, wells MW-30 and MW-34 can be considered hydraulically down-gradient of MW-41.

2.3 SUMMARY OF SA GEOLOGY AND HYDROGEOLOGY BASED ON RFI FINDINGS

This section provides a brief summary of the geology and hydrogeology of the SA based on the findings of the RFI. A more complete description of site conditions is contained in the RFI report. In addition, complete boring logs are included in Appendices C and D of the RFI report. Selected figures from the RFI report, including geologic cross-sections and potentiometric surface maps are included in Appendix A to this report.

2.3.1 Geology

According to the "Surficial Geologic Map of New York - Hudson-Mohawk Sheet, 1987", a majority of the WVA is underlain by recent alluvial deposits. These are defined as fine sand and gravel deposits overlain by silt. The SA, which is at a lower elevation than the main manufacturing area of the WVA located to the east, is generally underlain by a layer of fill (sand, shale fragments, slag, cinders, brick, wire, wood and concrete). Alluvium, lenses of peat, and lacustrine clay deposits were encountered beneath the layer of fill material.

According to the "Geologic Map of New York - Hudson-Mohawk Sheet, 1970", the site is underlain by Normanskill Shale of the Lorraine, Trenton, and Black River Groups. This formation is comprised of minor mudstone and sandstone and is dark gray to black in color. However, based on recent field observations, and the absence of sandstone, it is likely that the bedrock beneath the site is the Snake Hill Formation mapped by LaFleur (New York State Geological Association Guidebook, 1961), which is comprised mainly of dark gray shale. This unit lies stratigraphically above the Normanskill Shale. During the SA investigation, highly weathered shale was encountered from approximately three and a half to 31.0 ft-bgs. In general, competent bedrock was encountered at approximately 12.0 ft-bgs. The upper portion of the competent bedrock was found to be fissile and highly fractured with 45 to 60 degree bedding planes. The depth to competent bedrock was based on auger refusal during drilling.

2.3.2 Hydrogeology

Groundwater flows generally to the north-northwest in the NE Quadrant of the SA, and generally to the west across the remainder of the SA. Groundwater level data indicates that the SA is a local recharge area. The water table responds quickly to recharge events, and during times of low precipitation the water table may occur in the shale bedrock over portions of the SA. However, on the average, the water table is encountered in the overburden.

Surface water in the SA that does not infiltrate is generally directed into the existing storm sewers. The storm sewer is connected to the City of Watervliet storm sewer network. According to the City of Watervliet Water Department, the storm and sanitary sewer is a combined network which is carried via a 66-inch water main to the Albany County Sewage Treatment Plant, except during wet weather. Following treatment, the water is discharged into the Hudson River. All flows in excess of approximately 2.5 times the average dry weather flow, from the combined sewer system discharges to the Hudson River. No surface water bodies exist within the SA. See Appendix A for potentiometric surface maps generated during the RFI.

2.4 LONG-TERM GROUNDWATER MONITORING

MPI developed a long-term monitoring plan for the MMA and SA of the WVA to act as an interim/long-term monitoring program following the completion of site investigation activities and prior to the implementation of long-term remedial activities. Groundwater sampling data from investigations conducted in support of the RFI of the SA and the CMS of the SA were reviewed to determine the magnitude and frequency of chemical contaminant detections in groundwater at each monitoring well location. Chemical detections were grouped into four categories as follows: inorganics (filtered and unfiltered), semi-volatile organic compounds (SVOCs), VOCs, and Pesticides/PCBs. The results of the analysis for each group were compared to the previous analytical results for that well and compared to the results of the analysis for groundwater collected from wells in the immediate vicinity and to the applicable groundwater quality standards (i.e., NYS Class GA Standards). Wells which contained elevated concentrations of chemical contaminants were selected for inclusion into the long-term groundwater sampling program (MPI, 1999).

Wells at the MMA and the SA are sampled on a semi-annual basis as part of the long-term monitoring program. Long-term groundwater monitoring events were performed during August

1999, April 2000, October 2000 and May 2001. Pertinent results of the long-term monitoring events are discussed in later sections of this report.

3.0 SIBERIA AREA CHEMICAL OXIDATION PILOT STUDY

The Siberia Area chemical oxidation pilot study will be located in the NE Quadrant of the SA. Currently, there are several other pilot studies in progress in the NE Quadrant. A permeable reactive wall is in place to treat overburden groundwater contaminated with chlorinated VOCs and a landfarming pilot study is in place to treat soils contaminated with polycyclic aromatic hydrocarbons (PAHs). The chemical oxidation test is not expected to impact the other pilot studies, with the potential exception of the permeable reactive wall (see discussion in subsequent sections).

3.1 REMEDIATION TECHNOLOGY DESCRIPTION

As discussed in Section 2.0, chlorinated organic contamination in the bedrock aquifer at the SA is found in a localized 'hot spot' in the vicinity of MW-41. The highest concentrations were detected at a depth interval of 14 to 54 feet bgs.

The objective of the pilot study at the SA was to select a remedial technology capable of treating chlorinated VOC contamination within the fracture network as well as in the rock matrix. The WVA is underlain by shale, which is referred to as a fractured porous medium because its primary porosity typically ranges from 5 to 10 percent. It is the presence of fractures in the shale that provides the main pathways for flow through the rock because the rock pores are generally small and not interconnected. The ratio of the void space due to the presence of fractures to the bulk rock volume (fracture porosity) is expected to be several orders of magnitude lower than the matrix porosity, and is estimated to be between 0.01 to 0.0001 percent. This large difference between fracture and matrix porosities greatly influences the distribution of chlorinated solvent mass in these deposits. The net result is that at field sites where solvents have contaminated rock for a few decades, essentially all of the contaminant mass resides in the low permeability rock matrix, not in the fractures.

Chemical oxidation was selected as the most feasible remedial technology for treating chlorinated VOC contamination within the fracture network and in the rock matrix. Both Fenton's

reagent (hydrogen peroxide) and potassium permanganate ($KMnO_4$) were evaluated as potential chemical oxidants. Potassium permanganate was ultimately chosen for several reasons:

- Permanganate is effective over a wider range of pH than Fenton's reagent, which is most effective in acidic conditions
- Fenton's reagent is a stronger oxidant than permanganate; therefore, it degrades more rapidly in the environment. Fenton's short active life is not conducive to the longer diffusive time scales required to treat the rock matrix. Permanganate is more stable and is expected to remain active in the subsurface for weeks or months.
- There is a higher risk of excess pressure building in the subsurface by using Fenton's reagent rather than permanganate

Since unreacted potassium permanganate in solution is relatively stable, it can diffuse into media with low permeabilities (e.g., silt, clay, porous rock) over time, further enhancing oxidant delivery to hard-to-treat contaminated zones. This is particularly advantageous at the SA, since it is believed that a significant portion of the contaminant mass has diffused into the rock matrix. As contaminant concentrations decrease in the fractures following the permanganate injection (see below), the concentration gradient will lead matrix contamination to diffuse out of the rock matrix into the fractures. Application of excess potassium permanganate will allow for diffusion of permanganate into the matrix at the same time as contamination is diffusing out of the matrix (i.e., the reactants will be moving towards each other) speeding the treatment of contamination sorbed to the rock matrix.

3.1.1 Potassium Permanganate Summary

The oxidation of PCE (C_2Cl_4) and TCE (C_2Cl_3H) by potassium permanganate ($KMnO_4$) is governed by the following reactions:

$$C_2Cl_4 + 2KMnO_4 \rightarrow 2\,CO_2\,(aq) + 2MnO_2\,(s) + 2KCl + Cl_2 \quad (1)$$

$$C_2Cl_3H + 2KMnO_4 \rightarrow 2\,CO_2\,(aq) + 2MnO_2\,(s) + 2KCl + HCl \quad (2)$$

Chemical oxidation occurs at both the soil interface and free-phase interface (for non-aqueous phase liquid, NAPL, situations) and within the interstitial pore spaces in the saturated subsurface (for dissolved compounds).

Recent pilot and field demonstrations at other facilities have used potassium permanganate to treat dense non-aqueous phase liquid (DNAPL) sources within both the saturated and unsaturated zones. Potassium permanganate can oxidize a wide range of inorganic and organic compounds including:

- Chlorinated solvents (VOCs)
- Polycyclic aromatic hydrocarbons (PAHs)
- Phenolics (including creosols)
- Cyanides

Organic compounds that contain carbon-carbon double bonds (alkenes) are more readily oxidized by potassium permanganate than compounds having single carbon-carbon bonds (alkanes). Thus, potassium permanganate should be more effective at remediating chlorinated VOCs consisting of TCE or PCE rather than 1,1,1-trichloroethane (TCA).

Environmental parameters that influence the rate and degree of potassium permanganate oxidations include:

- pH (effective over a range of 3 to 12 with an optimum near 7)
- Temperature
- Contact (or reaction) time
- Oxidant concentration

3.1.2 Potential Limitations

Some potential limitations to the use of potassium permanganate include the following:

- The potential to alter subsurface biogeochemistry and locally mobilize co-contaminants (e.g., redox sensitive metals such as Cr).
- The potential for manganate (Mn^{4+}) to be reduced to dissolved divalent manganese (Mn^{2+}) under low-pH or redox conditions.

Hazardous intermediate compounds may be formed due to incomplete oxidation caused by insufficient quantity of the oxidant, the presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagents, and/or inadequate mixing or contact time between contaminant and oxidizing agent.

The by-products (HCl, Cl_2, etc.) released into the subsurface are generally not considered harmful in the environment. However, it is important to understand the fate of the primary by-products in order to minimize adverse impacts to the treatment zone.

- **CO_2 – carbon dioxide** will combine with water to form the carbonate series and lower the pH of the ground water.
- **Cl_2 – chlorine gas** is highly reactive, and it will readily combine with water to form hypochlorous acid (HOCl) and hypochlorite (OCl^-). These two compounds are also very strong oxidants.
- **HCl – hydrochloric acid** will be neutralized in carbonate environments.
- **MnO_2 – manganese dioxide** will precipitate out, coating the subsurface. The buildup of manganese dioxide, and other manganese oxides that may be formed, may reduce matrix permeability over time.

3.2 PILOT STUDY DESIGN

3.2.1 Pre-Injection Phase

3.2.1.1 Rock Core Sampling

One 6-inch diameter injection well (MW-78) was drilled adjacent to MW-41 in December 2001 in accordance with a drilling work plan submitted under separate cover to provide a baseline characterization of the rock matrix prior to the injection of $KMnO_4$ solution. As MW-78 was being drilled, rock cores samples were collected, crushed, specially preserved, and then sent to the University of Waterloo for VOC analysis. In addition, several of the rock core samples were preserved for a diffusivity study to determine the rate of $KMnO_4$ diffusion into the rock matrix. Procedures for rock core sample collection and analysis are provided in Appendix B. Well MW-78 will serve as an injection point during the subsequent injection phase of the pilot study. During installation of MW-78, a black, oily LNAPL was detected to be floating on top of the water column. This is discussed further in Section 3.2.1.2 below.

In addition to measuring VOC concentrations in the rock matrix, several physical and chemical properties will also be measured in the rock cores. These parameters, listed below, are required to provide a basis for generalizing the $KMnO_4$ invasion information from the laboratory tests and the field cores (see Section 3.2.5 for a discussion of $KMnO_4$ invasion):

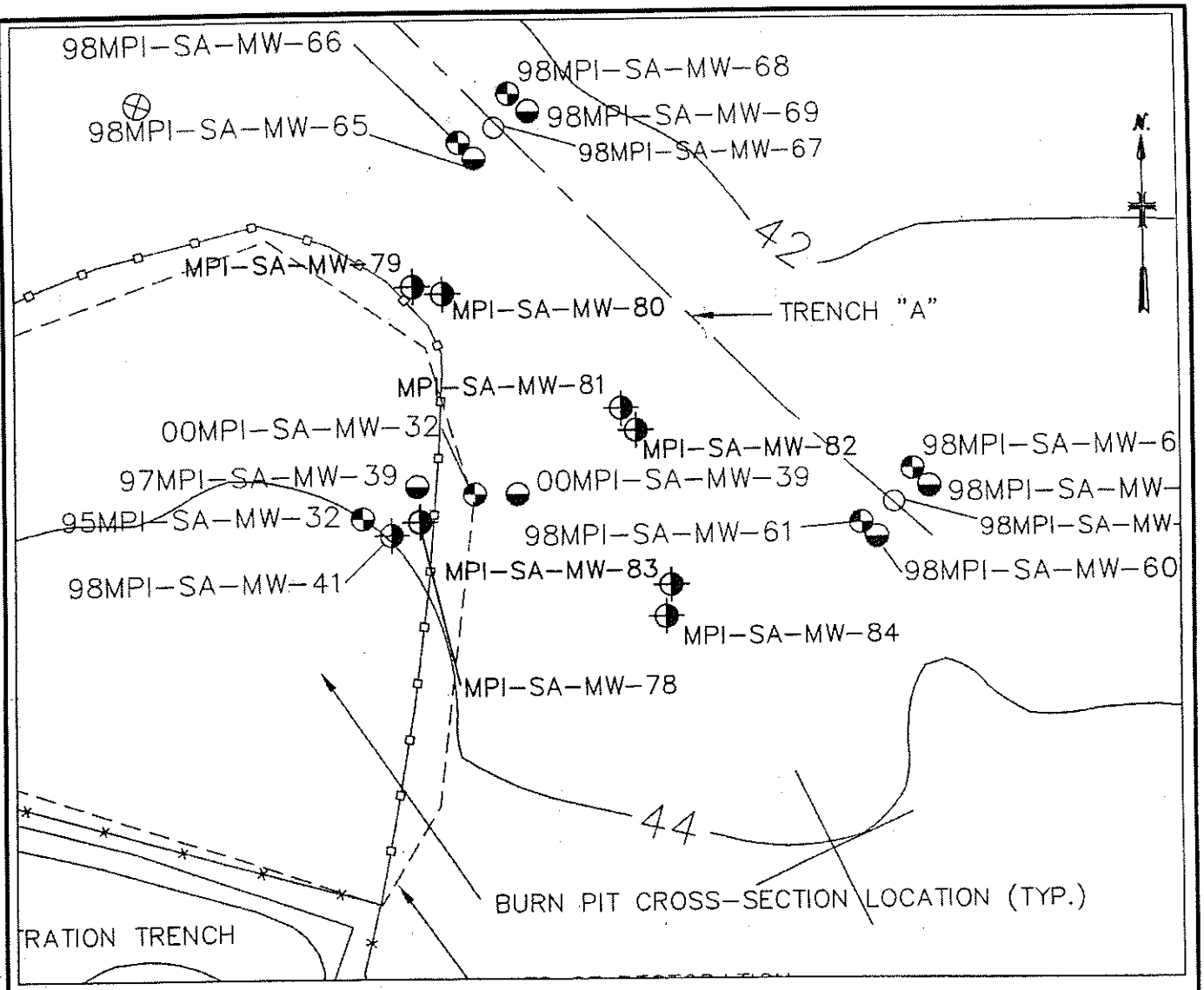
- Porosity (n)
- Saturated bulk density (ρ_{bw})
- Solid-phase organic carbon (f_{oc})
- Total carbonate-mineral content (C_T)
- The effective diffusion coefficient for chloride (D_e^{Cl}) will be measured on a smaller number of the samples.

A sufficient number of core samples will be analyzed to determine the variability of these properties. The shale is relatively uniform in its visual features; however, finer-grained layers that are visually distinct from the rest of the shale may be present at some depths. Samples from the rock core will be selected to determine whether these layers have properties appreciably different from the other shale. These measurements will determine whether the diffusion of $KMnO_4$ into the matrix can be limited by the finer-grained material that has been observed in some cores.

The physical/chemical parameters will be measured on approximately five to ten samples selected from the core hole. The samples will be taken primarily from points close to the most transmissive zones. The samples will be selected to discern vertical variations in the core. The physical/chemical parameters will also be measured on samples from very close to the core segments used for the laboratory $KMnO_4$ tests. This will be done so that associations can be made between $KMnO_4$ invasion and the rock properties governing diffusion, sorption and $KMnO_4$ consumption by rock organic matter and other rock constituents.

3.2.1.2 Baseline Groundwater Sampling

Three two-well monitoring well clusters were installed down-gradient of MW-78 to monitor the efficacy of the pilot injection. The six new wells were designated WVA-SA-MW-79, -80, -81, -82, -83, and –84 (see Figure 3-1). The 'shallow' well in each well cluster was drilled to 34 feet bgs with an open interval from 14 feet bgs to 34 feet bgs. The 'deep' well in each cluster was drilled



LEGEND

- OVERBURDEN WELL
- WEATHERED BEDROCK WELL
- BEDROCK WELL

SCALE IN FEET

0 12.5 25 50

User: LaPlante Spec: PIRNIE STANDARD File: I:\ACAD\PROJ\0285\890\890-FIG3-1.DWG Scale: 1:1 Date: 02/28/2002 Time: 14:01 Layout: Layout1

MALCOLM PIRNIE

WATERVLIET ARSENAL SIBERIA AREA
USAC CONTRACT NO. DACA31-94-D-0017

CHEMICAL OXIDATION INJECTION PILOT

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FIGURE 3-1

to a depth of 54 feet bgs with an open interval from 34 feet bgs to 54 feet bgs. The use of clustered shallow and deep wells will allow for discreet zone monitoring of the contaminated depth intervals (see well construction details in Appendix I). LNAPL was detected in the bedrock injection well (MW-78) during development. The thickness of the LNAPL was difficult to measure due its viscous nature; however, the approximate thickness of the LNAPL was less than one inch. LNAPL was not detected in the new bedrock monitoring wells. Hydraulic testing was conducted during development of the injection well to evaluate the degree of connection to the newly installed bedrock monitoring wells. The results of the testing showed a direct connection to five of the six newly installed monitoring wells.

The injection well and the monitoring wells were sampled on February 6-7, 2002. The groundwater samples were analyzed for VOCs, SVOCs, petroleum hydrocarbons (diesel fuel and motor oil), total organic carbon (TOC), and iron. The results of the baseline sampling are attached in Appendix I. The purpose of the SVOC and petroleum hydrocarbon analyses was to determine whether the detected LNAPL was partitioning into the aqueous phase. Based upon the low SVOC and petroleum hydrocarbon concentrations, it was determined that very minimal partitioning is occurring from the LNAPL to the aqueous phase. Given the low degree of aqueous phase partitioning, and since the KMnO4 injection will be performed via a packer system well below the top of the water column, it is assumed that the presence of the LNAPL will not interfere with treatment of chlorinated VOCs in the bedrock groundwater.

3.2.2 Potassium Permanganate Injection

Potassium permanganate will be injected into MW-78 at two depth intervals: 14 to 34 feet bgs and 34 to 54 feet bgs. The two discrete depth intervals will be separated during injection using an arrangement of packers. Approximately 200 kilograms (440 pounds) of solid $KMnO_4$ will be mixed with water and injected into MW-78. Assuming a water temperature of approximately 50°F, it is anticipated that a 2.5% solution of $KMnO_4$ will be achievable. This will yield approximately 2,100 gallons of solution; approximately 1050 gallons will be injected in the shallow interval and 1050 gallons in the deep interval. Assuming that injection will proceed at a rate of 2.0 gallons per minute, the injection period will span approximately two to three days.

of permanganate (i.e., the water is purple) or measurable concentrations of permanganate, the water will be containerized in U.S. Department of Transportation (DOT)-approved, close-topped 55-gallon steel drums. One water sample will be collected from each drum for VOC analysis using the methods described in Sections 5.0 and 6.0. If VOC concentrations exceed New York State Class GA standards, the water will be disposed off-site. If VOC concentrations are below New York State Class GA standards, the water will be discharged down-gradient of the reactive wall at the Siberia Area to avoid permanganate interference with the wall.

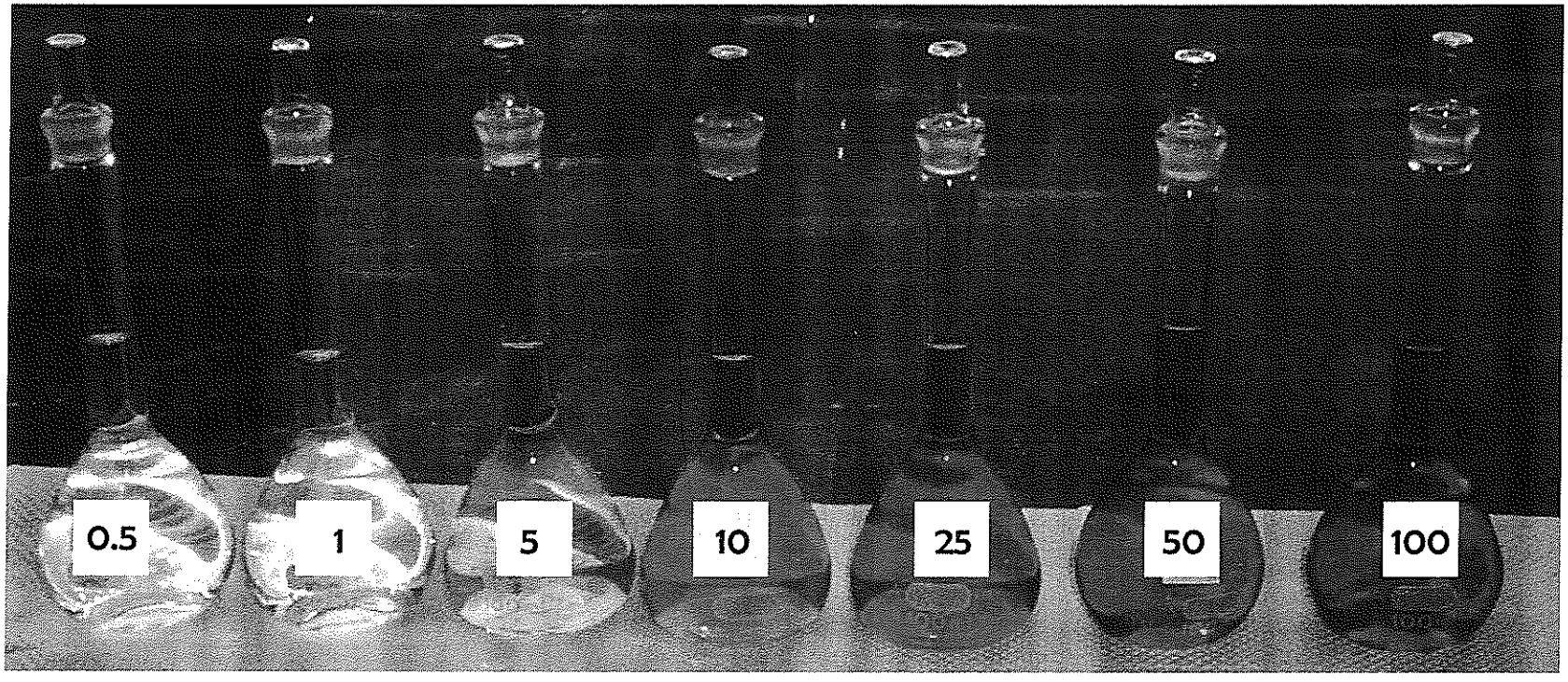
Some disposable personal protective equipment (PPE) and decontamination fluids will be generated. Attempts will be made to wash surface contamination off so that PPE (i.e., gloves and other disposable items) may be disposed of as ordinary solid waste. If contamination is suspected, these materials will be collected and containerized in DOT-approved, 55-gallon steel drums (separately from contaminated groundwater) and disposed of off-site.

During injection at MW-78, $KMnO_4$ concentrations will be monitored in the nearby monitoring wells (i.e., MW-79, 80, 81, 82, 83, and 84). Groundwater samples will be collected by lowering a bailer into each monitoring well. The concentration of permanganate in water can be determined by observing the color (pink to purple) and comparing this color to standard solutions in glass vials. Permanganate concentrations may be visually estimated between the range of approximately 1 mg/L to 100 mg/L (see Figure 3-2). Permanganate concentrations lower than 1 mg/L have no purple color; those higher than 100 mg/L have a uniform deep purple color. In addition to visual color observations, a spectrophotometric method will be used to analytically measure aqueous concentrations of permanganate. If no permanganate is detected in MW-79, 80, 81, 82, 83, or 84 by the end of the injection period, then additional permanganate solution will be applied to MW-78 until permanganate is detected in at least one of the listed monitoring wells.

Several reactive wall wells (see Table 4-1) will also be monitored periodically during the injection to see if any $KMnO_4$ is detected. Samples from these wells will also be collected by lowering a bailer into the wells. If any $KMnO_4$ is detected in the reactive wall wells, injection of $KMnO_4$ solution will be immediately halted, and the well(s) where $KMnO_4$ was detected will be flushed with potable water to prevent $KMnO_4$ from contacting the reactive wall and oxidizing the iron in the wall.

3.2.3 Post-Injection Monitoring

The goals of post-injection monitoring are to determine the spatial distribution of $KMnO_4$ that results from the injection at MW-78 and to measure changes in groundwater quality. There will be two types of sampling events for the Siberia Area pilot study: full monitoring events and field monitoring events. During full monitoring events, groundwater samples will be collected for field analysis as well as for analytical laboratory analysis. During field monitoring events, Malcolm Pirnie staff will measure field parameters only. Two full monitoring events will be conducted, one at approximately one month after the end of injection, and one at approximately two months following the end of the injection. Field monitoring events, during which only the permanganate concentration will be measured, will be conducted approximately weekly for three months and will be staggered between the full monitoring events. Table 3-1 lists the parameters to be measured



Permanganate Concentration, milligrams $KMnO_4$ / Liter = ppm

Note: ppm x 10,000 = %

Source: Carus Chemical Company
Technical Information Disk: Groundwater
& Soil Remediation, May 2001, v 1.0

MALCOLM PIRNIE	WATERVLIET ARSENAL BUILDING 25 AND 40 PILOT STUDY WORKPLAN **PERMANGANATE COLOR AS A FUNCTION OF CONCENTRATION**	MALCOLM PIRNIE, INC. **Figure 3-2**

during the Siberia Area pilot study. Although SVOCs and TPH were detected only at trace concentrations during the baseline sampling event (see Appendix I), these parameters will be analyzed in future rounds to detect potential mobilization that could occur as a result of the $KMnO_4$ injection.

Table 3-1: Analytical Parameters for the Siberia Area Pilot Study

Analytical Parameter
Volatile Organic Compounds (VOCs)
Semi-Volatile Organic Compounds (SVOCs)
Total Petroleum Hydrocarbons (TPH)
Total Organic Carbon (TOC)
*Temperature
*pH
*Oxidation/Reduction Potential (ORP)
*Electrical Conductivity (EC)
*Dissolved Oxygen
*Turbidity
**Permanganate

*Analyzed in the field via water quality instrumentation only during baseline sampling event
**Analyzed in the field using a spectrophotometer

3.2.4 Matrix Diffusion Studies

The rates of $KMnO_4$ invasion into the shale matrix will be determined from laboratory tests as well as from field results. The laboratory tests will involve experiments in which cores are put in contact with $KMnO_4$ solution for a period of time during which diffusion into the core will take place. After a period of several weeks to a few months, the cores will be examined to determine the distance of $KMnO_4$ invasion. This will be done by splitting the core to observe the invasion distance from the $KMnO_4$ contact surface visually based on color change and also by chemical analyses of small samples obtained from the core by saw cutting or miniature core drilling. Samples of the visible diffusion zone will be chipped from the core as well as samples farther from the fracture surface. These samples will be analyzed for Mn and K concentrations, and also for VOCs and total carbonate mineral content. Previous studies of $KMnO_4$ diffusion into clay cores has shown that the visible invasion zone has elevated Mn and K and little or no VOCs. The total carbonate mineral

analysis will be done to determine whether the acid produced by VOC oxidation has caused carbonate-mineral decline in the diffusion zone. This information is needed in order to assess the long-term buffering capacity of the shale, which is an important factor pertaining to the geochemical impacts. Several of these core diffusion experiments will be set up to run concurrently so that the invasion distances after different invasion period can be determined. The cores will be selected to be representative of the shale at different depths in the MW-78 core hole.

Approximately three months after the injection phase, one new core hole will be drilled adjacent to MW-78. Cores collected from this hole will be carefully inspected for visual evidence of $KMnO_4$ invasion into the rock matrix. The $KMnO_4$ will cause a visible color change (from black to dark brown) of the shale in the zones where diffusion has occurred (i.e., diffusion halos). This color change may not be evident on the fracture surfaces because of the wash effect of the drilling circulation water. Therefore, core segments at all brown or suspected fractures will be split to allow examination on fresh surfaces in the rock matrix. It is anticipated that $KMnO_4$ invasion distances from fractures will vary between a few millimeters and a few centimeters. Invasion distance predictions will be refined once information is obtained from the laboratory tests for matrix diffusion. The number of core segments that will be selected for this small-scale sampling to determine $KMnO_4$ invasion distances will depend on the number of fractures at which diffusion halos are identified and on the size of the halos. The halos will be sampled in both directions from each fracture, where possible. In addition, rock samples from the cores will be sampled for VOC analyses with the equipment and procedures used at MW-78 (see Appendix B).

3.2.5 Rebound Monitoring

It is anticipated that after the end of the injection phase, $KMnO_4$ concentrations will gradually diminish to below detection and VOC concentrations may gradually rise from below detection to detectable values. The VOC values would rise due to reverse diffusion from the rock matrix.

After the end of the injection, groundwater sampling of the pilot study monitoring wells will be performed to monitor the rate at which $KMnO_4$ concentrations diminish. Initially, monitoring will be performed on a weekly basis and samples will be analyzed in the field for $KMnO_4$

concentration only. Over time, monitoring will be scaled back to a bimonthly or monthly frequency depending upon the rate of $KMnO_4$ concentration dissipation. When KMnO4 concentrations decrease to approximately 5 mg/L (i.e., the visible range of potassium permanganate detection), a round of VOC monitoring will be performed. VOC monitoring will then be continued on a quarterly basis for a duration to be determined based upon VOC results. In order to expedite pilot-scale reporting, the results of rebound monitoring will not be included in the pilot study report, but will be submitted separately.

4.0 FIELD SAMPLING PLAN (FSP)

This section of the Work Plan includes the Field Sampling Plan (FSP) that will be used at the SA Pilot Study. The objectives of the FSP are to:

- Provide detailed information regarding sampling locations and frequency
- Provide detailed sampling methodology
- List analytical methods to be used for sample analysis

4.1 GROUNDWATER SAMPLING LOCATIONS

Six groundwater monitoring wells (three clusters of two wells each) were installed to monitor the Siberia Area pilot study. Wells located adjacent to the overburden reactive wall will also be monitored to determine whether potassium permanganate is migrating towards the reactive wall. Reactive wall well testing will be limited to lowering a bailer into the wells to visually determine presence of $KMnO_4$. Table 4-1 describes the locations and types of wells to be monitored.

Table 4-1. Pilot Monitoring Well Selection Summary

Cluster Number	Well	Well Location	Stratum of Well Opening	Total Depth of Well (ft. bgs.)
1	MW-79	Source Area	Bedrock	54
1	MW-80	Source Area	Bedrock	34
2	MW-81	Source Area	Bedrock	54
2	MW-82	Source Area	Bedrock	34
3	MW-83	Source Area	Bedrock	54
3	MW-84	Source Area	Bedrock	34
	MW-65	Reactive Wall**	Weathered Bedrock	
	MW-66	Reactive Wall**	Overburden	
	MW-70	Reactive Wall**	Weathered Bedrock	
	MW-71	Reactive Wall**	Overburden	
	MW-60	Reactive Wall**	Weathered Bedrock	
	MW-61	Reactive Wall**	Overburden	

** Reactive wall wells will be monitored for visual evidence of $KMnO_4$ only

4.2 SAMPLING FREQUENCY

Table 4-2 summarizes the sequence of sampling and the sampling frequency of each analytical parameter for the Siberia Area pilot study. Groundwater samples were collected prior to potassium permanganate injection to measure baseline conditions in the aquifer. Two post-injection full monitoring events will be conducted. The first will be performed one month after injection, and the second will be performed two months after the end of injection. Field monitoring (for $KMnO_4$ concentrations only) will initially be performed on a weekly basis and then may be scaled back to a bimonthly or monthly frequency depending upon the rate of $KMnO_4$ concentration dissipation.

4.3 SAMPLING METHODS

All wells will be sampled according to the United States Environmental Protection Agency (USEPA) protocol for Low Stress (Low Flow) Purging and Sampling (USEPA, 1998). Prior to collecting groundwater samples, static water levels will be measured in all monitoring wells to be sampled. Bladder pumps, peristaltic pumps, or submersible pumps will be used to sample the wells. A flow-through cell will be used to measure field parameters during well purging and after sample collection. All non-dedicated equipment and instrumentation will be decontaminated before and after use (see Section 5.0 for decontamination procedures). Parameters to be analyzed, analytical procedures, holding times, preservatives, and containers to be used are listed in Table 4-3.

4.4 INVESTIGATION DERIVED WASTE

Purge water that is collected prior to potassium permanganate injection will be discharged to the infiltration trench for the pilot landfarming study at the Siberia Area, which is located up-gradient of the reactive wall. Purge water from wells that have not been influenced by the permanganate injections (as determined by permanganate field test kit measurements) will also be discharged up-gradient of the reactive wall in the infiltration trench. In the case of purge water that is collected after the onset of potassium permanganate injections, and that contains visible evidence

Table 4-2
Siberia Area Pilot Study Sequence and Monitoring Parameters

					Field Monitoring		Laboratory Analyses				
Work Phase and Frequency	Sampling Location	Sample Depth Interval (feet bgs)	# of Events	Samples/ Event	Permanganate	EC/Redox/DO/Turbidity/pH	VOCs	SVOCs	TPH	Total Organic Carbon	Total # of Samples
Baseline Sampling One Event	MW-79	34	1	1		X	X	X	X	X	1
	MW-80	54	1	1		X	X	X	X	X	1
	MW-81	34	1	1		X	X	X	X	X	1
	MW-82	54	1	1		X	X	X	X	X	1
	MW-83	34	1	1		X	X	X	X	X	1
	MW-84	54	1	1		X	X	X	X	X	1
	Matrix Spike		1	1			X	X	X	X	1
	Duplicate		1	1			X	X	X	X	1
Injection Period Twice a day over 8 hour period (maximum of 3 days)	MW-79	34	6	1	X						6
	MW-80	54	6	1	X						6
	MW-81	34	6	1	X						6
	MW-82	54	6	1	X						6
	MW-83	34	6	1	X						6
	MW-84	54	6	1	X						6
	MW-60	Weathered Bedrock	6	1	X						6
	MW-61	Overburden	6	1	X						6
	MW-65	Weathered Bedrock	6	1	X						6
	MW-66	Overburden	6	1	X						6
	MW-70	Weathered Bedrock	6	1	X						6
	MW-71	Overburden	6	1	X						6
Field Monitoring Every week for duration of pilot study (three months)	MW-79	34	10	1	X						10
	MW-80	54	10	1	X						10
	MW-81	34	10	1	X						10
	MW-82	54	10	1	X						10
	MW-83	34	10	1	X						10
	MW-84	54	10	1	X						10
	MW-60	Weathered Bedrock	10	1	X						10
	MW-61	Overburden	10	1	X						10
	MW-65	Weathered Bedrock	10	1	X						10
	MW-66	Overburden	10	1	X						10
	MW-70	Weathered Bedrock	10	1	X						10
	MW-71	Overburden	10	1	X						10
Full Monitoring One month after injection Two months after injection	MW-79	34	2	1	X		X	X	X	X	2
	MW-80	54	2	1	X		X	X	X	X	2
	MW-81	34	2	1	X		X	X	X	X	2
	MW-82	54	2	1	X		X	X	X	X	2
	MW-83	34	2	1	X		X	X	X	X	2
	MW-84	54	2	1	X		X	X	X	X	2
	Matrix Spike		2	1			X	X	X	X	2
	Duplicate		2	1			X	X	X	X	2
	MW-60	Weathered Bedrock	2	1	X						2
	MW-61	Overburden	2	1	X						2
	MW-65	Overburden	2	1	X						2
	MW-66	Weathered Bedrock	2	1	X						2
	MW-70	Overburden	2	1	X						2
	MW-71	Weathered Bedrock	2	1	X						2

Reactive Wall Wells — To be checked for permanganate via visual observation only

Table 4-2
Siberia Area Pilot Study Sequence and Monitoring Parameters

					Field Monitoring		Laboratory Analyses				
Work Phase and Frequency	Sampling Location	Sample Depth Interval (feet bgs)	# of Events	Samples/ Event	Permanganate	EC/Redox/DO/Turbidity/pH	VOCs	SVOCs	TPH	Total Organic Carbon	Total # of Samples

TABLE 4-3
SAMPLE ANALYTICAL PROCEDURES, HOLDING TIMES, PRESERVATIVES, AND CONTAINERS
INTERIM CORRECTIVE MEASURE DESIGN AND INSTALLATION
SIBERIA AREA, WATERVLIET ARSENAL, WATERVLIET, NEW YORK
US ARMY CORPS OF ENGINEERS - BALTIMORE DISTRICT

PARAMETER	MATRIX	ANALYTICAL PROCEDURE	HOLDING TIME	PRESERVATIVE	CONTAINER
Analytical Laboratory Samples					
VOCs[1]	Groundwater	SW-846 5030B/8260B	7 days	Ice to 4 deg. C	3 X 40 mL glass, Septa vial
Semi-Volatile Organic Compounds	Groundwater	SW-846 3520C/8270C	7 days	Ice to 4 deg. C	2 x 1-L Amber glass
Total Petroleum Hydrocarbons	Groundwater	SW-846 8015B	7 days	Ice to 4 deg. C	2 x 1-L Amber glass
Total Organic Carbon	Groundwater	EPA 9060	28 days	Ice to 4 deg. C, H_2SO4 to pH<2	2 x 250-mL Amber glass
Field Test Kits					
Permanganate	Groundwater	Spectrophotometer	NA	NA	NA

Note 1: These samples must be collected in containers with zero headspace.

General Notes:
One trip blank will be sent per cooler containing volatiles or gases.
Rinse blanks will be collected at the rate of one per decon event per type of equipment, not to exceed one per day.
The laboratory will provide a temperature blank to be sent per cooler.
Samples containing potassium permanganate will be quenched with sodium bisulfite or glucose solution prior to shipment to the laboratory.

of permanganate (i.e., the water is purple) or measurable concentrations of permanganate, the water will be containerized in U.S. Department of Transportation (DOT)-approved, close-topped 55-gallon steel drums. One water sample will be collected from each drum for VOC analysis using the methods described in Sections 5.0 and 6.0. If VOC concentrations exceed New York State Class GA standards, the water will be disposed off-site. If VOC concentrations are below New York State Class GA standards, the water will be discharged down-gradient of the reactive wall at the Siberia Area to avoid permanganate interference with the wall.

Some disposable personal protective equipment (PPE) and decontamination fluids will be generated. Attempts will be made to wash surface contamination off so that PPE (i.e., gloves and other disposable items) may be disposed of as ordinary solid waste. If contamination is suspected, these materials will be collected and containerized in DOT-approved, 55-gallon steel drums (separately from contaminated groundwater) and disposed of off-site.

5.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

5.1 INTRODUCTION

The objective of this Quality Assurance Project Plan (QAPP) is to ensure that data produced from this study is of sufficient quality and quantity to measure the success of the Siberia Area pilot study. To meet this objective, the following six topics are presented and discussed in this section:

- Project organization and responsibilities
- Data quality objectives and analytical requirements
- Sample collection procedures
- Sample integrity
- Field data collection procedures
- Field instrument calibration and maintenance

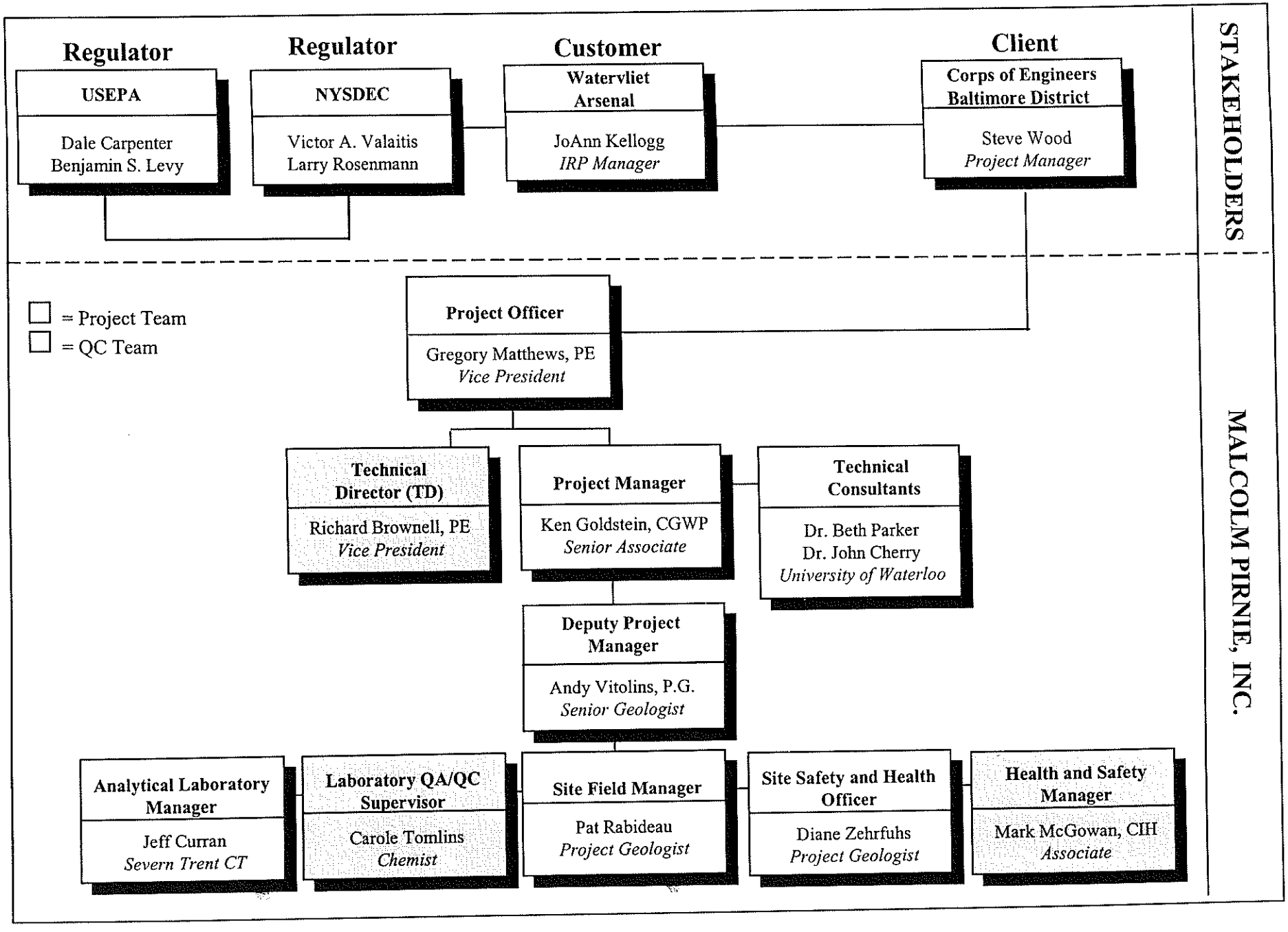
Samples collected during the Siberia Area pilot study will be analyzed by a laboratory located at the University of Waterloo and by PSC Analytical Services, a commercial laboratory. The University of Waterloo has developed special analytical methods for samples with matrices exhibiting high ionic strengths. The methods will be used to analyze groundwater samples with high concentrations of potassium permanganate. Malcolm Pirnie staff will measure field parameters. The rock coring analysis field and laboratory methods were submitted under separate cover and are included in Appendix B to this work plan.

5.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

MPI will conduct or supervise all engineering and field operations. An Organization Chart, showing the Project Officer, Project Manager, and field team personnel is presented in Figure 5-1.

The MPI Project Officer is the representative with contract authority. The Project Officer is responsible for appointing the Project Manager, supervising staff in the performance of project duties, and providing corporate support. The Project Manager, in turn, is responsible for managing the project staff and communicating with the USACE, assuring that all project QC procedures are

Figure 5-1
Organizational Chart



followed, and providing additional authority, when required, to support the Technical Director Delegate (TDD).

The MPI Technical Director (TD) appoints the TDD, and is responsible for supervision of the TDD in performance of project duties. The TDD provides guidance on technical matters and reviews all technical documents relating to the project. Furthermore, the TDD maintains MPI's overall corporate QA program and interacts with the corporate officers, division managers, and client QA/QC personnel to correct problem situations as necessary.

The Analytical Laboratory Manager is responsible for the overall management of the analytical laboratory, including the appointment and supervision of departmental managers, and for approving all analytical procedures and associated QC procedures.

The Laboratory QA/QC Supervisor acts as liaison between MPI field and laboratory operations and is responsible for:

1. Ensuring that field personnel are familiar with and adhere to proper sampling procedures, field measurement techniques, sample identification, and chain-of custody procedures.
2. Coordination of sample analyses to meet project objectives.
3. Preparations of analytical reports, including coordination with the TDD to assure that the data are validated prior to release outside of the analytical laboratory.
4. Review of laboratory data for compliance with precision, accuracy, and completeness objectives.
5. Review of any QC deficiencies reported by the Analytical Laboratory Manager.
6. Coordination of any data changes resulting from review by the TDD and/or Project Manager.

The Project Manager and Laboratory QA/QC Supervisor are responsible for providing consistent and accurate field or laboratory data and technical reports produced by analysts, project scientists or engineers, and sampling personnel under their supervision. These individuals are responsible to the Project Officer for ensuring that all personnel under their direction are knowledgeable of the QA/QC requirements of the project and that all QC and technical review procedures are followed, and documentation is provided.

It is the responsibility of all project personnel, as well as the laboratory analysts, project scientists, and field team members, to perform and document the required QA/QC procedures. It is the responsibility of laboratory analysts to perform preliminary QC checks to ensure that each batch of data being generated passes all required QC criteria. Field team members must bring any unusual observations or analytical problems to the immediate attention of the Project Manager.

5.3 DATA QUALITY OBJECTIVES

The overall data quality objective is to ensure that data of known and acceptable quality are generated. The quality of data is measured through qualitative and quantitative parameters, known collectively as the PARCCS parameters (Precision, Accuracy, Representativeness, Completeness, Comparability, and Sensitivity). All analytical work shall be conducted using laboratory validated procedures. Table 4-3 lists the analytical methods to be used for this investigation.

- ***Precision*** is a measure of mutual agreement among individual measurements of the same property, usually under prescribed conditions. Assessing precision measures the random error component of the data collection process. Precision is determined by measuring the agreement among individual measurements of the same property, under similar conditions. The degree of agreement, expressed as the relative percent difference (RPD), is calculated using the formula below.

$$\text{RPD} = \frac{(V_1 - V_2)}{\frac{(V_1 + V_2)}{2}} \times 100$$

where: V1 = value 1; V2 = value 2

Analytical precision is assessed by analyzing matrix spike/matrix spike duplicate pairs and laboratory duplicate samples. Field precision is assessed by measurement of field duplicate samples. The objective for precision is to equal or exceed the precision demonstrated for similar samples and should be with the established control limits for

the methods. Precision control limits and QC RPD limits can be found in the laboratory's SOP for each analytical parameter.

- ***Accuracy*** is the degree of agreement of a measurement with an accepted reference or true value. Accuracy measures the bias or systematic error of the entire data collection process. Sources of these errors include the sampling process, field and laboratory contamination, sample preservation and handling, sample matrix interferences, sample preparation methods, and calibration and analytical procedures. To determine accuracy, a reference material of known concentration is analyzed or a sample which has been spiked with a known concentration is reanalyzed. Accuracy is expressed as a percent recovery and is calculated using the following formula:

$$\%\ \text{Recovery} = 100 \times \frac{\text{measured value}}{\text{true value}}$$

Recoveries are assessed to determine method efficiency and matrix interference effects. Analytical accuracy is measured by the analysis of calibration checks, system blanks, quality control samples, surrogate spikes, matrix spikes, and other checks required by the selected analytical methods. Sampling accuracy is assessed by evaluating the results of filtration and trip blanks. Sampling accuracy is also maintained by frequent and thorough review of field procedures. The objective is to meet or exceed the demonstrated accuracy for the analytical methods on similar samples and should be within established control limits for the methods. Accuracy control limits and MS/MSD and surrogate recovery limits are located within each laboratory SOP, where applicable.

- ***Representativeness*** expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is achieved through proper development of the FSP. The FSP must be designed so that the samples collected are as representative as possible of the medium being sampled and that a sufficient number of samples will be collected.

- ***Completeness*** is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Data is complete and valid if it meets all acceptance criteria including accuracy, precision, and any other criteria specified by the particular analytical method being used. Completeness is calculated as follows:

  $$\% \text{ Completeness} = 100 \times V/n$$

  where : V = *number of measurements judged valid*

  n = *total number of measurements*

  The objective is to generate a sufficient database with which to make informed decisions. To help meet the completeness objective, every effort must be made to avoid sample loss through accidents or inadvertence. The completeness goal for field collection is 100%. The completeness goal for laboratory analysis is 95%. The Project Manager has the responsibility of deciding whether re-sampling and re-analysis are required to meet the data quality objectives. The Project Manager will discuss the situation with the project team and then inform the Laboratory QA/QC Supervisor and the TDD of the decision.

- ***Comparability*** expresses the confidence with which one data set can be compared to another. Comparability cannot be described in quantitative terms, but must be considered in designing the sampling program. Thus, this objective will be met by using standard methods for sampling and analyses and by following techniques and methods set forth in this Workplan.

- ***Sensitivity*** is a measure of a method's detection limit and ability to distinguish between two values. Sensitivity is determined through the laboratory's Instrument Detection Limit (IDL) and Minimum Detection Limit (MDL) studies. The DL for the analytical parameters have been reviewed and satisfy the program objectives.

Proper execution of each project task is needed to yield consistent information, results that are representative of the media and conditions being measured, and data that are useful for meeting the intended project objectives.

The analytical laboratory will perform the analyses for specified compounds using standardized methods, thereby generating data to provide a baseline for establishing control limits (for precision, accuracy, reporting limits) for daily analyses. The Standard Operating Procedures (SOPs) for the laboratories that will perform the analysis are provided in Appendix C of this document.

5.4 LABORATORY ANALYTICAL PROCEDURES

The University of Waterloo will be used as the off-site laboratory to analyze for VOCs. SVOCs, TPH, and TOC will be analyzed by PSC Analytical. Permanganate, ORP, EC, DO, pH, temperature, and turbidity will be analyzed using field instrumentation. Table 4-3 lists analytical procedures for the parameters to be analyzed. Table 4-3 also presents the required sample volume, required preservative, and the maximum allowable holding times prior to analysis. Laboratory SOPs included in Appendix C present the expected detection limits for each analytical method.

5.5 SAMPLE COLLECTION PROCEDURES

The sampling procedures described in this plan are designed to insure collection of representative samples for analysis, and are based on the following sources:

1. USEPA Region II Groundwater Sampling Procedure, Low Stress (Low Flow) Purging and Sampling, March, 1998 (Appendix D).
2. USEPA Region II CERCLA Quality Assurance Manual, October, 1989.
3. NYS Department of Environmental Conservation Analytical Services Protocol 9/89, Revisions 12/91, and any subsequent modifications.
4. RCRA Quality Assurance Project Plan Guidance, NYS Department of Environmental Conservation, Division of Hazardous Substances Regulation, 3/29/91.
5. USEPA RCRA Ground Water Monitoring Technical Enforcement Guidance Document, September 1986.

The objectives for each field team member are to:

1. Collect a sample that is representative of the matrix being sampled.
2. Maintain sample integrity from the time of sample collection to receipt by the laboratory.

5.5.1 Decontamination of Sampling Equipment

Cross contamination of samples from any source is to be avoided. All sampling equipment must be clean and free from the residue of any previous samples. To accomplish this, the following procedures will be followed:

- All non-dedicated sampling equipment must be cleaned initially and prior to being reused. The following is the procedure for decontamination.
- Wash and scrub with low phosphate detergent.
- Rinse with tap water.
- Rinse with ten percent nitric acid if metals analysis is required.
- Rinse with tap water.
- Rinse with isopropanol (pesticide grade).
- Rinse thoroughly with analyte-free deionized water.
- Air dry.
- Wrap in aluminum foil for transport.

In order to decontaminate the sampling pumps, the following procedure will be followed after each well is sampled:

- Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes.
- Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes. Use the detergent sparingly.
- Rinse: Operate pump in a deep basin of potable water for 5 minutes.
- Final Rinse: Operate pump in a deep basin of distilled/deionized water to pump out 1 to 2 gallons of this final rinse water.

Field filtration equipment will be decontaminated prior to use using a deionized water rinse. Field instrumentation should be cleaned per manufacturer's instructions. Probes, such as those used in pH and conductivity meters and thermometers must be rinsed prior to and after each use with analyte-free deionized water.

5.5.2 Sampling Equipment

The following equipment will be needed to collect groundwater samples for laboratory analysis and to perform field test kits analyses:

- Electric water level indicator
- Bladder pump or peristaltic pump
- Air compressor
- Generator
- Polyethylene discharge tubing
- Horiba U-10 Water Quality Checker
- Dissolved oxygen and redox meters
- Photoionization Detector (PID)
- Hach® DR 890 Series Colorimeter
- Hach® 16900 Series Digital Titrator
- Permanganate test kit (Type to Be Determined)

- Field logbook and field logs
- Preservatives
- Laboratory prepared sample containers
- Roll of polyethylene sheeting
- Decontamination equipment

5.5.3 Sampling Procedures

Groundwater sampling will be conducted in accordance with the USEPA Region II Low-Flow Sampling protocol (USEPA 1998), (Appendix D).

A piece of polyethylene sheeting will be fitted over the monitoring well and laid on the ground. The sampling equipment will be placed on the polyethylene sheeting. The access port through the well cap will be removed, and the concentration of volatile organic vapors emanating from the monitoring well will be measured with the 10.2 eV PID. The PID will be calibrated before the start of each sampling event.

The well will be purged using a bladder pump, submersible pump, or a peristaltic pump at a steady rate of 200 to 500 milliliters per minute (ml/min) while maintaining a drawdown of no more than 0.3 feet in the well. Based on the results of the baseline sampling, some of the monitoring wells may exceed a drawdown of 0.3 feet. In these cases, the well will be purged at three well volumes or dryness, whichever occurs first. Measurements of field parameters consisting of pH, specific conductance, temperature, DO, ORP and turbidity will be made in each monitoring well prior to, during, and after purging (just before sampling) through the use of a Horiba U-22 Water Quality Meter. Water levels will be measured in each monitoring well prior to, during, and after purging (just before sampling). The Horiba U-22 Water Quality Meter will be calibrated for water temperature before each sampling event. It will not be possible to use the Horiba Meter when collecting samples that contain potassium permanganate because several of the probes would be damaged.

The volume of water removed from each monitoring well will be dependent upon the amount of time required for stabilization of the field parameters. In general, the well will be considered

stabilized for sample collection when field parameters have stabilized for three consecutive readings as follows:

- pH: +/- 0.1 standard units
- Specific Conductance: +/- 3%
- Reduction Potential: +/- 10 millivolts
- Dissolved Oxygen +/- 10%
- Turbidity +/- 10%

When the field parameters have stabilized, the volume of water will be recorded, and groundwater in the monitoring well will be sampled through the pump at a flow rate between 100 and 250 ml/min. The purge water will be discharged in accordance with Section 4.4, (Investigation Derived Waste).

Three 40-ml vials for volatile organic analysis will be filled first, without leaving any headspace. Sample pH will be checked by the analytical laboratory, and analyzed accordingly. All other sample bottles will be filled such that some headspace remains in the bottle. The analytical parameters and order of sample collection for groundwater samples will be:

1. In-situ measurements: temperature, pH, specific conductance, turbidity, dissolved oxygen, reduction potential, permanganate and PID measurement
2. Volatile organics
3. Semi-volatile organics
4. Total Organic Carbon
5. TPH
6. Potassium permanganate

The sample bottles will be pre-preserved by the laboratory according to the analytical protocols. The sample bottles will be immediately placed in a cooler and covered with double-bagged ice.

Permanganate will be analyzed using a spectrophotometric method. Specific procedures for field analysis of these parameters are presented in the instrument manuals attached in Appendix E.

Disposable gloves will be worn by the sampling personnel and changed between sampling points. While performing any equipment decontamination, blue latex gloves will be worn in order to prevent contamination of the sampling equipment by interaction between the gloves and the organic solvent(s).

5.5.4 Field Documentation

Data to be recorded in the field logbook will include the date, start and finish times, purging and sampling methods, depth to water, volume of water removed during purging, sample depth interval, field parameters, field-analyzed chemical measurements and PID readings. In addition, the field technician shall note the weather during sampling, samples taken, instrument maintenance and calibration, and any field changes, problems or corrective actions.

5.5.5 Containers, Preservatives, and Holding Times

Sample integrity is preserved through the use of proper sample containers, addition of the correct preservatives to the samples, and meeting designated holding times (the time from sample collection to sample analysis).

The field team leader is responsible for proper sample collection, labeling, preservation, and shipment to the laboratory to meet required holding times. Table 4-3 identifies the proper containers, preservation techniques, and maximum holding times.

The analytical laboratory will supply MPI with commercially-cleaned sample containers. The containers will meet or exceed cleaning and quality control requirements of USEPA OSWER Directive 9240.0-05, Specifications for Obtaining Contaminant-Free Sample Containers. Sample containers will be stored in clean, dust-free areas that are segregated from the analytical laboratory and solvent/reagent storage areas.

5.5.6 Quality Control Samples

Rinse blanks, trip blanks, temperature blanks, and field duplicate samples will be collected to ensure proper field QA/QC accuracy and precision techniques are followed. These samples will be prepared and submitted for analysis along with the actual samples. QA/QC samples in the form of blind duplicates, rinse blanks, matrix spikes (MS) and matrix spike duplicates (MSD) will be

collected to access field and laboratory accuracy and precision techniques. Because of the nature of the potassium permanganate injections, the identification of matrix interferences is a critical component of this study; therefore, MS/MSD samples will be collected at a frequency of one per six environmental samples. Test kits used for field monitoring sample analysis will be performed in duplicate to measure field precision on one sample per event. The collection procedures and frequency of collection of these samples are presented below.

- ***Trip Blanks*** - When collecting environmental aqueous samples for volatile organic compound analysis, a trip blank is taken into the field as part of the sampling kit (the set of appropriate containers used to collect the samples). Trip blanks consist of demonstrated analyte-free water sealed in 40 ml Teflon®-lined septum vials. A clean pair of latex gloves must be worn when preparing a trip blank. These blanks are used to determine whether collected samples have been contaminated by outside sources during shipment or storage. One trip blank sample will be prepared and carried with every shipment of aqueous samples that are to be analyzed for volatiles.

- ***Equipment Blanks*** - Equipment blanks are used to determine whether non-dedicated sampling equipment has been properly decontaminated and assure that there is no cross-contamination of samples due to unclean equipment. Equipment blanks are prepared by pouring demonstrated analyte-free water over decontaminated sampling equipment (using a clean pair of latex gloves), and collecting the rinse water in sample bottles. The collected samples are then preserved and handled in the same manner as the samples, and will be analyzed for the same parameters as the actual samples.

- ***Field duplicates*** - are collected in such a manner that they are equally representative of parameters of interest at a given point in space and time. They are separate from laboratory duplicates, which demonstrate analytical precision. Field duplicates will be collected at a rate of one per six environmental samples for the Siberia Area pilot study. The field duplicate samples will be "blind" duplicates, meaning that the laboratory must

Guidance ER 1100-1-263, Chemical Data Quality Management for Hazardous Waste Remedial Activities, and are modeled after standard USEPA procedures.

Field activities will be documented in a field notebook. All field notes will be recorded in indelible ink on standard forms or in bound notebooks. All standard forms used during the field investigation will be bound in a notebook and centrally located on-site at the end of each day. The notebook will be signed and dated at the end of each day. Similarly, significant events occurring during the day will be reported to the project manager at the end of each day.

At a minimum, the notebook will contain the following sample particulars:

- Sample number
- Date and time of sample collection
- Sample location
- Name of collector
- Analytical work to be done
- Type of sample, and whether the sample is a duplicate, quality assurance, or quality control sample
- Volume of sample taken
- Type of container, number of containers/samples
- Any field observations or measurements (e.g. pH, temperature, specific conductance)
- Type of concentration: low, medium, high
- Preservatives used
- Sampling methodology/special features
- Sampler's signature
- Method of shipment to the laboratory

After samples are collected, chain-of-custody records will be used to trace the possession and handling of the samples. A chain-of-custody record is a printed form that accompanies a sample or group of samples as custody is transferred from person to person. Figure 5-2 provides the typical chain-of-custody document.

As soon as practical after sample collection, the following information must be entered, in indelible ink, on the chain-of-custody record:

CHAIN-OF-CUSTODY RECORD

Page ____ of ____

REPORT TO		INVOICE TO		
COMPANY	PHONE	COMPANY	PHONE	LAB PROJECT #:
NAME	FAX	NAME	FAX	
ADDRESS		ADDRESS		TURNAROUND TIME:
CITY/ST/ZIP		CITY/ST/ZIP		

CLIENT PROJECT NAME:	CLIENT PROJECT #:	CLIENT P.O.#:

SAMPLE IDENTIFICATION	DATE/TIME SAMPLED	COMPOSITE	GRAB	WATER	SOIL	OTHER	LAB ID	# OF CONTAINERS	REQUESTED ANALYSES	COMMENTS
	/									
	/									
	/									
	/									
	/									
	/									
	/									
	/									
	/									
	/									
	/									

TSF#	RELINQUISHED BY	DATE/TIME	ACCEPTED BY	DATE/TIME
1		/		/
2		/		/
3		/		/

ADDITIONAL REMARKS:

COOLER TEMP:

WHITE: LABORATORY COPY **YELLOW**: REPORT COPY **PINK**: CLIENT'S COPY

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TYPICAL CHAIN-OF-CUSTODY

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FIGURE 5-2

1. Project number.
2. Project name.
3. Sampler(s) signature(s).
4. Sample identification code for each sample contained in the shipment. This code appears on the sample label.
5. The date-of-collection of each sample, entered as six-digit number indicating the year, month, and day.
6. The time-of-collection of each sample, entered as a four-digit number indicating the military time of collection; for example, the time entered for a sample collected at 1:54 p.m. would be 13:54 hrs.
7. The matrix of each sample (e.g. soil, aqueous, sludge).
8. The analysis and analytical method to be performed for each sample.
9. The number of containers for each sample identification code (when analyzing for several chemical parameters, a number of containers are filled at each sampling location).
10. Remarks. Enter any appropriate remarks.

A person is in custody of a sample if the sample is:

- In that person's physical possession;
- In view after being in that person's physical possession;
- Placed in a locked repository by that person, or;
- Placed in a secure, restricted area by that person.

Custody of the samples may be transferred several times prior to their arrival at the laboratory. For example, a field team shipper may be designated to receive all samples from field team members. When transferring custody to another responsible individual, perform the following:

1. Enter the date and time of sample transfer on the chain-of-custody form, and sign the form, under the "Relinquished by:" entry.
2. Make certain that the individual receiving custody signs the "Received by:" entry.

When transferring custody to a common carrier (e.g. Federal Express), perform the following:

1. Enter the date and time of sample transfer on the chain-of-custody form, and sign the form, under the "Relinquished by:" entry.
2. Enter the name of the carrier under the "Received by:" entry.
3. Enter the bill-of-lading or Federal Express airbill number under the "Remarks:" entry.
4. Follow the packaging procedures presented in Section 6.7.3 (Sampling Shipping)

5.7.3 Sample Shipping

The following procedures shall be followed for packaging and shipping of samples:

1. Coolers shall be used to ship samples.
2. All labels shall be written with indelible ink.
3. Approximately 3 inches of inert cushioning material such as vermiculite shall be placed in the bottom of the cooler.
4. Each sample container shall be enclosed in a clear plastic bag through which the labels are visible, and the bag sealed. The containers shall be placed upright in the cooler in such a way that they do not touch, and will not touch during shipping.

- Additional vermiculite packing material shall be placed in the cooler to partially cover the sample containers (more than halfway). Bags of ice shall then be placed around, among, and on top of the sample containers.
- The cooler shall then be filled with cushioning material.
- The original chain-of-custody form shall be placed in a waterproof plastic bag and placed inside the cooler. Retain a copy of the form with the field records.
- The drain of the cooler shall be taped shut.
- The cooler lid shall be secured by taping. The cooler shall be wrapped completely with strapping tape at a minimum of two locations in such a way that no labels are covered.
- The shipping label shall be attached to top of cooler.
- "This Side Up" labels with arrows and "Fragile" labels shall be placed on at least two sides of the cooler.

- Numbered and signed custody seals shall be affixed on the front right and back left sides of the cooler, across the lid and body of the cooler. These seals shall be covered with wide, clear tape. A sample custody seal is shown on Figure 5-3.

The laboratory addresses are as follows:

University of Waterloo
Paul Johnson (BFE Bldg.)
Department of Earth Sciences
University of Waterloo
200 University Avenue West
Waterloo, Ontario N2L 3G1
Canada
Phone: (519) 888-4567 ext. 6750 or ext. 2658

PSC Analytical Services
200 Bluewater Road
Bedford Nova Scotia, B4B 1G9
phone: (902) 420-0203, fax: (902) 420-8612

5.7.4 Sample Custody in the Laboratory

Once the samples arrive at the laboratory, custody of the samples will be maintained by laboratory personnel. Each sample will be identified upon receipt by the laboratory and cross-referenced to the chain-of-custody record. Any inconsistencies will be noted on the custody record. Laboratory personnel will immediately notify the MPI Laboratory QA/QC Supervisor, Site Field Manager, or Project Manager if inconsistencies are identified.

The analytical laboratory will have written SOPs for maintaining security of samples and tracking the work performed on samples through the entire analytical process. The SOP requires that sample receipt, sample extraction/preparation, sample analysis, data reduction and data reporting be documented by the laboratory.



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SAMPLE CUSTODY SEAL

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FIGURE 5-3

5.7.5 Document Control

Document control consists of maintaining a project file, an analytical laboratory batch file, a project field file, and a QA project file. The project file will be maintained by the MPI Project Manager and will contain all original documents. Project personnel may keep their own files; however, all original documents will be kept in the project file. All laboratory records, including batch forms, log sheets, and computerized worksheets, will be kept by the analytical laboratory in a batch file in the sample control center. Field logs will be maintained by the Project Manager in a project field file. The Laboratory QA/QC Supervisor will independently maintain a QA project file. At the end of the project, the QA project file will be turned over to the Project Manager. The following documents will be placed in the QA project file:

1. QA records maintained throughout the investigation.
2. Documentation of QA system and performance audits.
3. Documentation of all unusual findings or observations.
4. Documentation of all QA corrective actions.
5. All official QA correspondence received or issued relating to the investigation, including records of telephone calls.
6. One copy of all QA deliverable review sheets.
7. Any other QA documents related to the project or follow-up activities related to the investigation.

5.8 EQUIPMENT CALIBRATION AND MAINTENANCE PROCEDURES

Instruments must be properly calibrated to produce technically valid data. Documented calibration and calibration check results verify that the instruments used for measurement are in proper working order and the data produced is reliable. The calibration requirements described or referenced in this section are necessary to support the data quality objectives for this project. When calibration requirements are met, the data will support the focused investigation decisions dealing with the nature and extent of contamination and safety concerns. In the event that the data is used in court, documented calibrations are necessary to ensure that the data is legally defensible.

5.8.1 Field Equipment Calibration

The following table provides a list of the tasks that will require field equipment, and the specific field instruments that will be used for each task and which require calibration.

Table 5-1. Field Equipment that Requires Calibration

TASK	FIELD INSTRUMENT
Groundwater Sampling	MiniRae Photoionization Detector Horiba U-22 Water Quality Meter

5.8.2 General Procedures

The operation and maintenance procedures for the field equipment to be used during groundwater sampling are provided in Appendix E. General calibration procedures and requirements are described below:

- All instruments will be calibrated at least once a month.
- All instruments will have the calibrations checked at a minimum at the start of each day before measurements are made.
- The calibration and calibration checks will indicate that the sensitivity of the instrument (practical detection limit) is adequate to meet project needs and that the instrument is accurate over the working range.
- All calibration information will be recorded in the field log book. This includes date and time, technician signature, calibration procedure, calibration results, calibration problems, recalibration and maintenance, and instrument serial numbers.
- All calibration standards will be of National Bureau of Standards (NBS) quality and their sources listed and documented so that standards are traceable. In addition, only technicians trained in the use of the field instruments will operate them. If the instrument readings are incorrect at the time of the initial calibration, the instrument will either be calibrated by the technician or returned to the manufacturer for calibration. If

the instrument readings are incorrect after a continuing calibration check, the preceding sample results will be reviewed for validity, and reanalyzed if necessary.

5.8.3 Laboratory Calibration Procedures

All samples shall be analyzed according to the analytical methods attached in Appendix C, and shall follow the procedures described by the methods. All calibration results shall be recorded and kept on file, and will be reviewed and evaluated by the data validator as part of analytical data validation procedures.

Instrument calibration will be checked with a reference standard prior to the analysis of any sample. The standards used for calibrations will be traceable and each calibration will be recorded in the laboratory notebook for the particular analysis. Any printouts, chromatograms, etc., generated for the calibration will be kept on file.

5.8.4 Corrective Actions

Corrective actions are those measures taken to rectify a laboratory or field measurement system that does not comply with this QAPP. The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system are:

1. Identifying and defining the problem.
2. Assigning of responsibility for investigating the problem.
3. Investigating and determining the cause of the problem.
4. Determining a corrective action to eliminate the problem.
5. Assigning and accepting responsibility for implementing the corrective action.
6. Implementing the corrective action and evaluating its effectiveness.
7. Verifying that the corrective action has eliminated the problem.

A nonconformance is defined as an identified or suspected deficiency in an approved document (e.g., technical report, analysis, calculation, computer program); an item where the quality of the end item itself or subsequent activities using the document or item would be affected by the deficiency; or an activity that is not conducted in accordance with the established plans or

procedures. Any staff member engaged in project work who discovers or suspects a nonconformance is responsible for initiating a nonconformance report (see Appendix F). The Laboratory QA/QC Supervisor shall evaluate each nonconformance report and shall provide a disposition, which describes the actions to be taken. The Project Manager shall ensure that no further project work dependent on the nonconforming item or activity is performed until approval is obtained and the nonconformance report is closed out. If the nonconformance is related to material, the Project Manager shall be responsible for marking or identifying, with the nonconformance report number, the nonconforming item (if practical) and indicating that it is nonconforming and is not to be used.

Samples that are analyzed prior to the resolution of a nonconforming event will be resampled if project staff are still in the field, and/or reanalyzed once the corrective action has been demonstrated to be effective.

A copy of each closed nonconformance report shall be included in the quality assurance file. Copies of all nonconformances shall be maintained by the Laboratory QA/QC Supervisor.

5.8.4.1 Field Corrective Actions

At the end of each sampling day, the sampling team shall report any problems requiring corrective action which were encountered during the day. Corrective action will be undertaken when a non-conforming condition is identified. A non-conforming condition occurs when QA objectives for precision, accuracy, completeness, representativeness or comparability are not met, or when procedural practices or other conditions are not acceptable. A report shall be filed which documents the problems encountered and the corrective action implemented. Corrective actions for field test kits and instrumentation involve ordering back up kits to be available. A stop-work order may be issued by the Laboratory QA/QC Supervisor, upon authorization by the Project Manager, if corrective action does not adequately address a problem, or if no resolution can be reached.

5.8.4.2 Laboratory Corrective Actions

If a particular analysis is deemed "out-of control," corrective action will be taken to ensure continued data quality. Actions which may be taken include, but are not limited to:

- Rechecking calculations

- Checking QC data on other samples
- Auditing laboratory procedures
- Reanalyzing the sample if the holding time requirements have not been exceeded
- Accepting data with the acknowledged level of uncertainty
- Discarding data

The coordinator of the laboratory's analytical section will be responsible for initiating laboratory corrective action when necessary. Recommendations for corrective actions outside the laboratory will be made by the Laboratory QA/QC Supervisor to the Project Manager.

6.0 REPORTING

6.1 PILOT TEST REPORT

Upon completion of the Siberia Area pilot test, a report addressing the following topics will be prepared:

- Site history and site conditions
- Discussion of pilot study activities
- Presentation of analytical results
- Conclusions drawn from the interpretation of the data
- Recommendations for additional work (if required)
- Supporting data, including analytical data packages and field log forms

A Pre-Draft report will be submitted to the USACE and WVA for review and comment prior to submittal to regulatory agencies. One set of revisions will be made to the report based on the USACE and WVA comments. The Draft Pilot Test Report will then be submitted to the regulators. The Final report will include one set of revisions based on comments from the regulatory agencies.

6.2 DATA ANALYSIS

Data from the Siberia Area pilot study will be used to estimate reductions in VOC groundwater concentrations in the vicinity of MW-41.

Results of matrix pore water VOC analyses conducted by the University of Waterloo will be evaluated with the following objectives:

1. Estimate the mass and concentration distributions of VOCs with depth;
2. Assess the extent of contaminant migration away from fractures into matrix blocks, and direction of diffusion into or out of the matrix blocks;
3. Compare rock matrix VOC concentrations to groundwater VOC concentrations in the pilot study monitoring wells to isolate fractures and matrix zones that contribute to the observed concentrations in the monitoring wells.

The results of the laboratory and field measurements will be used to decide whether additional oxidant injections are required to complete the destruction of chlorinated VOCs in the vicinity of MW-41.

7.0 REFERENCES

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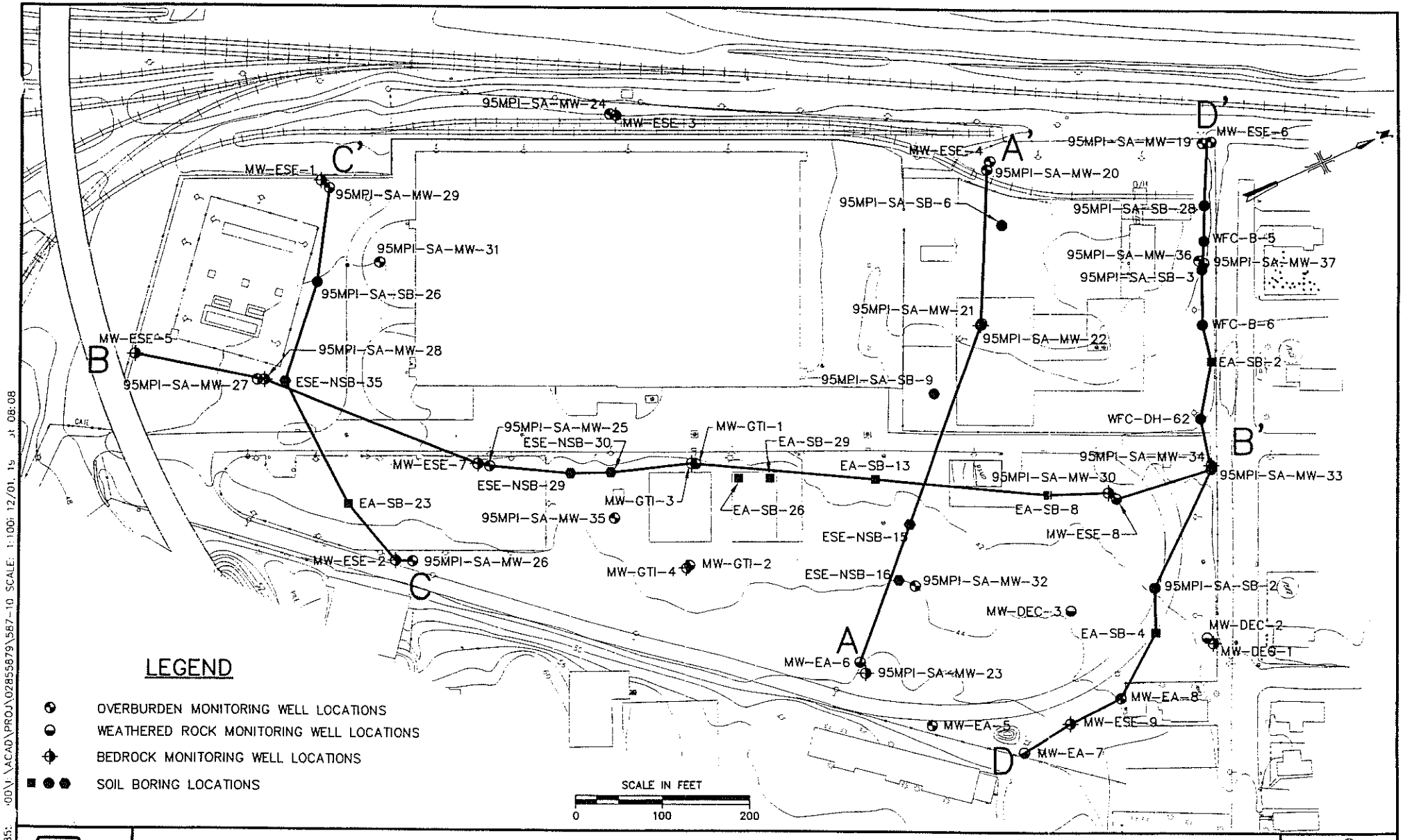
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APPENDIX A

Selected Figures from the RFI Report



US Army Corps of Engineers

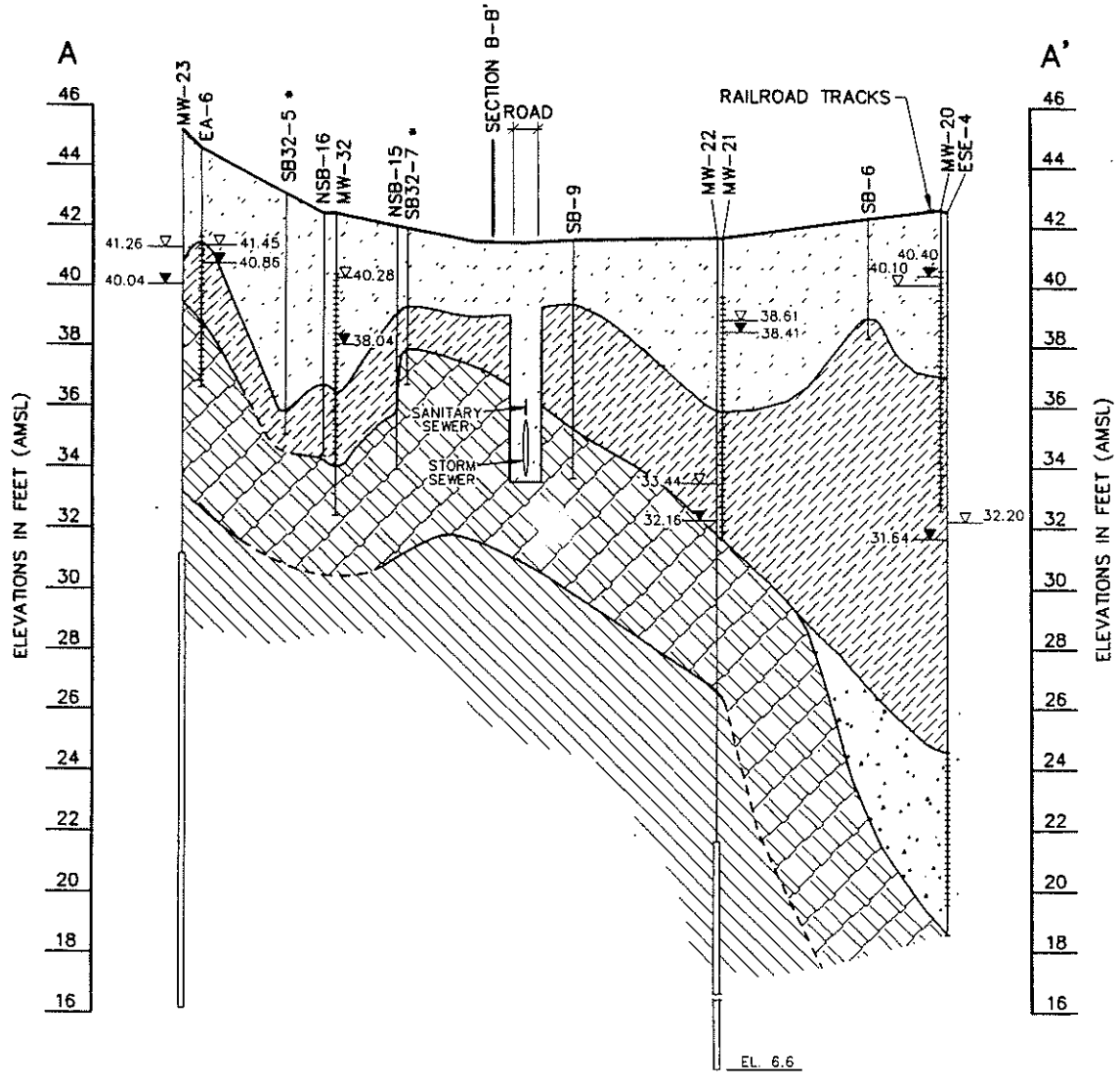
CROSS-SECTION LOCATIONS

WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-2

3705 : 0285: :00\ \ACAD\PROJ\02855879\587-10 SCALE: 1:100: 12/01, 1 at 08:08
XREF: X587-02



SCALE: HORZ. 1"=100'
VERT. 1"=4'

LEGEND

- FILL
- WEATHERED ROCK
- BEDROCK
- CLAYEY SILT
- SAND & GRAVEL
- GROUND SURFACE
- WELL RISER
- SCREENED INTERVAL
- WELL RISER
- OPEN INTERVAL
- * PROJECTED INTO SECTION
- WATER LEVEL ELEVATIONS MEASURED 7-20-95 (ROUND 1 OF GROUNDWATER SAMPLING)
- WATER LEVEL ELEVATIONS MEASURED 4-22-96 (ROUND 2 OF GROUNDWATER SAMPLING)

US Army Corps of Engineers

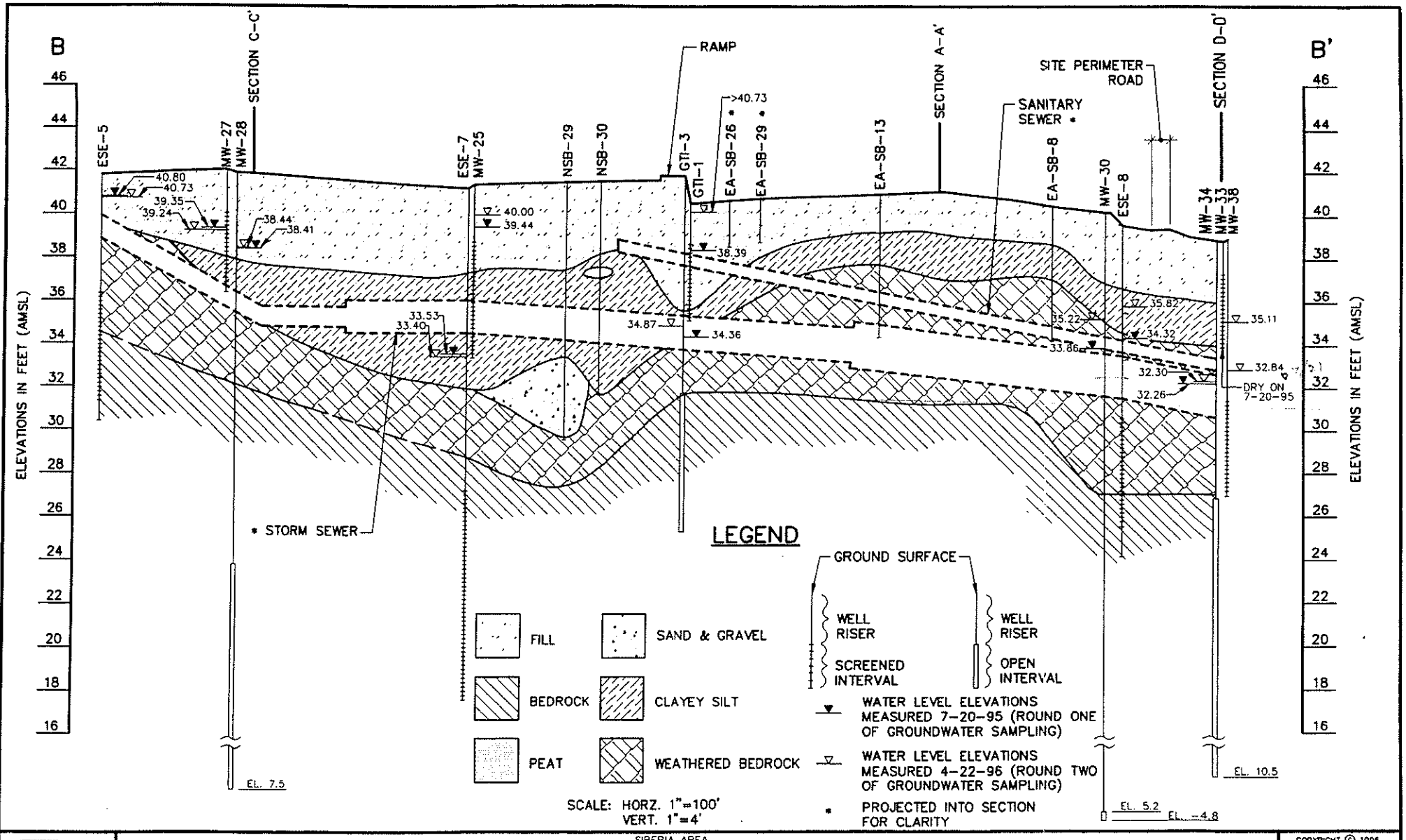
SECTION A-A'
GEOLOGIC CROSS-SECTION

WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-3

N:\ACAD\PROJ\02855919\591-07 SCALE: 1:1 07/17, 1996 5:41



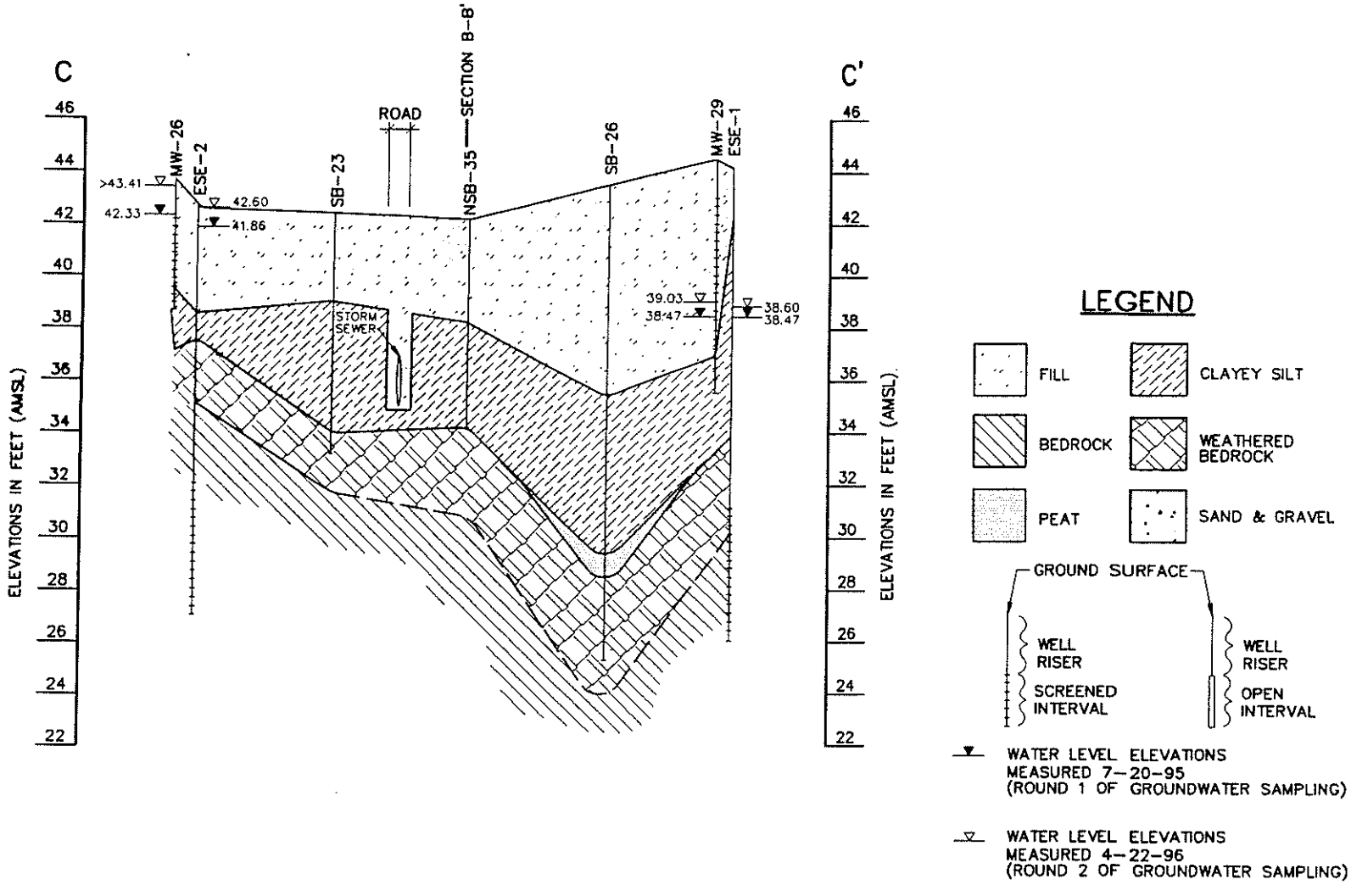
US Army Corps of Engineers

SIBERIA AREA
GEOLOGIC CROSS-SECTION
SECTION B-B'
WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-4

4871 : 02855919\U:\ACAD\PROJ\02855919\591-08 SCALE: 1:1 08/07, 1996 - 4:58



SCALE: HORZ. 1"=100'
VERT. 1"=4'

US Army Corps of Engineers

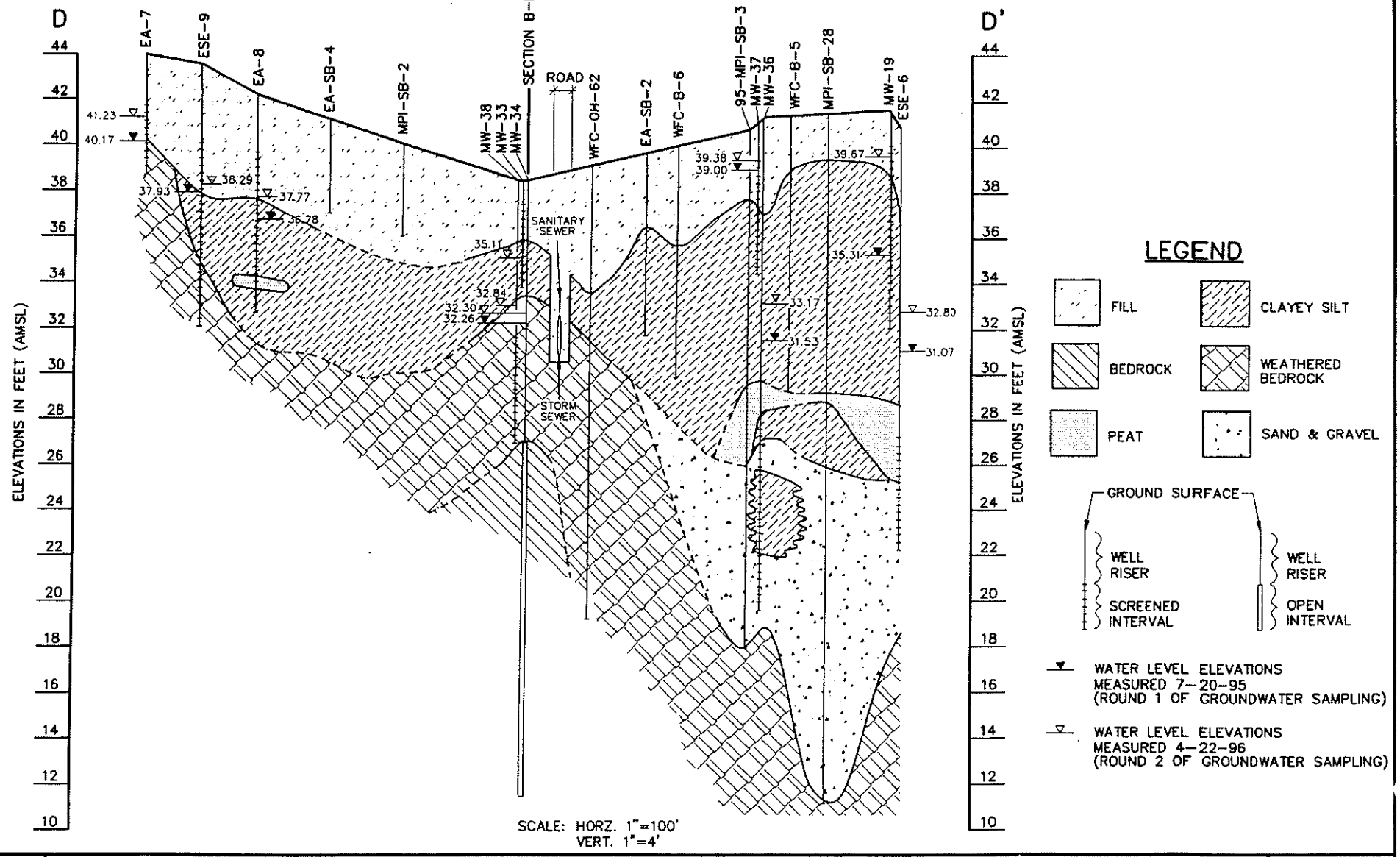
SIBERIA AREA
GEOLOGIC CROSS-SECTION C-C'

WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-5

3705 : 02855 0\I: \ACAD\PROJ\02855879\587-14 SCALE: 1:1 08/05, 1996 16:23



US Army Corps of Engineers

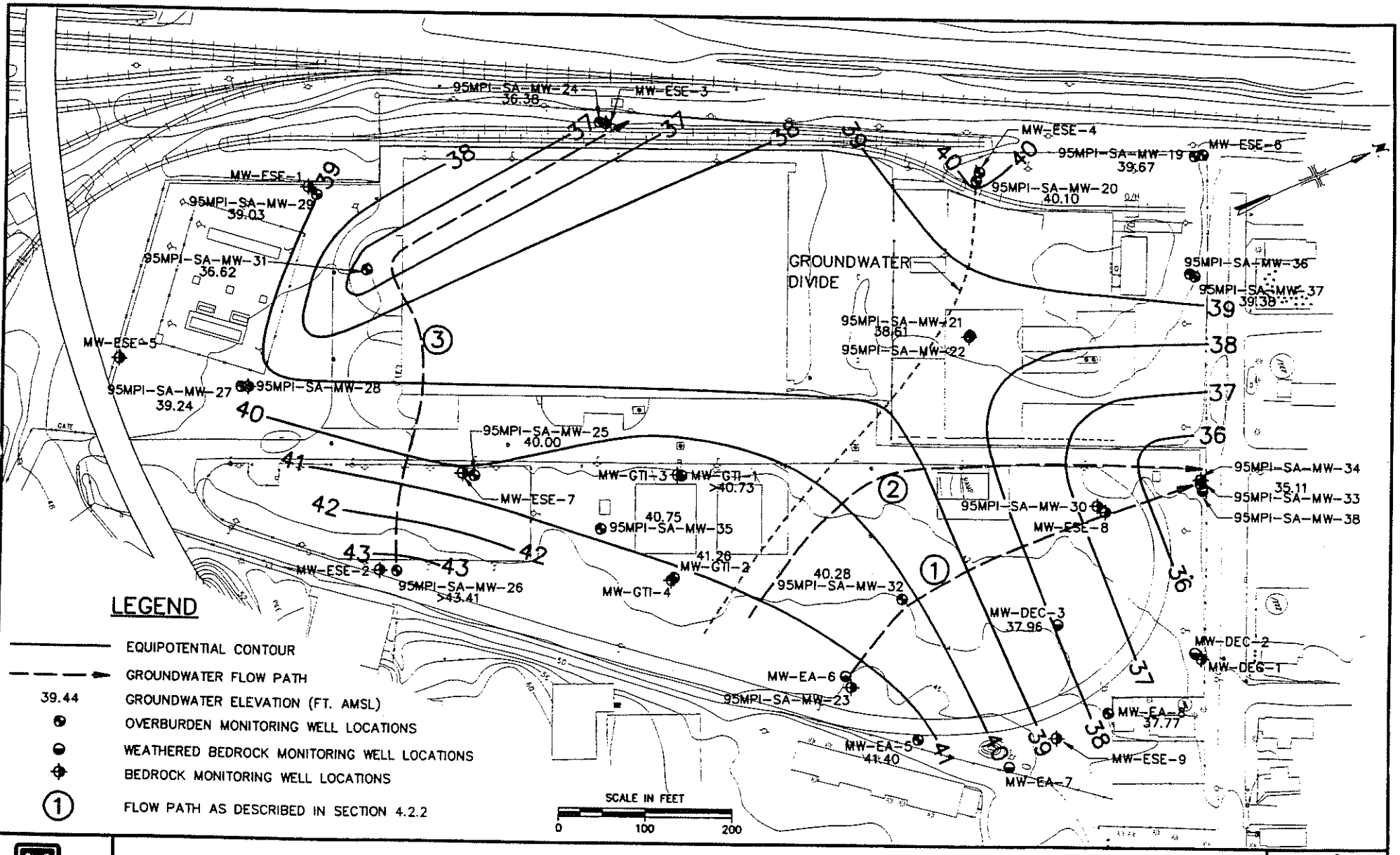
SIBERIA AREA
GEOLOGIC CROSS-SECTION D-D'

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FIGURE 4-6

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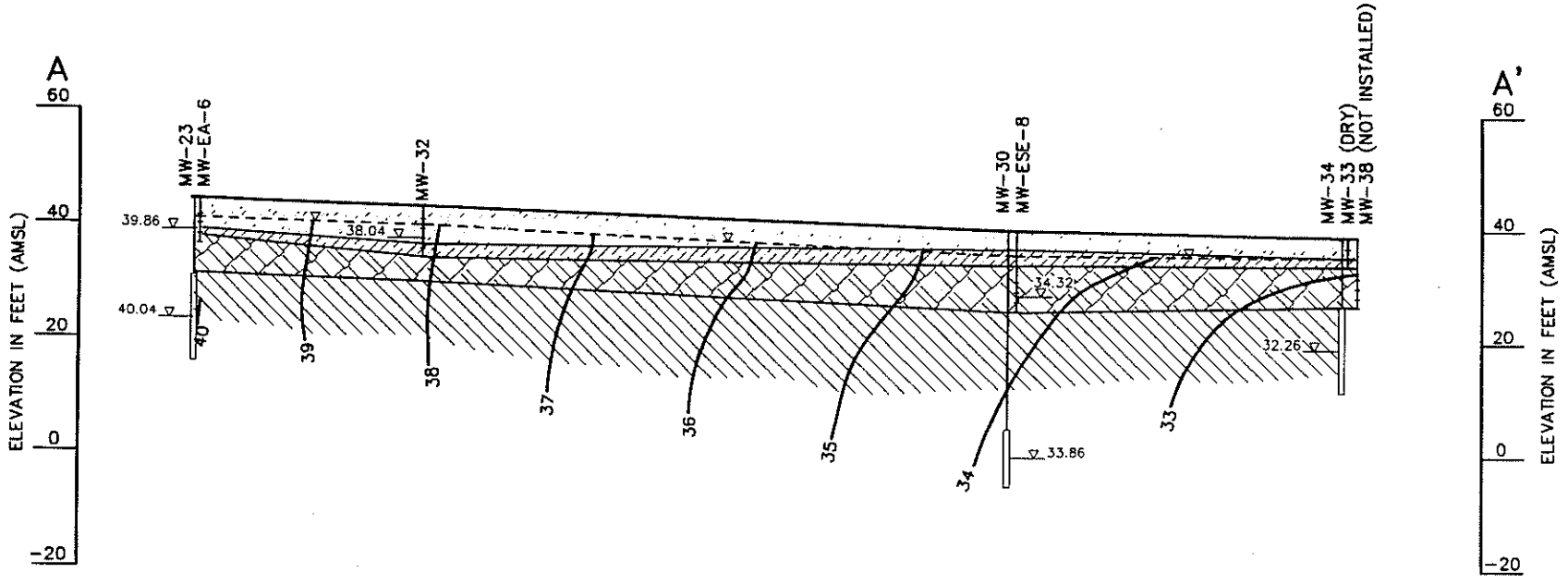


US Army Corps of Engineers

OVERBURDEN POTENTIOMETRIC CONTOUR MAP 4/22/96
SIBERIA AREA
WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-14



LEGEND

FILL
CLAYEY SILT
BEDROCK
WEATHERED BEDROCK

GROUND SURFACE
WELL RISER
SCREENED INTERVAL
WELL RISER
OPEN INTERVAL

32.51 POTENTIOMETRIC HEAD
POTENTIOMETRIC SURFACE
40 EQUIPOTENTIAL CONTOURS

SCALE: HORZ. 1"=50'
VERT. 1"=20'

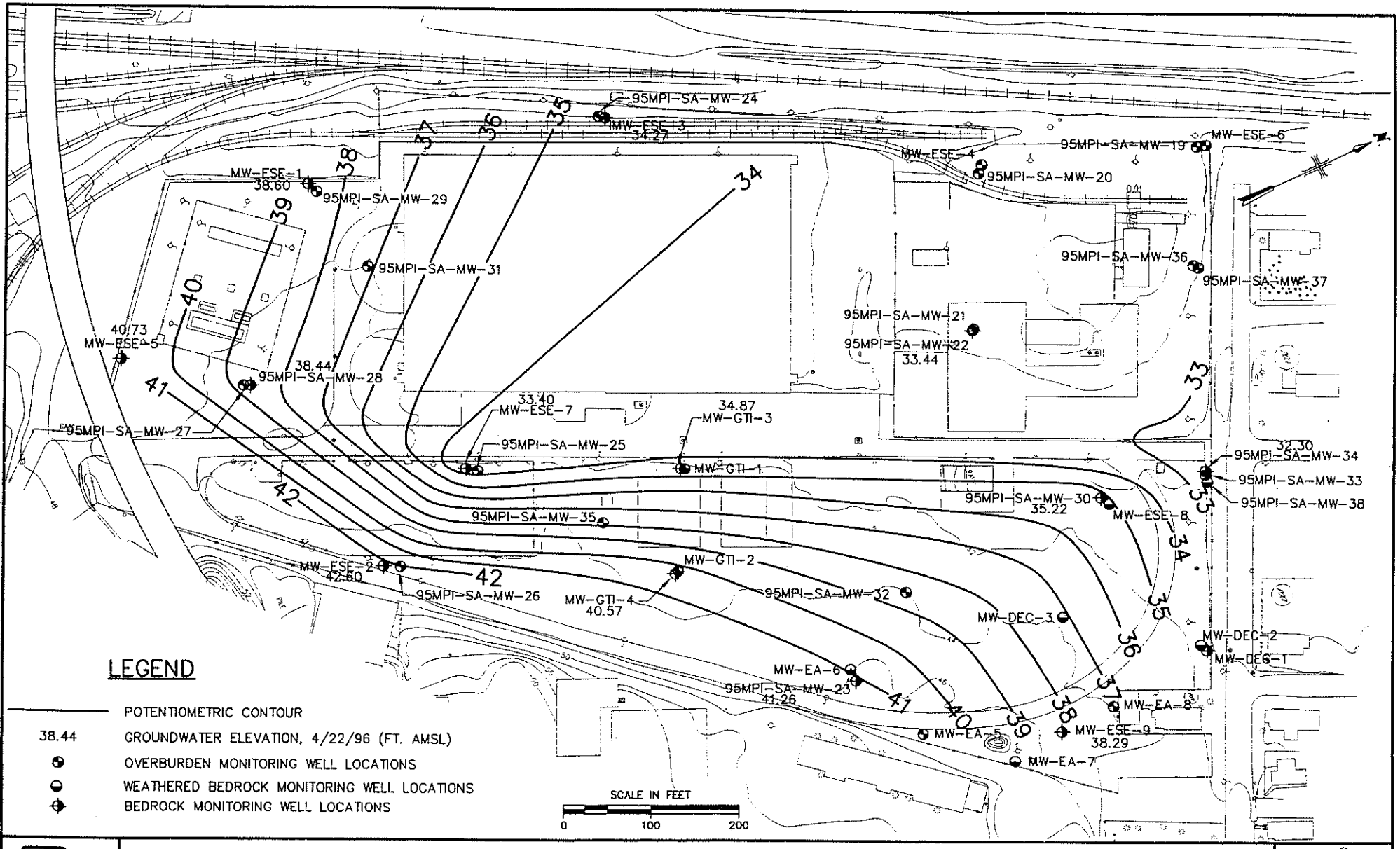
US Army Corps of Engineers

SIBERIA AREA
SCHEMATIC FLOW SECTION A-A', 7/20/96
WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-15

V:\ACAD\PROJ\02855919\591-28 SCALE: 1:1 08/15, 1996 8:10
4871 : 0285



US Army Corps of Engineers

BEDROCK POTENTIOMETRIC CONTOUR MAP 4/22/96
SIBERIA AREA
WATERVLIET ARSENAL
USACE CONTRACT NO. DACA31-94-D-0017

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FIGURE 4-18

4871 : 0285: ...00\c:\ACAD\PROJ\02855879\587-38 SCALE: 1:100i 07/31, 19: 01 15:23

XREF: X587-02

APPENDIX B

Rock Core Sample Collection and Analysis Procedure

PROTOCOL FOR COLLECTING AND ANALYZING ROCK CORE SAMPLES FOR VOLATILE ORGANIC CHEMICAL CONCENTRATIONS AND PHYSICAL PROPERTY MEASUREMENTS

PREPARED FOR MALCOLM PIRNIE, INC.

FOR THE WATERVLIET ARSENAL SITE

WATERVLIET, NEW YORK

Prepared By Beth L. Parker, Ph.D.

September 27, 2001

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FIGURE 2: Schematic Diagram of Rock Crusher

FIGURE 3: Outline of the Rock Core Sampling Procedure

shale, trends in monitoring well data, appropriate frequency of monitoring well sampling, and the nature of solvent fluxes toward receptors. These issues are at the heart of corrective action and long-term monitoring requirements. Hence, there is much potential for improvements and associated cost savings regarding approaches to site characterization at fractured rock sites.

The recommendations and protocols described below were prepared from a literature search for information on such methods used by others, and from previous studies conducted by the University of Waterloo (e.g. Parker and Sterling, 1999; Sterling, 1999) at several sites where chlorinated solvent contamination is present within sedimentary rock environments.

OBJECTIVES AND TECHNICAL APPROACH

The objectives for determining the volatile organic compound (VOC) concentrations in the rock matrix at the Watervliet Arsenal are several fold:

1. Determine the mass and concentration distributions with depth;
2. Determine the phase of contaminant distribution (e.g. magnitude of sorbed mass and likelihood of immiscible phase (DNAPL) persistence in fractures);
3. Assess the extent of contaminant migration away from fractures into matrix blocks, and direction of diffusion into or out of the matrix blocks;
4. Compare discrete level sampling in the rock matrix to discrete level monitoring of isolated zones using the Westbay MP system to isolate fractures and matrix zones that contribute to the observed concentrations in conventional monitoring wells.

The proposed data collection activities will provide the contaminant conditions within the source zones before and after pilot-scale remediation trials using potassium permanganate for in-situ mass destruction in order to assess the degree of success of this technology at the site source zones. In addition, the data will facilitate the overall site conceptual model for groundwater and DNAPL flow and contaminant migration. Determining the nature of

preserved in methanol will be analyzed at the University of Waterloo by direct, on-column injection into a gas chromatograph equipped with an electron capture detector (described later in more detail). Split aliquots of the methanol extract from 5% of the rock core VOC samples will be sent to a commercial, EPA certified laboratory for VOC analysis, using either EPA Method 8260B or 8021B, for laboratory and method comparison purposes. The samples for moisture content/porosity, diffusion coefficient, and matrix permeability will be analyzed by Golder Associates in Mississauga, Ontario.

2.1 THE ROCK CRUSHER

The University of Waterloo has developed a new rock crusher to replace the original manual version used in Sean Sterling's M.Sc. thesis (Sterling, 1999; Parker and Sterling, 1999). Motivation for the development of the new rock crusher was provided by the desire to reduce the difficulty and length of time required to decontaminate the crusher and to improve sample integrity by reducing the potential for losses due to volatilization during the crushing process. The new rock crusher uses the Enerpac™ system, which is a commercial hydraulic press that provides the crushing power necessary to break up the rock samples. The core sample is placed in a stainless steel crushing cell and crushed with a stainless steel piston head using pressures as high as 3000 psi (see Figure 2). The crushed sample is then pushed from the cylinder directly into a 125 mL, wide-mouth jar filled with a known volume of HPLC grade methanol. The amount of air passing by the sample while being crushed is minimized as well as the time required to completely crush the rock fragments into the desired particle size. The weight of the sample added to the sample jar containing the known volume of methanol is determined in the field with a field balance. VOC concentrations are determined on a total mass of VOC per unit mass of wet rock sample (ug/g). These concentrations can be converted to equivalent pore water concentrations by knowing the partitioning of the total mass between the aqueous and sorbed phases. For this calculation values for the following parameters are used: wet and dry bulk densities for the rock, matrix porosity and solid phase organic carbon content.

hydrogeologist are inspecting the core for selecting sample locations based on lithology, presence of fractures, bedding plane partings, and evidence for groundwater and/or DNAPL fluid flow (Figure 1). The hydrogeologist will flag/mark the sections of the core to be subsampled for any of the four following types of samples:

1. VOC analyses
2. Moisture content/porosity
3. Diffusion-based invasion tests/coefficient measurements
4. Matrix permeability/hydraulic conductivity
5. f_{oc}, mineralogy, thin sections

These sample types shall be taken in the order listed above, which is based upon the samples' relative sensitivity to VOC and/or moisture content loss.

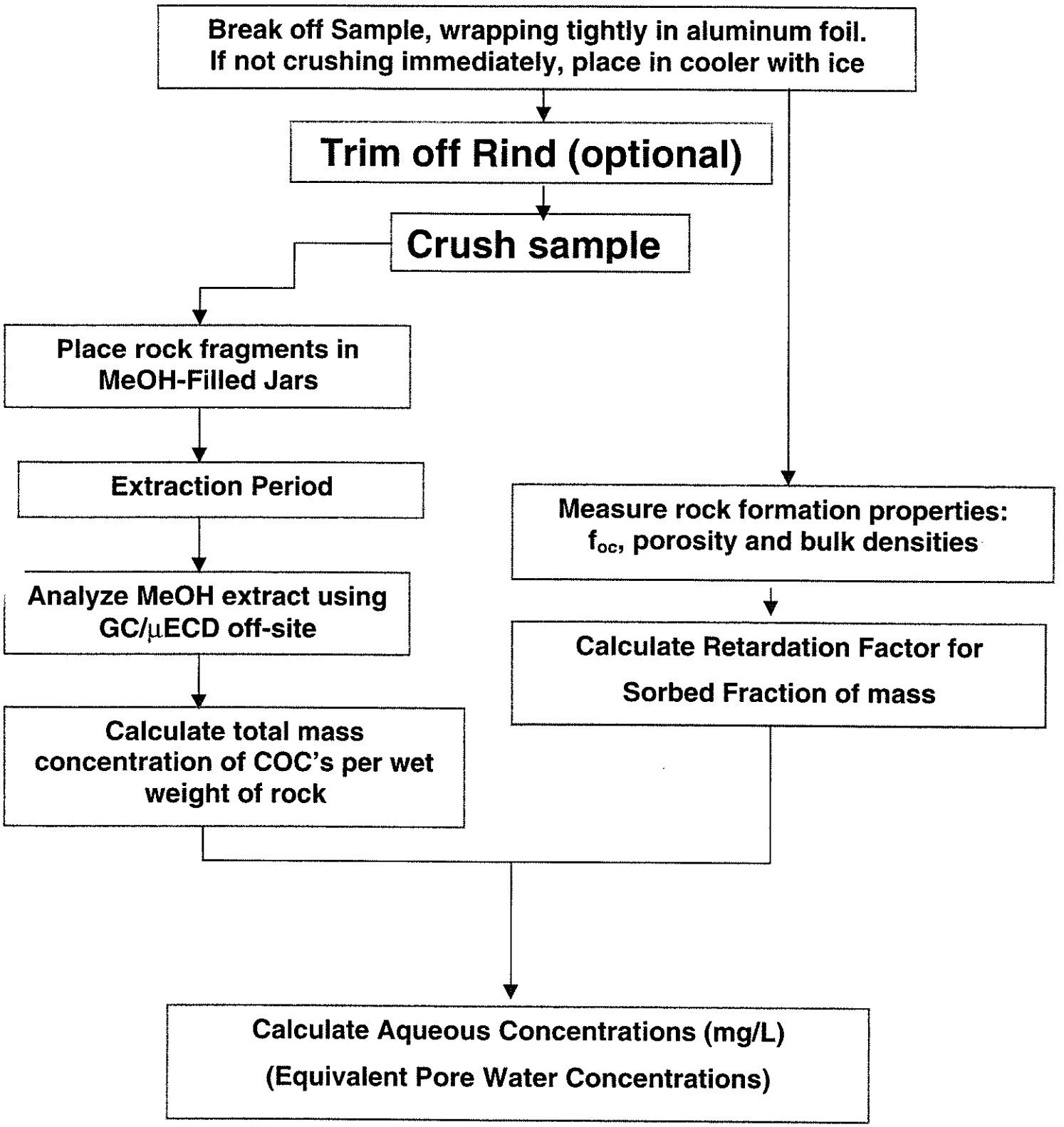
2.2.1 VOC Samples

Subsamples (i.e. core segments approximately 3-inches long) for determining VOC concentrations will be taken from the cores immediately to minimize chemical losses due to volatilization. The initial core logging will be performed to identify key features for subsampling purposes and sections of core will be quickly broken from the core using a chisel and hammer, and then wrapped in aluminum foil for VOC and moisture preservation. After these samples have been collected, the core will be logged in more detail for the full geologic description. Additional sample types will be selected and removed from the core to represent selected lithologies and depths. For future reference, wooden spacers will be placed in the core boxes where core sections have been removed. Each spacer will indicate the sample ID, length and depth of the removed section, the date, and the purpose for which the sample was removed (type of measurement).

There are four criteria for VOC sample selection. First, VOC samples will be taken adjacent to (less than 6 inches away) and 12 to 18 inches away from all identified fractures or partings, both above and below these features. All breaks in core should be suspected as being fractures in-situ, however, emphasis should be made on features with additional lines of evidence for active fluid flow (i.e. secondary mineral coatings/staining,

5. If a field duplicate is planned, the disc length should be doubled to six inches and split lengthwise along the core axis using the chisel to produce two samples of nearly equal size that cover the same depth interval.
6. Completely wrap each sample in a piece of clean aluminum foil with a sample ID to minimize volatilization losses, and place in a cooler containing ice prior to crushing.
7. Place sample in the clean, dry rock crusher and crush sample.
8. Empty crushed sample into sample jar containing a known volume (~60 ml) of HPLC grade methanol, taking extreme care to avoid splashing of methanol out of the jar. These sample jars and lids have been previously labeled and weighed both before and after filling with methanol, and again, immediately prior to their use in the field. There should be a minimum of 100 g of rock in each sample jar.
9. Record sample information (including a description (i.e. lithology pair, duplicate), the sample depth, location relative to any nearby fractures, etc.)
10. Clean rock crusher components, rock hammer, and chisel using the four part decontamination procedure explained in section 2.4.
11. During sample collection, trip blanks, eqiupment blanks and field duplicates will each be collected after every 20 samples (each QA/AC sample type representing 5% of total sample number).
12. Clean outside of sample jar and record total weight. Wrap screw cap lid-jar seam several revolutions with Teflon tape, place sample jar in plastic bag with seal and wrap completely with bubble wrap for shipping. Place in cooler with respective trip blanks (to remain with specific batch of samples throughout shipping, storage and analysis) and keep on ice.
13. Chain of custody (COC) forms will be filled out at the end of each day of sample collection and shipped with each cooler back to the University of Waterloo.
14. Upon receipt of samples at the University of Waterloo, the COC will be signed, each sample will be logged in, re-weighed and shaken on the orbital shaker for 15 minutes, and shaken once per week for every week prior to analysis. Its important that each batch of samples be handled as a unit including respective QA/QC samples (trip blanks, duplicates and equipment blanks).

Figure 3. Schematic of the VOC Subsampling Procedure



Finally, the sample will be completely submerged in slightly warm (liquid) wax (a mixture of 50% beeswax and paraffin is good for pliability and minimum stickiness). Each sample will be clearly labeled with the sample ID, lithology type, core location, depth, and date. Details and a full description of each sample will be recorded in the field notebook.

2.3.2 Diffusion Invasion Test Sample Collection

Cylindrical sections (4-6 inches in intact length at a minimum) of the HQ rock core (full diameter of 2.5 inches/6.35 cm) with several pieces representing from 10 to 20-inches of continuous core section will be collected and preserved in the same manner as the moisture content/porosity samples (see Section 2.3). Approximately fourteen sections will be selected to be representative of the formation lithology and variability along the three core holes in the first field episode. As with the porosity samples, these cores should first be wrapped (two to three times around) with a clean piece of aluminum foil, completely covering the whole core sample. Plastic wrap and tape follow this, and finally the sample is dipped into the beeswax/paraffin mixture and labeled with sample ID, core location, depth interval, measurement type, and date. These samples will also be shipped in a cooler with ice to the University of Waterloo for storage in the refrigerator at 4°C until use in laboratory measurements. A complete description of the core section, core location, depth interval and date collected should be recorded for future reference.

2.3.3 Chloride Diffusion Coefficient and Permeability Sample Collection

Six samples will be selected from existing core stored on-site to represent the bedrock formation over the relevant depth interval. Six to twelve inch lengths of core (full diameter) will be selected, wrapped in aluminum foil and plastic wrap and taped with a label indicating the core location, depth interval, and date of coring and date of sample collection.

fluids will be collected and treated or disposed of in the proper manner by Malcolm Pirnie, Inc.

2.5 FIELD QA/QC

One equipment blank, consisting of HPLC grade methanol rinsed through the rock crusher, will be taken after every 20 samples. Trip blanks equaling 5% of the total sample number or at least one trip blank per batch of samples being stored in a cooler or box will be brought and stored with the methanol-preserved crushed rock samples for later analysis at the University of Waterloo. A trip blank is HPLC grade methanol contained in a 125 mL VOC sample container, is shipped to and from the field, stored with the VOC samples, and unopened untill time for analysis of the methanol aliquot. Duplicate samples will be taken every 20 samples on core sections of double length split along core axis so that the samples are taken from the same depth interval. All QA/QC samples will be identified on the chain of custody forms and tracked throughout the sample handling and analysis process.

3 Laboratory Methods

The University of Waterloo will conduct the majority of the analyses. Duplicate analyses of the methanol extract will be performed on 5% of the rock VOC samples and internal standards by a commercial, EPA certified laboratory for method and laboratory comparison purposes. Chloride diffusion coefficient, matrix permeability, porosity and fraction of solid phase organic carbon measurements on six rock core samples will be performed by Golder Associates (Mississauga, ON).

3.1 SAMPLE ANALYSES METHODS

3.1.1 VOC Sample Extraction

Methanol extraction is expected to remove the sorbed as well as the dissolved phase contaminants from the matrix and prevent loss of these volatile constituents from the sample container during the extraction time period required.

previous contract laboratory (Table 2). These improved detection limits in methanol have been converted to equivalent pore water concentrations for those compounds studied in our method development. The GC specifications for the new methanol direct on-column injection technique are summarized below:

- GC: HP 6890 with autosampler
- Column: HP-1 30m, 0.32mm ID, 4μm stationary phase
- Injection: 1μL liquid, cold on-column
- Carrier gas: Helium
- Detector: μ–ECD
- Analysis turnaround time: 17 minutes

Table 3. A Comparison of Old and New Method Detection Limits (MDL)

Analyte	New Method MDL (µg/L): On-column injection (µg/L MeOH)	Old Method MDL (µg/L pentane):	New MDLEquiv. GW Conc. (µg/L)*
1,1 DCE	7	35.0	0.41
t-DCE	5.5	75.0	0.43
c-DCE	3.5	50.0	0.34
TCE	0.07	2.0	0.27
PCE	0.07	1.0	0.12

***Note:** $\rho_{b\ wet}$=2.45 g/cm^3 ; ϕ_m=12.86%; $R_{1\text{-}1\text{-}DCE}$=2.2; $R_{t\text{-}DCE}$=2.1; $R_{c\text{-}DCE}$=2.6; R_{TCE}=3.3; R_{PCE}=7.6 and assuming 40 cm^3 of rock in 60 mL of MeOH.

3.1.3 Moisture Content/Porosity Measurements

The preserved samples will be placed in a cold storage room (4°C) until ready for gravimetric determinations. The samples will be unwrapped, placed on a pre-weighed aluminum weighing tray, and weighed. The sampled will then be oven-dried at 105°C for four days, allowed to cool to room temperature in a desiccator, and a final weight determined. The volume of the sample will be determined by submerging the oven-dried sample (completely sealed using a latex membrane of negligible volume) in a container of fluid (water) and measuring its displacement volume. This allows calculation of sample porosity, moisture content, and wet and dry bulk densities. These data, along with the VOC analyses, will be used for calculating matrix pore water concentrations.

3.1.4 Matrix Diffusion Coefficient, Porosity, and Permeability Measurements

Six samples selected from existing stores of rock core from the site shall be sent to the Golder Associates laboratory in Mississauga, Ontario. Measurements of matrix porosity, chloride diffusion coefficient and related tortuosity factor, permeability and fraction of organic carbon content will be measured on each sample.

3.2 LABORATORY QA/QC

A minimum of five percent of all methanol preserved subsamples will have aliquots of the methanol extract removed after the samples have been allowed to fully extract. These

Sterling, S.N. 1999. Comparison of Discrete Depth Sampling Using Rock Core and a Removable Multilevel System in a TCE Contaminated Fractured Sandstone. M.Sc. Thesis, Department of Earth Sciences, University of Waterloo, 108 pp.

U.S. Environmental Protection Agency (EPA). 1996. Test methods for evaluation solid waste, physical/chemical methods. *SW-846, Final Update III*, Revision 2. Method 8021B, Aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors.

C:\MyDocuments\Watervliet\SOP Rock VOC.doc

APPENDIX C

Laboratory Standard Operating Procedures (SOPs)

METHOD SUMMARY

Title: Sample Collection, Pretreatment and Storage

SOP #: 4005
Reference:
Effective Date: February, 1996 **Revision Date:** August, 1998

1. Scope and Application

This procedure is used most often by Customer Service personnel. It provides test-specific guidelines on the size and type of collection bottle required, the addition of preservatives, sample storage conditions, and initial steps in sample preparation.

2. Summary of Method

SAMPLE COLLECTION AND PRESERVATION

WATER SAMPLES - INORGANICS

Test	Bottle Size	Bottle Type	Storage	Preservation
Acidity	50 mL	plastic	N/A	N/A
BOD	500 mL	plastic	4°C or Freeze	N/A
COD	50 mL	plastic	4°C	Sulphuric acid
Cyanide	250 mL	plastic	N/A	Na Hydroxide
Fluoride	50 mL	plastic	N/A	N/A
Mercury	125 mL	glass	N/A	K Dichromate/ Nitric acid
Sulphide	125 mL	glass	N/A	Zn Acetate
TKN	50 mL	plastic	4°C	Sulphuric Acid
Total Phosphorous	50 mL	plastic	4°C	Sulphuric Acid
Total Solids	500 mL	plastic	4°C	N/A
Surfactants	100 mL	plastic	4°C	N/A
Tannin & Lignin	50 mL	plastic	4°C	N/A

WATER SAMPLES - ORGANICS

All samples submitted for organic analysis should be collected in duplicate with zero headspace.

Test	Bottle Size	Bottle Type	Bottle Cap	Storage	Preservation
TPH (GC-FID)	125 mL	Amber glass	Teflon Liner	4°C	N/A
TPH (GC/MS)	40 mL	Amber glass	Teflon Septa	4°C	N/A
Oil & Grease	125 mL	Amber glass	Teflon Liner	4°C	N/A

METHOD SUMMARY

WATER SAMPLES - ORGANICS (Continued)

All samples submitted for organic analysis should be collected in duplicate with zero headspace.

Test	Bottle Size	Bottle Type	Bottle Cap	Storage	Preservation
PAH	1 Litre	Amber glass	Teflon Liner	4°C	N/A
PCB	1 Litre	Amber glass	Teflon Liner	4°C	N/A
THM	40 mL	Amber glass	Teflon Septa	4°C	N/A
THM Chlorinated Water	40 mL	Amber glass	Teflon Septa	4°C	Na Thiosulphate
Volatiles	40 mL	Amber glass	Teflon Septa	4°C	N/A

SOIL SAMPLES

Test	Size	Type	Bottle Cap	Storage	Preparation
Metals	125 mL	glass	Unlined Plastic	4°C	Air-dry & Sieve < 1mm
Mercury	125 mL	glass	Unlined Plastic	4°C	Air-dry & Sieve < 1mm
PCB	125 mL	glass	Unlined Plastic	4°C	N/A
PAH	125 mL	glass	Unlined Plastic	4°C	N/A
TPH	125 mL	glass	Unlined Plastic	4°C	N/A
Oil & Grease	125 mL	glass	Unlined Plastic	4°C	N/A
Total Carbon (TOC)	250 mL	glass	Unlined Plastic	4°C	Air-dry & Sieve < 1mm
Particle Size	125 mL	glass	Unlined Plastic	4°C	Aliquot (250mL Jars)

INITIAL SAMPLE PREPARATION

ICP-MS METALS

Test/Aliquots	Tube Size	Tube Type	Tube Cap	Storage	Preparation
ICP-MS Metals	50 mL	Plastic	N/A	N/A	Add Nitric Acid
ICP-MS Metals	12 mL	Centrifuge	red	N/A	Add Nitric Acid

RCAP

Submit sample in a 250 mL plastic bottle and a 50 mL plastic tube; mix surface water thoroughly prior to aliquoting.

Test/Aliquots	Tube Size	Tube Type	Tube Cap	Storage	Preparation	Duplicates
Colour	12 mL	Centrifuge	purple	4°C	Centrifuge as required	1 in 14 (min)
DOC	12 mL	Centrifuge	yellow	4°C	Centrifuge as required	1 in 14 (min)
pH/Conductivity	12 mL	Round Bottom	parafilm	4°C	Parafilm tightly	1 in 14 (min)
ICP-ORS Metals	12 mL	Centrifuge	green	N/A	Add Nitric Acid	1 in 14 (min)
Turbidity	Ground water samples must be allowed to settle for 1 hour minimum prior to decanting for					

METHOD SUMMARY

Title: Major Metals in Aqueous Samples by ICP-OES

SOP #: 3120
Reference: USEPA Method #200.7
Effective Date: August 1995 **Revision Date:** July, 1997

1. Scope and Application

This method is applicable to a variety of metals in drinking, surface, seawater, domestic and industrial waste waters. The LOQs are as follows:

Analyte	LOQ (mg/L)
Sodium	0.1
Potassium	0.1
Calcium	0.1
Magnesium	0.1
Iron	0.02
Manganese	0.01
Copper	0.01
Zinc	0.01
Phosphorus	0.1

2. Summary of Method

In direct aspiration optical emission spectroscopy, a sample is aspirated and atomized in an argon plasma. The atomized sample is then ionized causing the individual ions to emit characteristic wavelegths upon returning to stable conditions. The wavelengths emitted are split via a polychrometer and the focused signals are measured using a charged coupled segmented array detector. The raw signals are converted to concentrations by comparison to the emission strengths of calibration standards.

3. Quality Assurance

Quality control effort includes the analysis of certified reference materials, method spikes, matrix spikes, duplicates and method blanks. A minimum QC effort of 10% is maintained.

METHOD SUMMARY

Title: Analysis of Alkalinity in Water/Seawater

SOP #: 2010/2015
Reference: USEPA Method #310.2
Effective Date: October, 1993 **Revision Date:** July, 1997

1. Scope and Application:

This method is applicable to the determination of alkalinity in surface, ground or sea water, as well as industrial wastes. The samples must be free of turbidity and high colour, as only clear samples can be analyzed. Samples with suspended or particulate matter that can be centrifuged or filtered out are acceptable. The limit of quantitation is 1 mg/L as $CaCO_3$.

2. Summary:

Using a Centrifugal analyzer (Cobas/Fara or Hitachi 911), samples are combined with a methyl orange reagent. Methyl orange is used as an indicator because its pH range is the same as the equivalence point for total alkalinity. The methyl orange has been mixed with a weak buffer to maintain a pH of 3.1, just below the equivalence point. Any alkalinity due to the sample when mixed with the methyl orange will cause a decrease in color which is measured at 550 nm.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Sulphate in Water/Seawater

SOP #: 4060/4065
Reference: USEPA Method #375.4
Effective Date: October, 1993 **Revision Date:** July, 1997

1. Scope and Application:

This method is applicable to drinking and surface waters,domestic and industrial wastes. The limit of quantitation is 2 mg/L.

2. Summary:

Sulfate ion is precipitated under controlled conditions in a hydrochloric acid (HCl) medium with barium chloride so as to form barium sulfate crystals of uniform size. Light dispersion caused by the crystal $BaSO_4$ suspension is measured by the spectrophotometric function of the Cobas/Fara or Hitachi 911 as absorbance and compared against calibration standards.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Chloride in Water/Seawater

SOP #: 2040/2045
Reference: USEPA Method #325.1
Effective Date: October, 1993 **Revision Date:** July, 1997

1. Scope and Application:

This method can be applied to natural waters and wastewaters with a chloride content in the range of 1.0 to 500 mg/l. Higher concentrations can be brought within this range by proper dilution.

2. Summary:

This method is based on the displacement of thiocyanate ion from mercuric thiocyanate by chloride ion and the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the coloured ferric thiocyanate complex. This complex is proportional to the original chloride concentration and is measured at 480 nm using an automated colorimeter (Cobas/Fara or Hitachi 911).

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Reactive Silica in Water/Seawater

SOP #: 2180
Reference: USEPA Method # 370.1
Effective Date: September, 1995 **Revision Date:** July, 1997

1. Scope and Application

This method is applicable to surface waters, ground waters, precipitation samples, saline waters, domestic and industrial waste waters. Some difficulty is encountered with samples that are highly colored or contain turbidity which cannot be removed by filtration. The LOQ for this procedure is 0.5 mg/L as SiO_2.

2. Summary of Method

A centrifugal analyzer system (Cobas/Fara or Hitachi 911) is used for automated reagent handling. The automated colorimetric method is based on the reduction of molybdosilicic acid to molybdenum blue by ascorbic acid. Silica combines with ammonium molybdate under acidic conditions to form a complex known as molybdosilicic acid. The molybdosilicic acid is reduced by ascorbic acid to form a blue complex "Molybdenum Blue". The absorbance of this compound at 660 nm is directly proportional to the silica concentration.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Nitrate + Nitrite in Water/Seawater

SOP #: 2110/2115
Reference: USEPA Method #353.1
Effective Date: January, 1994 **Revision Date:** July, 1997

1. Scope and Application

This method is applicable to surface waters, ground waters, precipitation samples, saline waters, domestic and industrial waste waters. Some difficulty is encountered with samples that are highly colored or contain turbidity which cannot be removed by filtration. The LOQ for this procedure is 0.05 mg/L NOx as N.

2. Summary of Method

Using a centrifugal analyzer system (Cobas Fara or Hitachi 911), the nitrate in an aqueous sample is reduced to nitrite using hydrazine sulfate. The nitrite ions then react with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthyl-ethlenediamine dihydrochloride to form an azo dye which is read at 520 nm. The absorbance at this wavelength is directly proportional to the NOx concentration.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Nitrite in Water/Seawater

SOP #: 2120
Reference: USEPA Method #354.1
Effective Date: August, 1995 **Revision Date:** July, 1997

1. Scope and Application

This method is applicable to surface waters, ground waters, precipitation samples, saline waters, domestic and industrial waste waters. Some difficulty is encountered with samples that are highly colored or contain turbidity which cannot be removed by filtration. The LOQ for this procedure is 0.01 mg/L NO_2 as N.

2. Summary of Method

Using the Cobas Fara centrifugal analyzer system, the nitrite ions react with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthyl-ethlenediamine dihydrochloride to form an azo dye which is read at 540 nm.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

METHOD SUMMARY

Title: Analysis of Ammonia in Water/Seawater

SOP #: 2100/2105
Reference: USEPA Method #350.1
Effective Date: February, 1993 **Revision Date:** July, 1997

1. Scope and Application:

This method is applicable to surface waters, ground waters and saline waters. Industrial and sewage wastewaters can be analyzed as long as after filtration they are free of turbidity and are not highly colored. The limit of quantitation is 0.05 mg/L as N.

2. Summary of Method

Using a centrifugal analyzer (Cobas/Fara or Hitachi 911), samples are mixed with EDTA to remove interferences. Alkaline phenol and sodium hypochlorite are added to react with ammonia to form indophenol blue. The concentration of the blue color is proportional to ammonia concentration and is measured at 630 nm.

3. Quality Assurance

Reagent blanks, internal reference materials, and method spikes are analyzed in the same manner as mentioned above for the samples. Spiking of samples at a level appropriate to the matrix is performed at a frequency of 10%. Duplicate samples are also analyzed at a frequency of 10 %.

mL glass vials with open-top screw cap with Teflon-lined septa. The samples are obtained after the system has purged three water volumes. Afterwards, a vial is completely filled leaving an inverted meniscus on top, avoiding headspace, and promptly capping, to avoid VOC volatilization. If the flow rate is too slow, and the porosity is too low, samples are taken using a 50-mL or 60-mL plastic syringe with an attached 3-way valve. Samples are taken in duplicates

12.0 Preservation

For CSIA, the concentration of the compounds of interest in the sample must be known. Therefore, samples need refrigeration and preservation. In addition, the samples should be collected with no headspace. At the time of sampling, it is recommended to add 0.2 mL of sodium Azide (for preservation). The samples should be kept at 4 °C until analysis (ideally for no more than 14 days).

13.0 Sample Analysis Procedure

When a sample arrives in the lab the relevant data should be recorded. These data should include the sample name, arrival date, arrival time, and sample identification (see Chain of Custody above). A minimum of 25 mL of water must be provided in order to ensure that all quality objectives can be met and that samples can be re-analyzed should the need arise.

When a sample is to be run, open vial and introduce a small headspace if direct SPME is used or a larger headspace (10% of vial volume) if headspace SPME is used. Add a magnetic stirring bar. In case of headspace SPME, stir for 15 min at 1100 rpm before starting the SPME extraction. Prepare a duplicate sample for one out of five samples.

13.1. Analysis of standards and samples

1. start the instrument according to general start-up section
2. place vials on magnetic stirrer at 1100 rpm
3. retract fiber in needle, retract needle completely in fiber holder
4. place fiber holder on top of vial. Move needle out of fiber holder by turning inner part of fiber holder (metal) while holding outer part (black), until septum is penetrated
5. Move fiber out of needle. Adjust needle such that the fiber does not contact the aqueous phase (headspace SPME)
6. Two minutes before finishing the extraction, make injector ready for injection by pressing **prep run**
7. after the extraction period is over, retract fiber into needle and remove fiber holder from vial
8. adjust needle position to 4 by turning inner part of fiber holder

9. insert needle into injector and immediately move fiber out of needle
10. star GC run
11. leave fiber in injector for 15 min
12. verify that all peaks of interest are completely separated by examining the 2/1 trace, which should show a typical S-shape caused by earlier elution of compounds with ^{13}C compared to compounds with ^{12}C. The S-shape curve should be bordered by a horizontal line on both sides

13.2. Sequence of analysis of samples and standards

1. Analyze two separate standard vials. The measured $\delta^{13}C$ of compounds should agree with the calibrated values within 0.5 ‰.
2. Analyze samples
3. Analyze a duplicate for every fifth sample. The duplicate should be injected at least 5 injections before or after the corresponding sample run

Since the fiber is completely re-usable, it does not have a duty cycle. A fiber is replaced when deemed appropriate by the analyst.

14.0 Data Collection

When the chromatographic run is completed, the results can be viewed by selecting "View...Results" and selecting the appropriate detector channel.

15.0 Data Analysis and Calculations

The GC-C-IRMS instrument contains an internal program that records the data, and calculates the isotope ratio for each run. Each compound has a characteristic retention time in the column, and this in turn is related to the appearance of the peak in the chromatograph. The peak for each compound is identified by comparing the retention time with that of the compound in the standard.

The height and area of the peak are related to the concentration of the compound in te sample. The system calculates the isotopic composition of each one of the compounds in the sample, and gives the carbon isotope ratio for each one of them.

16.0 Data and Records Management

All chromatograms are stored electronically with a specific format. The files are kept in subdirectories named after the project with a filename such as 37P12001.chr, where 37P is a field code corresponding to the well ID, 12 corresponds to the depth interval of the piezometer, and 001 refers to the run number of that particular sample. The subdirectories (folders) are identified by codes like: JQ21L01, where JQ are the initials of the person running the analysis, and 21L01 is the date (21 July 2001). The files can then

be found easily if the analysis date and file numbers are recorded. All electronic files are to be stored on removable media and archived daily. Any loose sample log sheets will be bound in a notebook or binder after the completion of a project or phase of work. Any anomalous observations, maintenance, or experiments will be detailed in the bound GC lab notebook.

17.0 Quality Control

The GC is calibrated every morning before samples are analyzed. A linearity test test is performed every morning to ensure that system is stable. The standard deviation of the 2/1 ratio of 10 consecutive reference gas pulses has to be smaller than $1.0*10^{-7}$. The deviation between the lowest and highest values should be less than $5.0*10^{-6}$. The standard deviation and the deviation between the lowest and the highest values are recorded in the instrument log book.

Every day, after starting up the instrument, the background intensity of the mass-44 ion beam is determined. At a GC oven temperature of 50°C, the intensity should be less than $5.0*10^{-9}$. The date of determination, type of GC column, oven temperature, and background intensity are recorded in the instrument log book.

The SPME fiber normally does not exhibit carryover when the fiber conditioner is used. However, carryover will be assessed by periodically analyzing fiber blanks as part of the QC set.

A blank containing organic-free nanowater is analyzed following the same procedure as the samples, daily, and prior to start analyzing samples. The 44-ion trace should remain below $1.0*10^{-10}$ during the entire run, except during the injection of the reference gas. If the acceptance criterion is met, "blank test passed" is recorded in the instrument log book; otherwise, "blank test failed" is recorded.

Standard solutions containing reference compounds with known carbon isotope ratios (external standards) are analyzed twice before starting to analyze the samples, and once after each 6 sample injections thereafter. The measured $\delta^{13}C$ value should deviate less than 0.5‰ from the calibrated value. The measured and the calibrated values of $\delta^{13}C$ for the standard solution are reported in the reference compound log book.

A duplicate is analyzed for every fifth sample (with a separation of at least five injections between this analysis and that of the sample). The deviation of $\delta^{13}C$ values between samples and duplicates should be less than 0.5‰. The $\delta^{13}C$ of samples and duplicates are recorded on the data sheet.

All $^{13}C/^{12}C$ ratios are reported in the usual delta notation ($\delta^{13}C$) referenced to the Vienna Peedee Belemnite (VPDB) standard. The $\delta^{13}C$ value is defined as $\delta^{13}C = 1000(R_s/R_r - 1)$, where R_s and R_r are the $^{13}C/^{12}C$ ratios of the sample and the international standard, respectively.

MONITORING IN SITU OXIDATION OF TCE BY PERMANGANATE USING CARBON ISOTOPES

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Laboratory and field studies have shown that oxidation of chlorinated ethenes by permanganate is potentially an effective method to destroy chlorinated ethenes present as dense non-aqueous liquid (DNAPL) in aquifers (Nelson et al., 2001; Schnarr et al., 1998). When implementing the permanganate method, monitoring tools are required to verify that the permanganate solution has come in contact with chlorinated ethenes and destruction of chlorinated ethenes occurs. Concentrations of chlorinated ethenes and Cl^- have been used as monitoring parameters. However, concentrations of chlorinated ethenes can decrease due to displacement of contaminated water by the injected permanganate solution rather than oxidation of chlorinated ethenes or concentrations may remain elevated even though destruction occurs due to continuous dissolution of chlorinated ethenes. While Cl^- concentrations may initially be a sensitive monitoring parameter, after a large amount of Cl^- has accumulated, interpretation of Cl^- data can become ambiguous since concentration changes may be due to the movement of fluids with different Cl^- levels induced by permanganate injection and density gradients.

Aim of the study was to evaluate if carbon isotopes can be used as a complementary tool to assess in situ destruction of chlorinated ethenes. Laboratory studies with dissolved chlorinated ethenes were performed to quantify the magnitude of isotope fractionation associated with oxidation of trichloroethene (TCE). Furthermore, the isotope method was tested at a field site with TCE present as DNAPL, which was treated by permanganate injection.

The laboratory study revealed that during oxidation of TCE by permanganate, large shifts in the $^{13}C/^{12}C$ ratios of TCE occur, which are due to differences in reaction rates between molecules with ^{13}C and ^{12}C, respectively. Shifts of the carbon isotope ratio ($\delta^{13}C$) from an initial value of –29.4‰ to values >+100‰ were observed after more than 99% of TCE had been oxidized. At the field site, permanganate was injected at several locations in consecutive episodes and samples for concentration and stable isotope analyses were taken from multi-level bundle samplers situated within 2 meters of the permanganate injection points and at the fringe of the source area. A strong enrichment of ^{13}C was observed at locations close to where permanganate had been injected with $\delta^{13}C$ values of up to 38.6‰, providing evidence that the TCE had been hit and oxidative destruction occurred. These results demonstrate that carbon isotope ratios can serve as a sensitive tool to assess in situ destruction of chlorinated ethenes by permanganate.

References:

Nelson, M.D., Parker, B.L., Al, T.A., Cherry, J.A. and Loomer, D., 2001. Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by $KMnO_4$ in a sandy aquifer. Environ. Sci. Technol., 35: 1266-1275.

Schnarr, M., Truax, C., Farquhar, G., Hood, E., Gonullu, T. and Strickney, B. 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichoroethylene and perchloroethylene DNAPLs in porous media. J. Contam. Hydrol., 29: 205-224.

Environ. Sci. Technol. 2000, 34, 2839–2844

Determination of Compound-Specific Carbon Isotope Ratios of Chlorinated Methanes, Ethanes, and Ethenes in Aqueous Samples

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Compound-specific carbon isotope ratio analysis is a promising tool to assess the origin and fate of organic contaminants in groundwater. The aim of this study was to develop and evaluate a reliable, fast method to determine carbon isotope ratios of chlorinated methanes, ethanes, and ethenes in aqueous samples. Direct solid-phase microextraction (dSPME) and headspace solid-phase microextraction (hSPME) were selected as extraction method and compared to headspace equilibration. For dSPME and hSPME, deviations between carbon isotope ratios in the aqueous phase and on the SPME fiber were ≤ 0.40‰. For headspace equilibration, molecules in the gas phase were enriched in ^{13}C compared to molecules in the aqueous phase by up to 1.46‰, in particular for chlorinated methanes. The absence of significant carbon isotope fractionation during dSPME and hSPME could be explained by the fact that both the aqueous phase and the SPME fiber coating discriminate against molecules with ^{13}C to a similar degree, and thus no net carbon isotope fractionation occurs. If aqueous phase/gas-phase carbon isotope fractionation during headspace equilibration is taken into account, all methods, dSPME, hSPME, and headspace equilibration, provide accurate $\delta^{13}C$ values with a similar precision. Direct SPME was the most sensitive method with detection limits as low as 130 ppb.

Introduction

Contamination of groundwater with chlorinated solvents is a common environmental problem due to the toxicity and persistence of these compounds (*1*). Recently, the use of compound-specific stable isotope ratios was proposed as a tool to investigate the behavior and fate of chlorinated solvents in the subsurface (*2*). Isotope ratios may be used to demonstrate intrinsic biodegradation of chlorinated solvents (*3*–*7*) or abiotic transformation of chlorinated solvents by reactive barriers (*8*). These applications are based on the fact that a kinetic isotope effect may occur during biotic or abiotic transformation of organic compounds. As a result, the remaining fraction of the compound becomes enriched in heavy isotopes, while the product is depleted in heavy isotopes. In the absence of biodegradation, isotope ratios analyses may help to distinguish between different events or sources of contamination (*2*). The aim of this study was to develop and evaluate a method to determine compound-specific carbon isotope ratios of chlorinated solvents and dechlorination products in aqueous samples.

A variety of techniques to extract organic compounds from the aqueous phase have been developed, among them headspace equilibration, solid-phase microextraction (SPME), solid-phase extraction, liquid–liquid extraction, and purge-and-trap. In this study, SPME was chosen as extraction method, since SPME is a solvent free, fast, and sensitive method. The SPME method involves exposing a fused silica fiber coated with a polymeric phase to the aqueous sample (*9*, *10*). The fiber can either be directly immersed into the aqueous phase of the sample (direct SPME) or placed in the headspace above the sample (headspace SPME). In this study, direct SPME is abbreviated as dSPME and headspace SPME as hSPME, while SPME refers to the SPME method in general. Compared to dSPME, the hSPME method has the advantage that extraction of nonvolatile compounds, which may disturb the chromatographic resolution of target compounds, can be minimized. The hSPME method has a similar sensitivity for concentration analyses of volatile hydrocarbons as purge-and-trap methods (*11*). Therefore, SPME was expected to be a very sensitive method for isotope analyses of chlorinated solvents in aqueous samples. The SPME method was compared to headspace equilibration (*12*), a method that was previously evaluated by Slater et al. (*13*) for carbon isotope analysis of trichloroethene (TCE). In contrast to techniques that involve solvents, SPME and headspace techniques can be used to analyze isotope ratios of compounds with low boiling points such as dichloromethane.

The extraction methods investigated in this study, dSPME, hSPME, and headspace equilibration, rely on phase transfer processes which may lead to differences in the isotope ratios of a compound in different phases (isotope fractionation). To be able to determine carbon isotope ratios accurately, the degree of isotope fractionation during partitioning of a compound between the involved phases has to be known. Dias and Freeman (*14*) investigated carbon isotope fractionation during aqueous phase/SPME fiber partitioning of various non-chlorinated hydrocarbons. They found that hydrophobic compounds extracted by a nonpolar fiber were slightly enriched in ^{13}C (≤0.5‰), while organic acids extracted by a polar fiber were depleted in ^{13}C (≤1.5‰). Isotope fractionation was attributed to mass-dependent energy shifts during partitioning of the organic compound between the aqueous phase and the SPME fiber coating. Harris et al. (*15*) used a hSPME method for carbon isotope analysis of gasoline range hydrocarbons in oils. They found a nonsystematic ^{13}C depletion or enrichment in the extracted compounds compared to results from a purge-and-trap method. Carbon isotope fractionation during headspace equilibration of toluene and trichloroethene (TCE) was investigated by Slater et al. (*13*), and differences in carbon isotope ratios between molecules in the aqueous phase and the headspace were found to be ≤0.5‰.

In this study, the precision, accuracy, and sensitivity of compound-specific carbon isotope analysis was investigated for nine chlorinated methanes, ethanes, and ethenes. The selected compounds are among the most frequently detected organic contaminants in groundwater (*16*). The compounds were extracted by dSPME, hSPME, and headspace equilibration from aqueous solutions and measured using a gas chromatography combustion isotope-ratio mass spectrometry (GC-C-IRMS) system. To determine the accuracy of the methods, carbon isotope fractionation during dSPME, hSPME, and headspace equilibration was evaluated. The occurrence of carbon isotope fractionation during dSPME and hSPME

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TABLE 1. List of Compounds

compound	abbreviation	mixture	purity (%)	manufacturer
vinyl chloride	VC	A	99.5[a]	Fluka, Buchs, Switzerland
trans-1,2-dichloroethene	tDCE	A	98[a]	Aldrich, Milwaukee, U.S.A.
cis-1,2-dichloroethene	cDCE	A	97[a]	Aldrich, Milwaukee, U.S.A.
trichloroethene	TCE	A	99.7[b]	Dow, Midland, U.S.A.
tetrachloroethene	PCE	A	99.8[b]	Dow, Midland, U.S.A.
dichloromethane	DCM	B	99.9[a]	EM Science, Gibbstown, U.S.A.
chloroform	CF	B	99.8[a]	Aldrich, Milwaukee, U.S.A.
carbon tetrachloride	CT	A	99.9[a]	Fisher, Fair Lawn, U.S.A.
1,2-dichloroethane	1,2-DCA	B	99.8[a]	Aldrich, Milwaukee, U.S.A.

[a] Specified by manufacturer. [b] Determined by GC-FID.

depends on the magnitude of mass dependent effects in the aqueous phase and the SPME fiber coating. The headspace studies provide information on isotope effects associated with the aqueous phase. To evaluate isotope effects during interaction of the compounds with the SPME fiber coating, gas phase/SPME fiber partitioning experiments were performed. Furthermore, aqueous phase/SPME fiber partition coefficients were determined, and the effect of salt addition on the SPME and headspace extraction efficiency was investigated to allow for comparison of the sensitivities of the SPME and headspace methods.

Material and Methods

Analytical System. Compound-specific carbon isotope ratios were determined in the Environmental Isotope Laboratory of the University of Waterloo using a GC-C-IRMS system. The GC-C-IRMS system consisted of a Agilent 6890 GC (Agilent, Palo Alto, U.S.A.) with a split/splitless injector, a Micromass combustion interface operated at 850 °C, a cold trap cooled to −100 °C using liquid nitrogen, and a Micromass Isochrom isotope-ratio mass spectrometer (Micromass, Manchester, U.K.). The GC was equipped with a DB-VRX column (60 m × 0.25 mm, 1 μm stationary phase, J&W Scientific, Folsom, U.S.A.). The following oven temperature program was used: 50 °C for 2 min, 12 °C/min to 100 °C, 20 °C/min to 220 °C, 220 °C for 2 min, and the injector was set at 270 °C. The isotope-ratio mass spectrometer was operated at a trap current of 400 μM to optimize for linearity. A higher trap current would lead to an increase in sensitivity of the instrument, however, at the expense of stability and precision. For all experiments, injection sizes were selected such as to obtain peak heights between 1.0 and 5.0 V. Within this peak size range, the linearity of the system was better than 0.14‰. The lower limit of peak sizes corresponded to a minimal amount of 1.5 nmol carbon (C) on the GC column.

For SPME injections, a narrow bore SPME sleeve was installed (Supelco, Bellefonte, PA). During SPME injections, the split vent was closed for 1 min. All SPME extractions were performed using 100 μM poly(dimethylsiloxane) (PDMS) fibers (Supelco). For gas injections, the injector was equipped with a split/splitless sleeve (Restec, Bellefonte, U.S.A.). A split ratio of 10:1 was chosen to maximize the sensitivity of the headspace method. All $^{13}C/^{12}C$ ratios are reported in the usual delta notation ($\delta^{13}C$) referenced to the VPDB (Vienna Peedee Belemnite) standard (*17*). The $\delta^{13}C$ value is defined as $\delta^{13}C = (R_s/R_r - 1) \times 1000$, where R_s and R_r are the $^{13}C/^{12}C$ ratios of the sample and the international standard, respectively.

Determination of Carbon Isotope Ratios of Pure Phase Chlorinated Methanes, Ethanes, and Ethenes. The $\delta^{13}C$ of the pure phase compounds used in this study (Table 1) were determined using (i) a CE Instruments elemental analyzer (CE Instruments, Rodano, Italy) coupled to a Micromass Isochrom isotope-ratio mass spectrometer (EA-IRMS) and (ii) the GC-C-IRMS instrument described above. For both systems, carbon isotope ratios of target compounds were determined relative to external CO_2 reference gas (*18*). In addition, various amounts of reference CH_4 with a known $\delta^{13}C$ (−43.04‰) was injected similarly as the target compounds. In case of EA-IRMS, 3−5 μL of pure phase compounds or 0.5 mL of vinyl chloride (VC) was injected onto the combustion tube of the elemental analyzer (EA) using a syringe injection port attached to the EA. The values of target compounds were normalized and linearity corrected against the reference CH_4, which led to adjustments of the $\delta^{13}C$ values between 0.10 and 0.23‰.

When using the second system (GC-C-IRMS), two mixtures of chlorinated methanes, ethanes, and ethenes (A and B) were prepared that contained the compounds at equimolar ratios with respect to carbon (Table 1). Aliquots of the mixtures were injected into 500 mL glass bottles that had been flushed with helium for 5 min and closed with an open screw cap containing a Teflon lined silica septum. Vinyl chloride gas was added using a Hamilton gastight locking syringe (Hamilton, Reno, U.S.A.). The final concentrations of each compound in the glass bottles were 15 and 60 μM C per compound, respectively. After allowing at least 30 min for evaporation of the compounds added as liquid phase, gas samples of 1 mL volume from the glass bottles were injected into the split/splitless injection port of the GC using a gastight locking syringe. Since the value of reference CH_4 determined by GC-C-IRMS (−43.08 ± 0.07‰, n = 9) corresponded well to its calibrated value (−43.04‰) and the instrument exhibited good linearity, the $\delta^{13}C$ value obtained relative to external CO_2 were not corrected. The mean $\delta^{13}C$ values are reported with the corresponding 95% confidence intervals, which were obtained by multiplying the standard uncertainties with a coverage factor based on the t-distribution (*19*).

Determination of Partition Coefficients. In contrast to aqueous phase/gas phase partition coefficients (Table 2), the aqueous phase/SPME fiber partition coefficients are not documented for all of the compounds used in this study. Since the detection limits of the SPME method depends on the aqueous phase/SPME fiber partition coefficients, they were determined. Partition coefficients are defined by

$$K_{yx} = \frac{C_y}{C_x} \quad (1)$$

where C_x and C_y are the concentration of the compound in phase x and y, respectively (w = aqueous phase, g = gas phase, f = SPME fiber coating). To determine aqueous phase/SPME fiber partition coefficients (K_{fw}), aqueous solutions were prepared by injecting aliquots of pure phase mixtures A and B, respectively, through a Teflon lined septum into bottles containing organic free distilled water and a magnetic stirrer. The solutions contained 10, 50, and 150 μM C of each compound. After at least 3 h of mixing, the solutions were transferred into 17 mL glass vials with open screw caps and Teflon lined septa. Prior to dSPME extraction, 0.8 mL of

TABLE 2. Dimensionless Partition Coefficients at 25 °C for Aqueous Phase/Gas Phase Partitioning (K_{gw}), Aqueous Phase/SPME Fiber Partitioning (K_{fw}), and Octanol/Aqueous Phase Partitioning (K_{ow})[e]

compd	aqueous/gas K_{gw}	aqueous/SPME fiber K_{fw}	aqueous/octanol K_{ow}	aqueous/gas K_{gw}^{NaCl}/K_{gw}	aqueous/SPME fiber K_{fw}^{NaCl}/K_{fw}
VC	1.080[a]	50	4[b]	4.6	nd[d]
tDCE	0.377[a]	95	123[c]	5.1	5.1
cDCE	0.154[a]	72		5.1	5.5
TCE	0.386[a]	380	263[b]	5.7	2.1
PCE	0.716[a]	1630	759[b]	4.1	1.0
DCM	0.087[a]	23	14[b]	4.8	3.8
CF	0.147[a]	84	85[b]	5.9	5.3
CT	1.230[a]	760	537[b]	4.5	1.4
1,2-DCA	0.044[b]	36	30[b]	4.6	4.9

[a] Reference *34*. [b] Reference *35*. [c] Reference *36*. [d] nd, not determined. [e] Increase of partition coefficients by adding 5 M NaCl to aqueous phase. Aqueous phase/SPME fiber partition coefficients were determined using 100 μm poly(dimethylsiloxane) SPME fibers.

solution was removed to avoid contact of the needle holding the SPME fiber with the aqueous phase and a 14 mm magnetic stir bar was added. Three standards of each concentration level were extracted for 20 min by immersing the fiber into the aqueous phase. The peaks were recorded with a FID detector and peak areas were calculated. Using the peak areas and response factors, the amount of each compound on the fiber was calculated. Based on the amount of each compound on the SPME fiber and the concentration in the aqueous phase, K_{fw} values were obtained (*10*). The standard uncertainty of K_{fw} was calculated based on standard uncertainties of peak areas and response factors (*19*). The average relative standard uncertainty was 14%.

Evaluation of Carbon Isotope Fractionation during SPME and Headspace Equilibration. ***Analysis of Aqueous Standards by dSPME and hSPME.*** Aqueous standards were prepared using two mixtures of chlorinated methanes, ethanes, and ethenes (Table 1). The concentrations in the aqueous standards were chosen such that 1.5 or 6 nmol C of each compound was on the fiber after extraction. The required concentrations in the aqueous phase were calculated based on partition coefficients, volume of standards, and volume of the fiber coating (*10*). To prepare aqueous standards, aliquots of the pure phase mixtures were injected into 125 mL glass bottles containing organic free distilled water. The solutions were stirred for at least 3 h. For dSPME studies, glass vials were completely filled with the prepared solutions. The volume of the vials (17 mL) was chosen such that only a small amount of each compound (≤6%) was extracted, which maximizes the sensitivity of the method (*20*). Before analysis, 0.8 mL of solution was removed, and a 14 mm long Teflon-coated magnetic stir bar was added. For hSPME studies, 30 mL of solution was transferred into a 42 mL vial containing a 21 mm Teflon-coated magnetic stir bar. Vinyl chloride was added as gas phase to the headspace. The vials were vigorously shaken by hand for 2 min and then placed on a lateral shaker (120 rpm) for at least 2 h.

To determine whether the duration of extraction influences $\delta^{13}C$ values, tests were conducted with extraction times of 10, 20, and 30 min. Peak areas and $\delta^{13}C$ values for different extraction times were similar within the range of analytical uncertainty. For all further experiments, an extraction time of 20 min was used. The required extraction time may vary depending on the stirring rate, and in the case of hSPME, it also depends on the headspace volume and the shape of the vial (*20*). Three measurements were made for standards of each concentration level using separate vials. Additional standards were prepared for dSPME in a 5 M NaCl solution using similar amounts of the compounds as for the lower concentration level of the standards described above. The effect of NaCl on the partition coefficients was quantified based on peak areas of standards with and without NaCl.

Analysis of Aqueous Standards by Headspace Equilibration. For headspace equilibration studies, aqueous standards were prepared similarly as for SPME studies. Aqueous phase concentrations were chosen such that similar equilibrium concentrations of each compound in the headspace (15 or 60 μM C) were obtained. The concentrations corresponded to approximately 1.5 or 6 nmol C per compound on the GC column when 1 mL was injected at a split ratio of 10:1. To prepare aqueous standards, aliquots of the pure phase mixtures were injected into bottles containing organic free distilled water. The pure phase mixtures contained the same compounds as for the SPME experiments but at different ratios taking into account differences in partition coefficients. After 3 h of stirring, a headspace was introduced into bottles by replacing 20 mL of the aqueous phase by 99.995% helium. The bottles were shaken vigorously by hand for 2 min and then placed on a lateral shaker (120rpm) for at least 2 h in a water bath set to 25 °C. Headspace gas samples of 1 mL were injected into the GC using a locking gastight syringe. Three separate bottles were analyzed for each concentration level. Additional standards were prepared for headspace equilibration in a 5 M NaCl solution using similar amounts of the compounds as for the lower concentration level of the standards described above. The effect of NaCl on the partition coefficients was quantified based on peak areas of standards with and without NaCl.

Evaluation of Carbon Isotope Fractionation during SPME of Gaseous Standards. To investigate carbon isotope fractionation during partitioning of the compounds into the fiber coating, gas-phase standards were prepared using pure phase mixtures. The pure phase mixtures contained the compounds in ratios such that a similar amount of each compound was extracted. The compound ratios in the pure phase mixtures were calculated based on the gas phase/SPME fiber partition coefficients, which were estimated using the following equation (*10*)

$$K_{fg} = \frac{K_{fw}}{K_{gw}} \tag{2}$$

where K_{fw} is the aqueous phase/SPME fiber partition coefficient and K_{gw} is the aqueous phase/gas phase partition coefficient. Gas-phase standards were prepared by injecting aliquots of the pure phase mixtures and gaseous VC into 500 mL glass bottles, which had been flushed with helium for 5 min and closed with an open screw cap containing a Teflon-lined septum. After allowing at least 30 min for evaporation of the compounds added as liquid phase, the SPME fiber was exposed to the gas phase for 20 min.

Calculation of Fractionation Factors. Isotope fractionation during phase transfer processes can be expressed using the enrichment factor ϵ, which corresponds approximately to the difference between the isotope ratios of a compound in phase y and x (*21*)

$$\epsilon_{yx} \approx \Delta\delta^{13}C_{yx} = \delta^{13}C_y - \delta^{13}C_x \tag{3}$$

where $\delta^{13}C_y$ and $\delta^{13}C_x$ are the equilibrium isotope ratios of a compound in phase y and x, respectively.

For two-phase systems, the following equation is obtained that relates ϵ_{yx} to the initial $\delta^{13}C$ value of the added compound and the measured $\delta^{13}C$ of compound in phase y

$$\epsilon_{yx} \approx \delta^{13}C_y - \delta^{13}C_x = \frac{\delta^{13}C_y - \delta^{13}C_o}{r_x} = \frac{\Delta\delta^{13}C_{yo}}{r_x} \tag{4}$$

where $\delta^{13}C_o$ is the initial isotope ratio of the added compound and f_x is the fraction of compound in phase x.

For hSPME (w = aqueous phase, f = SPME fiber coating, g = gas phase), the enrichment factor can be calculated using the following equation

$$\epsilon^*_{fw} \approx \delta^{13}C_f - \delta^{13}C_w = \frac{\delta^{13}C_f - \delta^{13}C_o}{f_w} + \frac{f_g(\delta^{13}C_g - \delta^{13}C_f)}{f_w} = \frac{\Delta\delta^{13}C_{fo}}{f_w} + \frac{f_g\epsilon_{gf}}{f_w} \quad (5)$$

where f_g and f_w are the fractions of compound in the gas phase and aqueous phase, respectively.

The enrichment factors were calculated based on the GC-C-IRMS $\delta^{13}C$ values of the compounds, which were considered to represent $\delta^{13}C_o$, and the average $\delta^{13}C$ of all measurements in each experiment. All ϵ_{yx} and ϵ^*_{fw} values are reported with the corresponding 95% confidence intervals, which were obtained by multiplying the standard uncertainties with a coverage factor based on the t-distribution (*19*). The standard uncertainties were calculated based on the standard uncertainties of the measured $\delta^{13}C$ values using the law of propagation of uncertainty. In this study, vials with larger volumes than required for practical applications were chosen to maximize f_x. Larger f_x lead to larger $\Delta\delta^{13}C_{yo}$ (eq 4) and thus make it possible to detect enrichment factors ϵ_{yx} with smaller values for a given standard uncertainty of $\delta^{13}C_o$ and $\delta^{13}C_y$.

If the isotopic enrichment factors are known, the original isotope ratio of compounds in samples that have been analyzed using dSPME and headspace equilibration can be calculated with the following equation

$$\delta^{13}C_o = \delta^{13}C_y - \epsilon_{yx}f_x \quad (6)$$

In case of hSPME, the following equation is valid

$$\delta^{13}C_o = \delta^{13}C_f - f_w\epsilon^*_{fw} + f_g\epsilon_{gf} \quad (7)$$

Results

SPME Partition Coefficients and Effect of Salt. The calculated K_{fw} values are listed in Table 2. For chlorinated ethenes and methanes, the values are higher the more chlorinated the compounds are. Chlorinated ethenes have higher K_{fw} values than chlorinated methanes with a corresponding number of chlorine atoms. Compounds with high octanol/water partition coefficients (K_{ow}) have high K_{fw} values (Table 2) as previously observed (*20*).

For compounds having a SPME partition coefficient (K_{fw}) below 300, addition of 5 M NaCl leads to an increase of the partition coefficient by a factor of 3.8–5.5, while for compounds having a K_{fw} larger than 300 little or no increase is observed (Table 2). For headspace equilibration, the increase of the partition coefficient is in the same range (4.1–5.9) for all compounds.

Stable Carbon Isotope Ratios of Pure Phase Chlorinated Methanes, Ethanes, and Ethenes. The $\delta^{13}C$ values determined by EA-IRMS and GC-C-IRMS are similar within the range of analytical uncertainty (Table 3). This indicates that split injection into the GC, which is used in the headspace experiments, does not cause significant carbon isotope fractionation. The standard uncertainties are slightly smaller for EA-IRMS than for GC-C-IRMS measurements, which reflects the larger number of handling steps and higher complexity of the GC-C-IRMS system.

Carbon Isotope Fractionation during SPME. Enrichment factors between compounds in the aqueous phase and on the SPME fiber were calculated for dSPME (ϵ_{fw}) and hSPME (ϵ^*_{fw}), respectively, using eqs 4 and 5, respectively. The enrichment factors are not significantly different from zero and within the range of analytical uncertainty, for all compounds except PCE and CT (Table 4). Extraction of PCE and CT by hSPME is accompanied by a detectable but small carbon isotope fractionation. Addition of 5 M NaCl does not lead to a significant change of carbon isotope fractionation during dSPME (Table 4). Enrichment factors ϵ_{gf} for extraction of gas standards by SPME were quantified using eq 4. Molecules in the gas phase are enriched in ^{13}C compared to molecules on the SPME fiber. The largest carbon isotope fractionation occurs for chlorinated methanes.

TABLE 3. Stable Carbon Isotope Ratios of Chlorinated Methanes, Ethanes, and Ethenes Determined Using an Elemental Analyzer Coupled to an Isotope-Ratio Mass Spectrometer (EA-IRMS) and a Gas Chromatograph Coupled to an Isotope-Ratio Mass Spectrometer (GC-C-IRMS)

compound	EA-IRMS $\delta^{13}C$ (‰ VPDB) $n = 4$	GC-C-IRMS $\delta^{13}C$ (‰ VPDB) $n = 6$
VC	−28.62 ± 0.14	−28.62 ± 0.31
tDCE	−22.23 ± 0.16	−22.44 ± 0.18
cDCE	−23.23 ± 0.11	−23.33 ± 0.07
TCE	−29.48 ± 0.08	−29.39 ± 0.20
PCE	−27.27 ± 0.08	−27.20 ± 0.24
DCM	−53.59 ± 0.10	−53.53 ± 0.14
CF	−63.62 ± 0.14	−63.43 ± 0.22
CT	−32.48 ± 0.22	−32.34 ± 0.15
1,2-DCA	−30.73 ± 0.02	−30.63 ± 0.25

Carbon Isotope Fractionation during Headspace Equilibration. Enrichment factors for aqueous phase/gas-phase partitioning (ϵ_{gw}) were calculated using eq 4. For all compounds, molecules in the gas phase are enriched in ^{13}C compared to molecules in the aqueous phase (Table 4). The magnitude of isotope fractionation is larger for chlorinated methanes than for chlorinated ethanes and ethenes. It does not significantly depend on the degree of chlorination within a compound class. In standards with NaCl, ϵ_{gw} is slightly smaller for most of the compounds than in standards without salt (Table 4); however, the differences are within the range of uncertainty for most compounds.

Detection Limit. The minimum detection limit of the SPME method is lower than that of the headspace method for all compounds except VC (Table 5). Addition of salt (salting out) leads to lower detection limits. For dSPME, salting out has a particularly large effect on compounds with a low K_{fw} and thus a high detection limit. By adding 5 M NaCl, a dSPME detection limit <1 ppm can be reached for all compounds except DCM. The reported detection limits are specific to the GC-C-IRMS system used in this study which requires a minimum of 1.5 nmol C on the GC column. For other GC-C-IRMS systems, the detection limits would differ depending upon the amount of carbon required.

Discussion

Our findings demonstrate that extraction of chlorinated methanes, ethanes, and ethenes by dSPME and hSPME is generally not accompanied by significant carbon isotope fractionation. In contrast, detectable isotope fractionation was observed during headspace equilibration, in particular for chlorinated methanes. This indicates that carbon isotope effects occur during interaction of the compounds with water molecules. The absence of significant isotope fractionation during extraction of aqueous standards by dSPME and hSPME suggests that in case of SPME, isotope effects in the aqueous phase are compensated with isotope effects in the fiber coating. This conclusion is consistent with the observation that enrichment factors for gas phase/aqueous phase and gas phase/SPME fiber partitioning have a similar magnitude

TABLE 4. Carbon Isotope Fractionation during Analysis of Aqueous Standards by Direct SPME (dSPME), Headspace SPME (hSPME), and Headspace Equilibration[a]

	dSPME ϵ_{fw}		hSPME ϵ^*_{fw}	headspace equilibration ϵ_{gw}		SPME of gas standards ϵ_{gf}
	dist water	5 M NaCl	dist water	dist water	5 M NaCl	
VC	nd[b]	nd[b]	−0.01 ± 0.14	0.33 ± 0.20	0.21 ± 0.16	0.39 ± 0.17
tDCE	−0.17 ± 0.33	−0.37 ± 0.27	−0.15 ± 0.16	0.38 ± 0.23	0.28 ± 0.19	0.80 ± 0.16
cDCE	−0.04 ± 0.35	−0.21 ± 0.23	0.05 ± 0.15	0.61 ± 0.26	0.69 ± 0.15	0.60 ± 0.14
TCE	−0.12 ± 0.25	0.06 ± 0.26	0.03 ± 0.24	0.59 ± 0.35	0.37 ± 0.24	0.68 ± 0.31
PCE	−0.25 ± 0.26	−0.29 ± 0.33	−0.37 ± 0.18	0.53 ± 0.37	0.17 ± 0.17	0.69 ± 0.26
DCM	0.28 ± 0.34	0.40 ± 0.22	0.04 ± 0.16	1.30 ± 0.28	1.27 ± 0.17	0.98 ± 0.50
CF	0.38 ± 0.44	0.40 ± 0.22	−0.18 ± 0.21	1.46 ± 0.34	1.03 ± 0.22	0.97 ± 0.24
CT	−0.29 ± 0.30	−0.09 ± 0.43	−0.26 ± 0.17	1.38 ± 0.42	1.29 ± 0.16	1.39 ± 0.38
12DCA	0.10 ± 0.21	−0.10 ± 0.19	0.01 ± 0.19	0.69 ± 0.26	0.06 ± 0.20	0.74 ± 0.33

[a] Carbon isotope fractionation during analysis of gas standards by SPME. Isotope fractionation is expressed as enrichment factors in ‰ (eqs 4 and 5) with the corresponding 95% confidence intervals ($n = 6$). [b] nd, not determined.

TABLE 5. Detection Limit for Carbon Isotope Analysis Using Direct SPME (100 μm Polydimethylsiloxane Fiber) and Headspace Equilibration, Respectively[a]

	direct SPME (ppm)		headspace equilibration (ppm)	
	no salt	5 M NaCl	no salt	5 M NaCl
VC	1.5	nd[b]	0.51	0.17
tDCE	1.2	0.24	2.1	0.49
cDCE	1.6	0.29	4.9	1.0
TCE	0.40	0.19	2.7	0.61
PCE	0.13	0.13	2.0	0.62
DCM	8.4	2.2	15.0	3.3
CF	3.3	0.63	13.0	2.8
CT	0.51	0.36	2.2	0.80
1,2-DCA	3.1	0.64	18.0	4.1

[a] The detection limit corresponds to the initial concentration required in the aqueous phase to obtain 1.5 nmol C on the GC column. [b] nd, not determined.

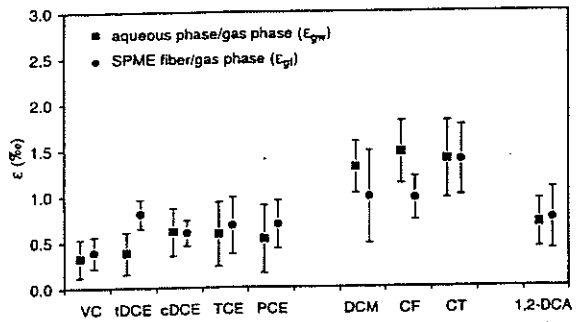


FIGURE 1. Carbon isotope fractionation during aqueous phase/gas phase and SPME fiber/gas phase partitioning. Positive enrichment factors ϵ signify an enrichment of ^{13}C in the gas phase. The error bars represent the 95% confidence intervals ($n = 6$).

(Figure 1). In both cases, an inverse isotope effect is observed whereby the molecules in the gas phase are enriched in ^{13}C compared to molecules in the aqueous and in the SPME fiber coating, respectively.

A similar inverse isotope effect is frequently observed during gas phase/liquid-phase partitioning in GC columns (*22*–*25*), which results in a slightly faster elution of molecules with heavy isotopes than molecules with light isotopes during GC separation. The SPME fiber has a similar chemical composition as nonpolar GC columns (dimethylpolysiloxane). Therefore, similar isotope effects during gas phase/liquid-phase partitioning are expected for SPME fiber and GC column. In this study, an inverse isotope effect during GC separation was observed for all compounds which is consistent with the observation that during SPME partitioning, molecules in the gas phase are enriched in ^{13}C compared to molecules on the fiber. An inverse isotope effect with respect to carbon has also been observed during evaporation of pure phase solvents such as CF, CT, and TCE (*26*–*30*). For example, Huang et al. (*29*) found that under equilibrium conditions, TCE in the gas phase was enriched in ^{13}C by 0.9‰ (25 °C) compared to pure phase TCE. The inverse isotope effect during evaporation and GC separation of organic compounds has been rationalized in terms of a mass-dependent effect of the van de Waals interactions on the vibrational energy of molecules in the liquid phase (*31*, *32*). Due to this effect, molecules with heavy isotopes have slightly higher energies in the liquid phase than molecules with light isotopes, which explains their higher volatility. A similar effect probably occurs during partitioning of chlorinated methanes, ethanes, and ethenes into the fiber coating.

When using dSPME and hSPME to analyze aqueous samples, the measured $\delta^{13}C$ can generally be considered to represent the $\delta^{13}C$ of the compounds originally dissolved in the aqueous phase, and no correction is required. A similar conclusion has been drawn by Dayan et al. (*8*) for carbon isotope analysis of PCE, TCE, cDCE, and tDCE by hSPME. However, when using headspace equilibration, isotope fractionation during gas phase/aqueous phase partitioning has to be taken into account, particularly for chlorinated methanes, and especially if values obtained by different analytical methods are compared (e.g. EA-IRMS for compounds present as nonaqueous phase liquid; GC-C-IRMS and headspace equilibration for dissolved compounds; GC-C-IRMS and gas injection for compounds in unsaturated zone). If carbon isotope fractionation during aqueous phase/gas phase partitioning is taken into account, dSPME, hSPME, and headspace equilibration techniques provide $\delta^{13}C$ values with a similar accuracy and precision. The 95% confidence interval of $\delta^{13}C_o$ (eqs 6 and 7), which can be considered as a measure of the overall analytical uncertainty of the method, ranges from 0.24 and 0.47 ‰ for dSPME, from 0.15 to 0.24 ‰ for hSPME, and from 0.29 to 0.57 ‰ for headspace equilibration. The good agreement between $\delta^{13}C$ values measured in standards without and with added NaCl indicates that for both SPME and headspace equilibration, the results are not affected by variations in ionic strength in aqueous samples.

The dSPME method has the advantage of having a lower detection limit and requires less sample volume than the headspace method. For hSPME, the detection limit is up to 30% higher than for dSPME, depending on K_{gw} of the compound (*20*), but is still lower than for headspace equilibration. By choosing other fibers than the one used in this study, lower detection limits than those given in Table 5 can be obtained for some compounds. For example, a detection limit of 150 ppb was reached for 1,2-DCA by using a PDMS-DVB fiber. For hSPME, a further decrease of the

detection limit could be reached by simultaneously heating the sample and cooling the fiber (*20*), for headspace equilibration by heating the sample (*13*). The headspace equilibration method has the advantage that in addition to obtaining isotope ratios of chlorinated solvents and degradation products, those of gaseous end products (ethene, CO_2, and CH_4) can be determined as well, using the same method or even during the same GC run (*5*).

Application in Groundwater Studies. The analytical techniques tested in this study can be easily adapted for analyzing chlorinated methanes, ethanes, and ethenes in groundwater samples. The results of this study make it possible to combine headspace equilibration, dSPME and hSPME methods according to their merits. For example, chlorinated compounds present in high concentration and gaseous end products can be analyzed by headspace equilibration and compounds at low concentration by dSPME. For such a combined analysis, no more than the content of a standard 40 mL VOC vial is required if the water that is displaced to create a headspace is used for dSPME. This approach was used to analyze groundwater samples from field sites, and a similar precision as reported in this study was achieved (*33*). Given the high precision of the measurements and given that shifts of $\delta^{13}C$ values during abiotic and biotic degradation of chlorinated solvents are in the range of tens of ‰ (*5–8*), the methods investigated in this study are very sensitive to trace abiotic and biotic transformation of these compounds in groundwater.

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Ion Chromatographic Determination of Anions in Aqueous Samples Containing Permanganate

Ion Chromatographic (IC) determination of major anions in aqueous environmental samples is a standard and well accepted technique (refer to US EPA Method 300.0[1]). However, for research programs involving *in situ* chemical oxidation, there are problems in using the IC method for samples that contain strong oxidants such as permanganate, because the oxidant can damage the exchange properties of the chromatographic column bed material. In order to overcome this problem, the IC method has been modified with a pre-treatment step in which glucose is used to reduce all of the oxidant (permanganate). Glucose is the preferred reductant because it does not require pH adjustment, and it does not contain the major anionic analytes of interest. The addition of glucose reduces Mn(VII) to Mn(IV), forming an MnO_2 floc which must be removed by centrifugation or filtration prior to the standard IC analytical procedure.

[1]The Determination of Inorganic Anions in Water by Ion Chromatography "; U.S. Environmental Protection Agency Method 300.0; Cincinnati, Ohio, 1993.

Analytical Methods for Major Ions and Inorganic Trace Constituents

Field Methods:

Samples are filtered through 0.45 μm cellulose acetate membranes, then split into two sub-samples. One of the sub-samples is acidified with 16 *N*, trace-metal grade HNO_3 to pH <1 for major cation and trace-metal analysis, and the unacidified sub-sample is used for anion analysis. All samples are refrigerated immediately and stored under refrigerated conditions until analyses are complete. Alkalinity is determined in the field on filtered sub-samples of 50 to 100 mL. Alkalinity is determined by potentiometric titration for samples that contain permanganate, and by colorimetric titration using methyl-red, bromcresol-green indicator for samples not affected by permanganate coloration.

Laboratory Methods:

Major-cation analyses are conducted by Inductively-Coupled-Plasma Optical-Emission Spectroscopy (ICP-OES) consistent with U.S. E.P.A. Method 200.7. Trace metals are determined by Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS) consistent with U.S. E.P.A. Method 200.8. The major anions (Cl, NO_3, PO_4 and SO_4) are determined by Ion Chromatography (IC) following US EPA Method 300.0. Ion Chromatographic determination of major anions in aqueous environmental samples is a standard and well accepted technique. However, for analytical programs involving *in situ* chemical oxidation, there are problems in using the IC method for samples that contain strong oxidants such as permanganate, because the oxidant can damage the exchange properties of the chromatographic column bed material. In order to overcome this problem, the IC method has been modified with a pre-treatment step in which glucose is used to reduce all of the oxidant (permanganate). Glucose is the preferred reductant because it does not require pH adjustment, and it does not contain the major anionic analytes of interest. The addition of glucose reduces Mn(VII) to Mn(IV), forming an MnO_2 floc which must be removed by centrifugation or filtration prior to the standard IC analytical procedure.

APPENDIX D

USEPA Region II Groundwater Sampling Procedure, Low Stress (Low Flow) Purging and Sampling, March, 1998.

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION II

GROUND WATER SAMPLING PROCEDURE
LOW STRESS (Low Flow) PURGING AND SAMPLING

I. SCOPE & APPLICATION

This Low Stress (or Low-Flow) Purging and Sampling Procedure is the EPA Region II standard method for collecting low stress (low flow) ground water samples from monitoring wells. Low stress Purging and Sampling results in collection of ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by minimizing stress on the geological formation and minimizing disturbance of sediment that has collected in the well. The procedure applies to monitoring wells that have an inner casing with a diameter of 2.0 inches or greater, and maximum screened intervals of ten feet unless multiple intervals are sampled. The procedure is appropriate for collection of ground water samples that will be analyzed for volatile and semi-volatile organic compounds (VOCs and SVOCs), pesticides, polychlorinated biphenyls (PCBs), metals, and microbiological and other contaminants in association with all EPA programs.

This procedure does not address the collection of light or dense non-aqueous phase liquids (LNAPL or DNAPL) samples, and should be used for aqueous samples only. For sampling NAPLs, the reader is referred to the following EPA publications: DNAPL Site Evaluation (Cohen & Mercer, 1993) and the RCRA Ground-Water Monitoring: Draft Technical Guidance (EPA/530-R-93-001), and references therein.

II. METHOD SUMMARY

The purpose of the low stress purging and sampling procedure is to collect ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by setting the intake velocity of the sampling pump to a flow rate that limits drawdown inside the well casing.

Sampling at the prescribed (low) flow rate has three primary benefits. First, it minimizes disturbance of sediment in the bottom of the well, thereby producing a sample with low turbidity (i.e., low concentration of suspended particles). Typically, this saves time and analytical

costs by eliminating the need for collecting and analyzing an additional filtered sample from the same well. Second, this procedure minimizes aeration of the ground water during sample collection, which improves the sample quality for VOC analysis. Third, in most cases the procedure significantly reduces the volume of ground water purged from a well and the costs associated with its proper treatment and disposal.

III. ADDRESSING POTENTIAL PROBLEMS

Problems that may be encountered using this technique include a) difficulty in sampling wells with insufficient yield; b) failure of one or more key indicator parameters to stabilize; c) cascading of water and/or formation of air bubbles in the tubing; and d) cross-contamination between wells.

Insufficient Yield

Wells with insufficient yield (i.e., low recharge rate of the well) may dewater during purging. Care should be taken to avoid loss of pressure in the tubing line due to dewatering of the well below the level of the pump's intake. Purging should be interrupted before the water level in the well drops below the top of the pump, as this may induce cascading of the sand pack. Pumping the well dry should therefore be avoided to the extent possible in all cases. Sampling should commence as soon as the volume in the well has recovered sufficiently to allow collection of samples. Alternatively, ground water samples may be obtained with techniques designed for the unsaturated zone, such as lysimeters.

Failure to Stabilize Key Indicator Parameters

If one or more key indicator parameters fails to stabilize after 4 hours, one of four options should be considered: a) continue purging in an attempt to achieve stabilization; b) discontinue purging, do not collect samples, and document attempts to reach stabilization in the log book; c) discontinue purging, collect samples, and document attempts to reach stabilization in the log book; or d) Secure the well, purge and collect samples the next day (preferred). The key indicator parameter for samples to be analyzed for VOCs is dissolved oxygen. The key indicator parameter for all other samples is turbidity.

Cascading

To prevent cascading and/or air bubble formation in the tubing, care should be taken to ensure that the flow rate is sufficient to maintain pump suction. Minimize the length and diameter of tubing (i.e., 1/4 or 3/8 inch ID) to ensure that the tubing remains filled with ground water during sampling.

Cross-Contamination

To prevent cross-contamination between wells, it is strongly recommended that dedicated, in-place pumps be used. As an alternative, the potential for cross-contamination can be reduced by performing the more thorough ▒daily▒ decontamination procedures between sampling of each well in addition to the start of each sampling day (see Section VII, below).

Equipment Failure

Adequate equipment should be on-hand so that equipment failures do not adversely impact sampling activities.

IV. PLANNING DOCUMENTATION AND EQUIPMENT

- Approved site-specific Field Sampling Plan/Quality Assurance Project Plan (QAPP). This plan must specify the type of pump and other equipment to be used. The QAPP must also specify the depth to which the pump intake should be lowered in each well. Generally, the target depth will correspond to the mid-point of the most permeable zone in the screened interval. Borehole geologic and geophysical logs can be used to help select the most permeable zone. However, in some cases, other criteria may be used to select the target depth for the pump intake. In all cases, the target depth must be approved by the EPA hydrogeologist or EPA project scientist.

- Well construction data, location map, field data from last sampling event.

- Polyethylene sheeting.

- Flame Ionization Detector (FID) and Photo Ionization Detector (PID).

- Adjustable rate, positive displacement ground water sampling pump (e.g., centrifugal or bladder pumps constructed of stainless steel or Teflon). A peristaltic pump may only be used for inorganic sample collection.

- Interface probe or equivalent device for determining the presence or absence of NAPL.

- Teflon or Teflon-lined polyethylene tubing to collect samples for organic analysis. Teflon or Teflon-lined polyethylene, PVC, Tygon or polyethylene tubing to collect samples for inorganic analysis. Sufficient tubing of the appropriate material must be available so that each well has dedicated tubing.

- Water level measuring device, minimum 0.01 foot accuracy, (electronic preferred for tracking water level drawdown during all pumping operations).

- Flow measurement supplies (e.g., graduated cylinder and stop watch or in-line flow meter).

- Power source (generator, nitrogen tank, etc.).
- Monitoring instruments for indicator parameters. Eh and dissolved oxygen must be monitored in-line using an instrument with a continuous readout display. Specific conductance, pH, and temperature may be monitored either in-line or using separate probes. A nephalometer is used to measure turbidity.

- Decontamination supplies (see Section VII, below).

- Logbook (see Section VIII, below).

- Sample bottles.

- Sample preservation supplies (as required by the analytical methods).

- Sample tags or labels, chain of custody.

V. SAMPLING PROCEDURES

Pre-Sampling Activities

1. Start at the well known or believed to have the least contaminated ground water and proceed systematically to the well with the most contaminated ground water. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations.

2. Lay out sheet of polyethylene for placement of monitoring and sampling equipment.

3. Measure VOCs at the rim of the unopened well with a PID and FID instrument and record the reading in the field log book.

4. Remove well cap.

5. Measure VOCs at the rim of the opened well with a PID and an FID instrument and record the reading in the field log book.

6. If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).

7. Measure and record the depth to water (to 0.01 ft) in all wells to be sampled prior to purging. Care should be taken to minimize disturbance in the water column and dislodging of any particulate matter attached to the sides or settled at the bottom of the well.

8. If desired, measure and record the depth of any NAPLs using an interface probe. Care should be taken to minimize disturbance of any sediment that has accumulated at the bottom of the well. Record the observations in the log book. If LNAPLs and/or DNAPLs are detected, install the pump at this time, as described in step 9, below. Allow the well to sit for several days between the measurement or sampling of any DNAPLs and the low-stress purging and sampling of the ground water.

Sampling Procedures

9. Install Pump: Slowly lower the pump, safety cable, tubing and electrical lines into the well to the depth specified for that well in the EPA-approved QAPP or a depth otherwise approved by the EPA hydrogeologist or EPA project scientist. The pump intake must be kept at least two (2) feet above the bottom of the well to prevent disturbance and resuspension of any sediment or NAPL present in the bottom of the well. Record the depth to which the pump is lowered.

10. Measure Water Level: Before starting the pump, measure the water level again with the pump in the well. Leave the water level measuring device in the well.

11. Purge Well: Start pumping the well at 200 to 500 milliliters per minute (ml/min). The water level should be monitored approximately every five minutes. Ideally, a steady flow rate should be maintained that results in a stabilized water

level (drawdown of 0.3 ft or less). Pumping rates should, if needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. As noted above, care should be taken to maintain pump suction and to avoid entrainment of air in the tubing. Record each adjustment made to the pumping rate and the water level measured immediately after each adjustment.

12. Monitor Indicator Parameters: During purging of the well, monitor and record the field indicator parameters (turbidity, temperature, specific conductance, pH, Eh, and DO) approximately every five minutes. The well is considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows (Puls and Barcelona, 1996):

    ±0.1 for pH
    ±3% for specific conductance (conductivity)
    ±10 mv for redox potential
    ±10% for DO and turbidity

    Dissolved oxygen and turbidity usually require the longest time to achieve stabilization. The pump must not be removed from the well between purging and sampling.

13. Collect Samples: Collect samples at a flow rate between 100 and 250 ml/min and such that drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft. VOC samples must be collected first and directly into sample containers. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container.

    Ground water samples to be analyzed for volatile organic compounds (VOCs) require pH adjustment. The appropriate EPA Program Guidance should be consulted to determine whether pH adjustment is necessary. If pH adjustment is necessary for VOC sample preservation, the amount of acid to be added to each sample vial prior to sampling should be determined, drop by drop, on a separate and equal volume of water (e.g., 40 ml). Ground water purged from the well prior to sampling can be used for this purpose.

14. Remove Pump and Tubing: After collection of the samples, the tubing, unless permanently installed, must be properly discarded or dedicated to the well for resampling by hanging the tubing inside the well.

15. Measure and record well depth.

16. Close and lock the well.

VI. FIELD QUALITY CONTROL SAMPLES

Quality control samples must be collected to determine if sample collection and handling procedures have adversely affected the quality of the ground water samples. The appropriate EPA Program Guidance should be consulted in preparing the field QC sample requirements of the site-specific QAPP.

All field quality control samples must be prepared exactly as regular investigation samples with regard to sample volume, containers, and preservation. The following quality control samples should be collected during the sampling event:

- Field duplicates
- Trip blanks for VOCs only
- Equipment blank (not necessary if equipment is dedicated to the well)

As noted above, ground water samples should be collected systematically from wells with the lowest level of contamination through to wells with highest level of contamination. The equipment blank should be collected after sampling from the most contaminated well.

VII. DECONTAMINATION

Non-disposable sampling equipment, including the pump and support cable and electrical wires which contact the sample, must be decontaminated thoroughly each day before use (※daily decon※) and after each well is sampled (※between-well decon※). Dedicated, in-place pumps and tubing must be thoroughly decontaminated using ※daily decon※ procedures (see #17, below) prior to their initial use. For centrifugal pumps, it is strongly recommended that non-disposable sampling equipment, including the pump and support cable and electrical wires in contact with the sample, be decontaminated thoroughly each day before use (※daily decon※).

EPA's field experience indicates that the life of centrifugal pumps may be extended by removing entrained grit. This also permits inspection and replacement of the cooling water in centrifugal pumps. All non-dedicated sampling equipment (pumps, tubing, etc.) must be

decontaminated after each well is sampled (▒between-well decon,▒ see #18 below).

17. **Daily Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Disassemble pump.

E) Wash pump parts: Place the disassembled parts of the pump into a deep basin containing 8 to 10 gallons of non-phosphate detergent solution. Scrub all pump parts with a test tube brush.

F) Rinse pump parts with potable water.

G) Rinse the following pump parts with distilled/ deionized water: inlet screen, the shaft, the suction interconnector, the motor lead assembly, and the stator housing.

H) Place impeller assembly in a large glass beaker and rinse with 1% nitric acid (HNO_3).

I) Rinse impeller assembly with potable water.

J) Place impeller assembly in a large glass bleaker and rinse with isopropanol.

K) Rinse impeller assembly with distilled/deionized water.

18. **Between-Well Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Final Rinse: Operate pump in a deep basin of distilled/deionized water to pump out 1 to 2 gallons of this final rinse water.

VIII. FIELD LOG BOOK

A field log book must be kept each time ground water monitoring activities are conducted in the field. The field log book should document the following:

- Well identification number and physical condition.
- Well depth, and measurement technique.
- Static water level depth, date, time, and measurement technique.
- Presence and thickness of immiscible liquid layers and detection method.
- Collection method for immiscible liquid layers.
- Pumping rate, drawdown, indicator parameters values, and clock time, at three to five minute intervals; calculate or measure total volume pumped.
- Well sampling sequence and time of sample collection.
- Types of sample bottles used and sample identification numbers.
- Preservatives used.
- Parameters requested for analysis.
- Field observations of sampling event.
- Name of sample collector(s).
- Weather conditions.
- QA/QC data for field instruments.

IX. REFERENCES

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Puls, R.W. and M.J. Barcelona, 1996, Low-Flow (Minimal Drawdown) Ground-water Sampling Procedures, EPA/540/S-95/504.

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APPENDIX E

Field Equipment Manuals

16900-08

Digital Titrator
Model 16900

© Hach Company, 1980-1998. Digital Titrator manufactured under U.S. Patent 4,086,062
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ap rev 2, 11/98

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GENERAL DESCRIPTION

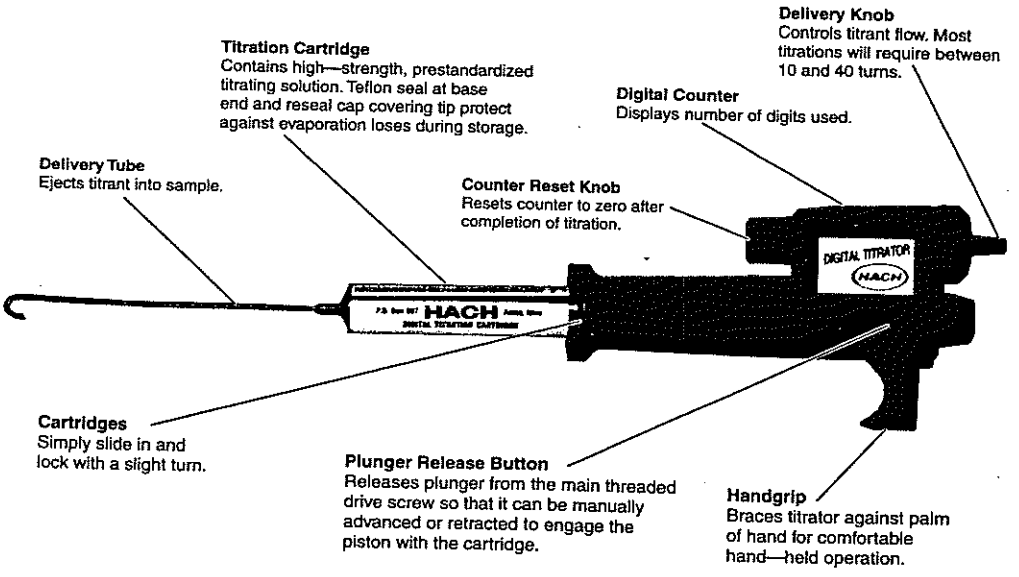
1.1 Introduction

Hach's Digital Titrator is a new concept in titrimetric analysis. It is a precision dispensing device fitted with compact cartridges that contain concentrated titrants. Accurate titrations are made without the bulk and fragility of conventional burets.

A main drive screw in the Digital Titrator controls a plunger which forces the solution from a titration cartridge in a carefully regulated flow. The titrator body is constructed of precision-molded, heavy-duty, chemical- and impact-resistant acetal plastic. Accuracy is rated at ±1% or better for a titration of more than 100 digits. For titrations less than 100 digits the accuracy is ±1 digit.

Titration solutions (titrants) are packaged in disposable polypropylene or Kynar® containers with Teflon-covered neoprene seals and polyethylene resealable closures to cover the cartridge tips. Each cartridge contains approximately 13 mL of titrating solution, enough for 50-100 average titrations. Titrant solutions are typically controlled to ±0.5% concentration with normality and tolerances listed on the label. Titrant concentrations are designed for titrations of 10 to 40 turns (100 to 400 digits) of the delivery knob. For the most commonly used concentration ranges, the digits appearing in the counter window correspond to the sample concentration.

Figure 1 Hach Digital Titrator



Both portable and fixed-position titrations are possible with the Digital Titrator. The instrument has a grip for hand-held operation or it can be clamped to a TitraStir® Stir Plate or laboratory stand for stationary setups. See *Figure 1*.

Each Digital Titrator comes with five delivery tubes and a methods manual, which covers the most commonly tested parameters and the corresponding titrant cartridges. Right-angle (ninety-degree) delivery tubes for stationary setups are available as an optional accessory.

1.1.1 Following a Procedure for the First Time

Each method is divided into five sections: Procedure, Accuracy Check, Interferences, Summary of Method, and Reagents and Apparatus. For more information about how to select a procedure or for answers to chemical questions, see Hach's *Water Analysis Handbook* (literature 8376). For more information about chlorine measurement, also see the technical booklet titled, *Current Technology of Chlorine Analysis for Water and Wastewater* (literature 7019).

The **Procedure** details how to perform the method step-by-step. To select the appropriate sample volume and titration cartridge based on expected sample concentration, use the tables provided in each procedure. If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

The ranges in the table overlap to offer more flexibility. In most procedures, the number of digits used for each concentration range will be 100 to 400 digits.

To determine the actual concentration of the sample, use the correct digit multiplier for the sample volume and titration cartridge used.

Throughout the procedure, the notes will provide additional information.

The **Accuracy Check** provides a way to verify the results and determine if interferences are present. It also provides a method for checking the performance of reagents, the Digital Titrator and the operator's technique. Further information is provided in *APPENDIX A, ACCURACY CHECK AND STANDARD ADDITIONS*.

The **Interferences** section identifies common interferences causing inaccurate results and describes how to eliminate their effects. The interference levels are based on the sample volume that has 1.0 as the digit multiplier. Higher interference levels may be tolerated if a smaller sample is used.

The **Summary of Method** section discusses the chemical reaction taking place and information that applies to the entire procedure.

The **Reagents and Apparatus** list concludes the procedure. All the items required to perform the test are listed first and are available from Hach. The items listed in the notes or interferences sections are included in the optional listings.

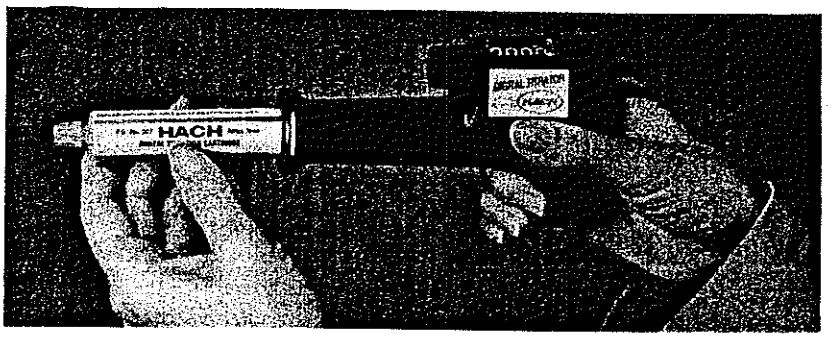
1.2 Step-By-Step

1. Select a sample volume and titration cartridge corresponding to the expected sample concentration from the table given in each procedure.

   If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

2. Slide the cartridge into the titrator receptacle and lock in position with a slight turn. See *Figure 2*.

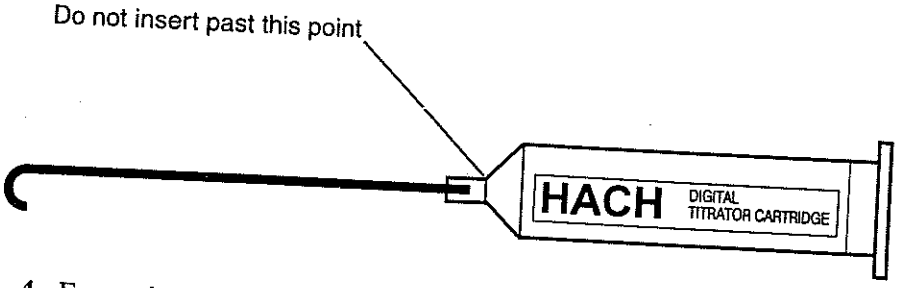
Figure 2 Sliding the Cartridge into Place



3. Remove the polyethylene cap and insert a clean delivery tube into the end of the cartridge until it is tight. See *Figure 3*. Use a straight tube with a hook at the end for hand-held titrations; use a 90° tube with a hook at the end for stationary setups.

   Do not insert tube past cartridge extension; see illustration below. In some instances, it might be necessary to remove a small burr on the leading edge of the tube before insertion.

Figure 3 Inserting the Delivery Tube



4. For stationary titrations, use a TitraStir Stir Plate or a clamp holder and clamp to attach the titrator to a laboratory stand. See *Figure 4* and *Figure 5*.

   The TitraStir Stir Plate holds the Digital Titrator during the titration and also stirs the sample at a constant speed, leaving the analyst free to detect the endpoint. When a TitraStir Stir Plate is used, substitute or add the following Optional Apparatus.

APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Delivery Tubes, 90° with hook for TitraStir Stir Plate	1	5/pkg	41578-00
Flask, Erlenmeyer, 125 mL	1	each	505-43
Flask, Erlenmeyer, 250 mL	1	each	505-46
Stir Bar, 28.6 x 7.9 mm	1	each	20953-52
TitraStir Stir Plate, 115 Vac	1	each	19400-00
TitraStir Stir Plate, 230 Vac	1	each	19400-10

Figure 4 Using the TitraStir Stir Plate

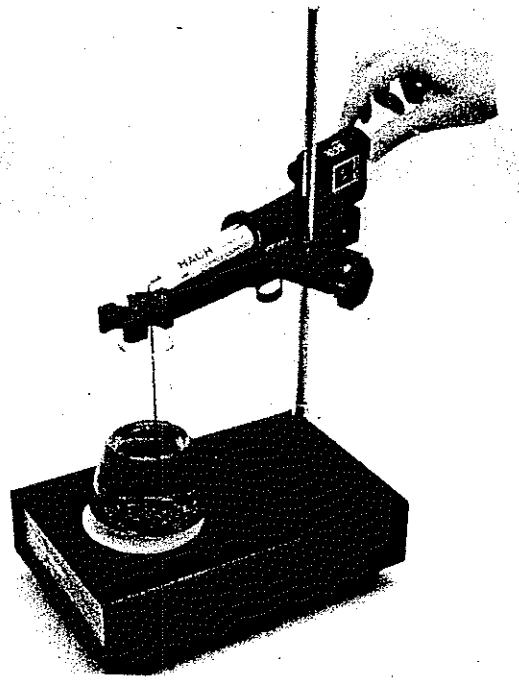


Figure 5 Using a Laboratory Stand



5. To start titrant flowing and flush the delivery tube, hold the tip of the cartridge up. Advance the plunger release button to engage the piston with the cartridge (push the button in and toward the cartridge). Do not expel solution when pushing the piston toward the cartridge. Turn the delivery knob until air is expelled and several drops of solution flow from the tip. As you turn the knob a drive screw pushes a piston against the cartridge seal and forces liquid out through the delivery tube. Then use the counter reset knob to turn the digital counter back to zero and wipe the tip. The tip can be rinsed with deionized water rather than wiped, if desired.

Figure 6 Titrating the Sample



6. Use the smallest appropriate graduated cylinder or pipet to measure the sample volume from the given table. Transfer the sample into a 125-mL or 250-mL Erlenmeyer flask. Dilute to the appropriate total volume with deionized water if necessary.

Note: *Sample volume measurements and dilutions (if required) must be made accurately. However, final total volume of titrated solution is not critical.*

7. Add the necessary reagents to the sample and swirl to mix.

8. Immerse the delivery tube tip in the solution and swirl the flask while titrating. Titrate by turning the delivery knob. Keep turning the knob and swirling the sample until the end point is reached. Record the number of digits that appear in the digital counter window. See *Figure 6*.

Note: *The number of digits required will usually range from 100 to 400. In nearly all of the procedures if the digits required is less than 100 or more than 400, an alternate sample volume or titrant cartridge should be used.*

Note: *Inaccurate results will occur if the delivery tube tip is held out of the solution rather than under the solution surface.*

9. Calculate the concentration of your sample by using the following formula:

Digits Required x Digit Multiplier = Sample Concentration

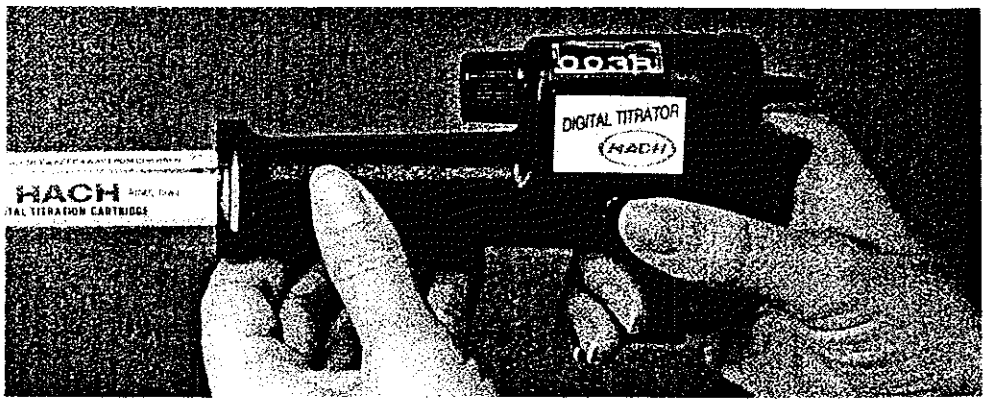
Where:

Digits Required = the number that appeared in the digital counter window in Step 8.

Digit Multiplier = the number from the table given in the procedure. It takes into account the sample dilution and titrant strength.

10. After completing testing for the day, press the plunger release button and manually retract the plunger into the body of the titrator. Remove the cartridge. Remove the delivery tube and reseal the cartridge with the polyethylene cap. See *Figure 7*.

Figure 7 Retracting the Plunger



11. Discard or clean the delivery tube immediately after use.
To clean, force water, then air, into the tube opening with a syringe or wash bottle.

1.3 Helpful Hints

1.3.1 To Reuse a Partially Emptied Cartridge

1. With the plunger fully retracted, attach cartridge to the titrator.
2. Press the plunger release; then manually push the plunger against the cartridge seal.
3. Attach a delivery tube. Hold the tip of the cartridge up. Eject air and a few drops of titrant, zero the counter, and wipe the tip.
4. Titrate as usual.

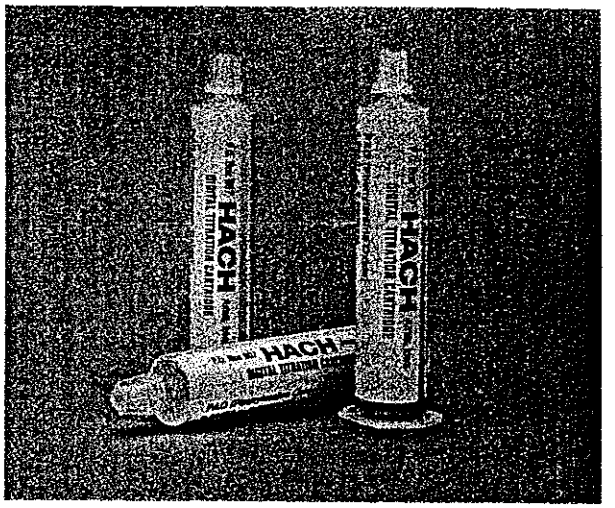
1.3.2 To Calculate Titrant Volume Used

Normalities of many Hach titration cartridge solutions have been designed so that the number of digits used in a titration corresponds to the sample concentration in mg/L. To determine the volume used in mL, divide the Digital Titrator reading by 800.

1.3.3 To Fill Your Own Titration Cartridges

Cartridges may be cleaned and refilled, or new empty cartridges, Cat. No. 14495-01, can be purchased from Hach Company. See *Figure 8*. When preparing to refill old cartridges, push the cartridge seal out of the cartridge with air pressure applied through the tip. Cap the tip, fill with solution and reinsert the cartridge seal using care to avoid wrinkling the Teflon sheath. Filling also can be accomplished at the tip with a syringe.

Figure 8 Digital Titrator Cartridges



1.3.4 Verifying Technique

Whenever procedures are changed or new equipment is used, it is helpful to run a sample of known concentration. This technique will confirm the operator is following the procedure correctly and the new equipment is working properly. One objective important to Hach Company is making our tests self-verifying. This means Hach makes the tools available so the operator can check their own work for accurate results without relying on an outside lab or chemist.

For most of the tests in this manual, Table 1 on page 12 lists each procedure, the suggested standard, the volume of standard needed, the titration cartridge used, and the number of expected digits when the test is performed correctly. The suggested standards are Voluette® or PourRite® Ampules whenever possible because of their superior accuracy and stability.

To use titration standards follow these steps:

1. Select the procedure of interest and order the appropriate standard. Use the given catalog numbers.
2. Measure the volume of standard to be used as the sample in the procedure using a TenSette® Pipet or Class A pipet.
3. Perform the procedure as written, adding deionized water as necessary.
4. After titrating, the required number of digits should approximately equal the expected digits.

Call Hach Technical and Customer Service (1-800-227-4224) for additional help.

Table 1 Titration Standards

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Acid-Base: Acid	0.500 N H_2SO_4 (2121-26)	1.0	1.600 N NaOH (14379-01)	250
		5.0	8.00 N NaOH (14381-01)	250
Base	0.500 N Na_2CO_3 (14278-10)	1.0	1.600 N H_2SO_4 (14389-01)	250
		5.0	8.00 N H_2SO_4 (14391-01)	250
Acidity	0.500 N H_2SO_4 (2121-26)	0.1	0.1600 N NaOH (14377-01)	250
		1.0	1.600 N NaOH (14379-01)	250
Alkalinity	0.500 N Na_2CO_3 (14278-10)	0.1	0.1600 N H_2SO_4 (14388-01)	250
		1.0	1.600 N H_2SO_4 (14389-01)	250
Calcium[1]: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		1.0	0.800 M EDTA (14399-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Carbon Dioxide	10,000 mg/L CO_2 (14275-10)	0.2	0.3636 N NaOH (14378-01)	100
		2.0	3.636 N NaOH (14380-01)	
Chloride	12,500 mg/L Cl (14250-10)	0.1	0.2256 N $Hg(NO_3)_2$ (14393-01)	125
		0.1	0.2256 N $AgNO_3$ (14396-01)	125
		1.0	1.128 N $AgNO_3$ (14397-01)	250
		1.0	2.256 N $Hg(NO_3)_2$ (921-01)	125

Table 1 Titration Standards (Continued)

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Chlorine	~50 mg/L Cl_2 (14268-20) (see certificate)	2.0	0.02256 N $Na_2S_2O_3$ (24091-01)	varies[2]
	~25 mg/L Cl_2 (26300-20)	0.5	0.00564 N FEAS (22923-01)	varies[3]
Chromate	1000 mg/L Cr (2231 mg/L CrO_4) (14664-42)	1.0	0.2068 N $Na_2S_2O_3$ (22676-01)	223
Hardness: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		0.1	0.0800 M CDTA (14402-01)	100
		1.0	0.800 M EDTA (14399-01)	100
		1.0	0.800 M CDTA (14403-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Iron	50 mg/L Fe (14254-10)	10.0	0.0716 M TitraVer (20817-01)	200
	1000 mg/L Fe (2271-42)	10.0	0.716 M TitraVer (20818-01)	100
Oxygen, Dissolved[4]	10 mg/L as DO (401-11)	100	0.2000 N $Na_2S_2O_3$ (22675-01)	500
		200	2.00 N $Na_2S_2O_3$ (14401-01)	100
Sulfite	5000 mg/L SO_3 (22674-10)	1.0	0.3998 N KIO_3-KI (14961-01)	250

1 One to two drops of Magnesium Standard Solution (10 g/L as $CaCO_3$) must be added to get a sharp endpoint. These added drops will not change the results.

2 The expected digits equal the volume of standard times the concentration on the certificate (e.g., 2 mL x 50 mg/L = 100 digits).

3 The expected digits equals the volume of standard times the concentration on the certificate times the constant, 4. (Example: 0.5 mL x 50 mg/L x 4 = 100 digits)

4 Add one Sulfamic Acid Powder Pillow to the volume of standard and follow Steps 10 to 12 in the Dissolved Oxygen Procedure. It is not necessary to add the first two reagents.

1.4 Adapting a Buret Titration to the Digital Titrator

Adapt any standard titration procedure using a buret to the Digital Titrator by using the following procedure.

1. Determine the approximate number of digits required. The Digital Titrator dispenses 1 mL per 800 digits on the counter. Using the following equation, determine the digits required for your buret method.

$$\text{Digits Required} = \frac{N_t \times mL_t \times 800}{N_c}$$

Where:

N_t = Normality of buret titrant
mL_t = milliliters of buret titrant required for an average titration
N_c = Normality of Digital Titrator cartridge

2. If the number of digits required is within the range of 70 to 350, you can use the procedure as written, substituting the Digital Titrator directly for the buret. Or, if the number of digits is outside of this range, make the following modifications:

   a) If the number of digits required is more than 350, reduce the sample size to save titrant.

   b) If the number of digits required is less than 70, increase the sample size to increase precision.

   c) If the sample size is altered, adjust the amount of buffering or indicating reagents by the same proportion.

3. When using the Digital Titrator for your buret method, note the number of digits required for a sample titration. To convert the digits required to the equivalent number of milliliters if the buret method was used, calculate:

$$\text{Equivalent Buret Milliliters} = \text{Digits Required} \times \frac{N_c}{800 \times N_t}$$

If the sample size was changed, adjust the equivalent buret milliliters accordingly. If the sample size was increased, reduce the equivalent buret milliliters; if the sample size was reduced increase the equivalent buret milliliters. Multiply the equivalent buret milliliters by any normally used factors to calculate concentration in oz/gal, g/L, etc.

Example: Adapt a buret procedure, which normally requires about 20 mL of a 0.4 N titrant, to the Digital Titrator. Try an 8.0 N titration cartridge. The first equation above gives:

$$\text{Digits Required} = \frac{0.4 \times 20 \times 800}{8.0} = 800 \text{ digits}$$

Because this would use excessive titrant, reduce the sample size to one fourth its normal size to reduce the digits required to 200, well within the recommended range.

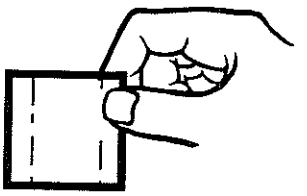
Upon completion of the titration using the smaller sample size, calculate the equivalent buret milliliters by the second equation above. If 205 were the digits required:

$$\text{Equivalent Buret Milliliters} = \frac{205 \times 8.0}{800 \times 0.4} = 5.13 \text{ mL}$$

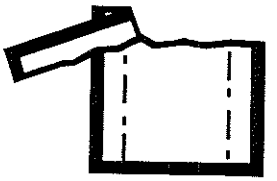
Multiply the 5.13 mL by 4 to account for the reduction in sample size to give the true equivalent buret milliliters of 20.5 mL. If the buret method called for multiplying the number of milliliters of titrant by a factor to calculate the concentration of a sample component, then multiply 20.5 by that factor.

1.5 Using PermaChem® Powder Pillows

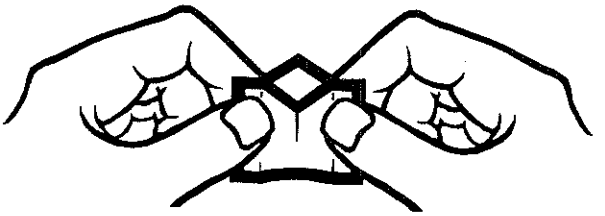
1. **Tap** the PermaChem on a hard surface to collect the powdered reagent in the bottom.



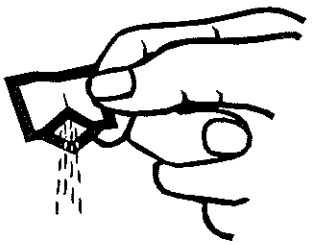
2. **Tear** across on the dotted pillow line marked 'TEAR' holding the pillow away from your face.



3. Using two hands, **Push** both sides toward each other until thumbs and forefingers form a diamond. Make sure to **Crease** the foil pack, so that it forms a spout.



4. **Pour** the pillow contents into the sample. The polyfilm lining is specially formulated to deliver all the powder necessary for accurate results (no tapping on the vessel edge is necessary).



1.6 Safety

Safety is the responsibility of each individual when performing analysis procedures, and the analyst must develop and maintain good safety habits. Because many of the procedures in this methods handbook use potentially hazardous chemicals and apparatus, it is important that the analyst practice good laboratory techniques to minimize accidents. The following paragraphs present several techniques applicable to water analysis in the laboratory and in the field. They are not all inclusive, of course, nor do they apply only to the procedures provided in this handbook. They are general in nature but emphasize practices that are often key factors in personal injury incidents.

- Read labels carefully. Never remove the label from a reagent container. When preparing a reagent or standard solution, be sure to label the container clearly and date it.
- A Material Safety Data Sheet (MSDS) comes with each reagent. This sheet contains helpful information on first aid, spill and disposal procedures, and precautionary measures and should be read before using the product.
- Warning labels also appear on some of the apparatus used with the test procedures.
- Wear protective clothing when handling chemicals that cause irritation or burns. Eye protection in particular is important to guard against spattering and splashes from accidental spills when caustic materials are being used.
- Use tongs or finger cots when transferring apparatus that is hot.

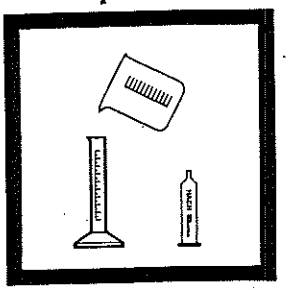
- Use mechanical pipetters: Mouth pipetting could result in accidentally ingesting dangerous chemicals. Make a habit of using mechanical pipet fillers for all pipetting. This will avoid mistakes that could cause serious injury.

- Use special care with dangerous chemicals and apparatus.

- Follow the test procedure steps carefully and observe all precautionary measures. It is good practice to read the entire procedure carefully before beginning the procedure. Use safety equipment, such as pipet fillers, protective clothing, and ventilating hoods, appropriate for the test being conducted. Wipe up all spills promptly. Do not smoke or eat in an area where toxic or irritating chemicals are used. Use reagents and apparatus only as they were meant to be used and use them only as directed in the test procedure. Do not use damaged labware and malfunctioning equipment.

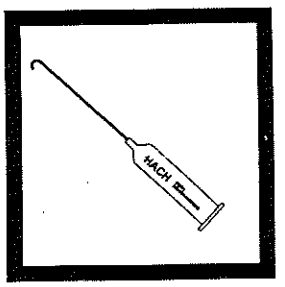
ALKALINITY (10 - 4000 mg/L as $CaCO_3$)

Phenolphthalein and Total Method

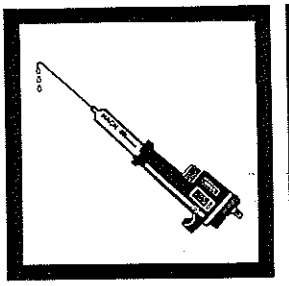


1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: See Sampling and Storage following these steps.

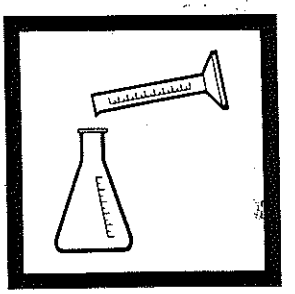


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14388-01	0.1
40-160	25	0.1600	14388-01	0.4
100-400	100	1.600	14389-01	1.0
200-800	50	1.600	14389-01	2.0
500-2000	20	1.600	14389-01	5.0
1000-4000	10	1.600	14389-01	10.0

11 → 451

SA 51 → 1390

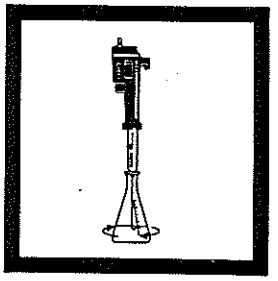
MMA 51 → 1310



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

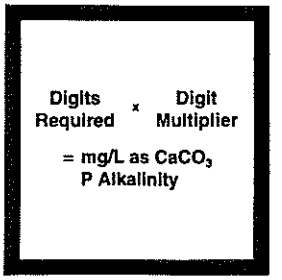
Note: A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end-point color.

Note: Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.



6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

Note: If the solution is colorless before titrating with sulfuric acid, the Phenolphthalein (P) Alkalinity is zero; proceed with Step 8.



7. Calculate:

Digits Required x Digit Multiplier = mg/L $CaCO_3$ P Alkalinity

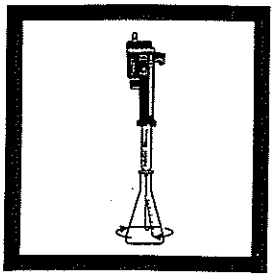


8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix.

Note: Four drops of Methyl Purple Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow. Titrate from green to a gray end point (pH 5.1).

Note: Four drops of Bromcresol Green-Methyl Red Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.





9. Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition; see *Table 2*. Record the number of digits required.

Note: A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pillow of the appropriate pH buffer in 50 mL of deionized water is recommended as a comparison for judging the proper end-point color. If the pH 3.7 end point is used, use a Bromphenol Blue Powder Pillow instead of a Bromcresol Green-Methyl Red and titrate to a green end point.

Total Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Total (T or M) Alkalinity

10. Calculate:

Total Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Total (T or M) Alkalinity

Note: Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.

Note: *meq/L Alkalinity = mg/L as $CaCO_3 \div 50$.*

Table 2

Sample Composition	End Point
Alkalinity about 30 mg/L	pH 5.1
Alkalinity about 150 mg/L	pH 4.8
Alkalinity about 500 mg/L	pH 4.5
Silicates or Phosphates present	pH 4.5
Industrial waste or complex system	pH 3.7

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

a) Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b) Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c) Multiply the phenolphthalein alkalinity by 2.

d) Select Row 3, 4, or 5 based on comparing the result of Step c with the total alkalinity.

e) Perform the required calculations in the appropriate row, if any.

f) Check your results. The sum of the three alkalinity types will equal the total alkalinity.

For example:

A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see Step a.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see Step b.

The phenolphthalein alkalinity multiplied by 2 = 340 mg/L, see Step c.

Because 340 mg/L is greater than 250 mg/L, select Row 5, see Step d.

The hydroxide alkalinity is equal to: (See Step e)

340 – 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 – 170 = 80

80 × 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.

Check: (See Step f)

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity
+ 0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Standard Solution Voluette Ampule, 0.500 N.

2. Use a TenSette Pipet to add 0.1 mL of standard to the sample titrated in Steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.

3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.

4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *APPENDIX A, ACCURACY CHECK AND STANDARD ADDITIONS.*

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.
- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this interference.

Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide.

REQUIRED REAGENTS

(varies with sample characteristics)

Alkalinity Reagent Set (about 100 tests) 22719-00
Includes: (1) 942-99, (1) 943-99, (1) 14388-01, (1) 14389-01

Description	Unit	Cat. No
Bromcresol Green-Methyl Red Powder Pillows	100/pkg	943-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N	each	14388-01
Water, deionized	4 L	272-56

ALKALINITY, continued

REQUIRED APPARATUS

Description	Unit	Cat. No
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46
Select one or more based on sample concentration		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

OPTIONAL REAGENTS

Alkalinity Standard Solution,		
Voluette Ampule, 0.500 N Na_2CO_3, 10 mL	16/pkg	14278-10
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	23292-32
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 4.5	25/pkg	895-68
Buffer Powder Pillows, pH 4.8	25/pkg	896-68
Buffer Powder Pillows, pH 5.1	25/pkg	897-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Methyl Purple Indicator Solution	100 mL MDB	21934-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32

OPTIONAL APPARATUS

Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir Stir Plate	5/pkg	41578-00
Hach One Combination pH Electrode with Temp	each	48600-22
pH Meter, EC10, portable	each	50050-60
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 25 mL	each	14515-40
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet, volumetric, Class A, 100 mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00

* Contact Hach for larger sizes.

OPTIONAL APPARATUS, continued

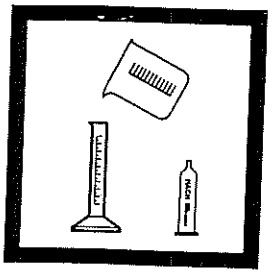
Description	Unit	Cat. No
Support Ring Stand	each	563-00
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10
Voluette Ampule Breaker Kit	each	21968-00

CHLORIDE

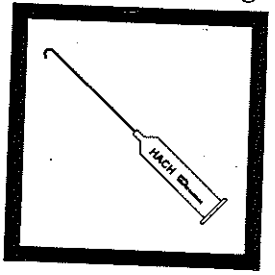
Mercuric Nitrate and Silver Nitrate Methods

Mercuric Nitrate Method (10 - 8000 mg/L as Cl^-)

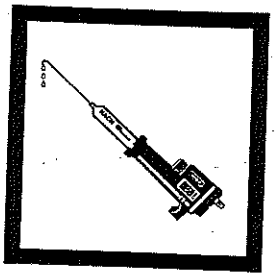
Method 8206



1. Select the sample volume and Mercuric Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 1*.

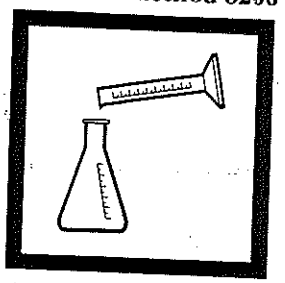


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step*, for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

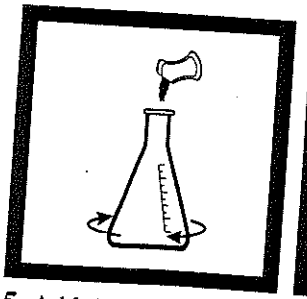
Note: See Sampling and Storage following these steps.

Table 1

Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $Hg(NO_3)_2$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14393-01	0.1
40-160	25	0.2256	14393-01	0.4
100-400	100	2.256	921-01	1.0
200-800	50	2.256	921-01	2.0
500-2000	20	2.256	921-01	5.0
1000-4000	10	2.256	921-01	10.0
2000-8000	5	2.256	921-01	20.00

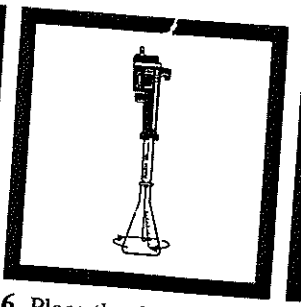
SA 64-406

MMA 43-496

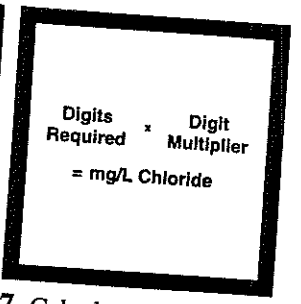


5. Add the contents of one Diphenylcarbazone Powder Pillow and swirl to mix.

Note: Results will still be accurate if a small amount of the powder does not dissolve.



6. Place the delivery tube tip into the solution and swirl the flask while titrating with silver nitrate from a yellow to light pink color. Record the number of digits required.



7. Calculate:

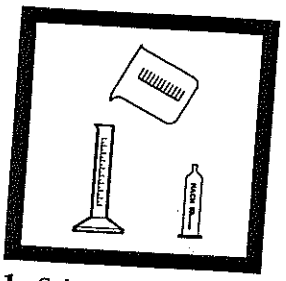
Digits Required x Digit Multiplier = mg/L Chloride

Note: Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.

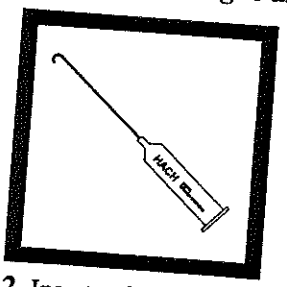
Note: meq/L Chloride = mg/L Cl^- ÷ 35.45.

Silver Nitrate Method (10 - 10000 mg/L as Cl^-)

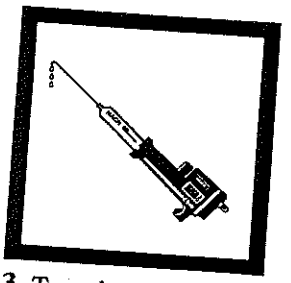
Method 8207



1. Select the sample volume and Silver Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 2*.

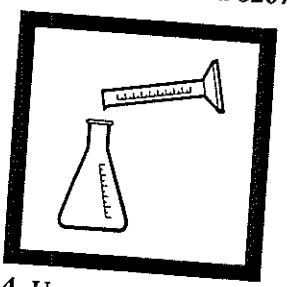


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step*, for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.

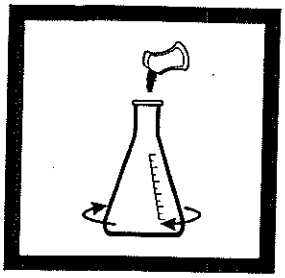


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Note: See Sampling and Storage following these steps.

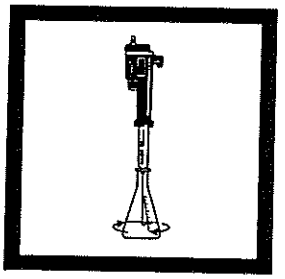
Table 2

Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $AgNO_3$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14396-01	0.1
25-100	40	0.2256	14396-01	0.25
100-400	50	1.128	14397-01	1.0
250-1000	20	1.128	14397-01	2.5
1000-4000	5	1.128	14397-01	10.0
2500-10000	2	1.128	14397-01	25.0

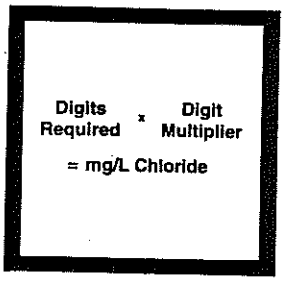


5. Add the contents of one Chloride 2 Indicator Powder Pillow and swirl to mix.

Note: Results will still be accurate if a small amount of the powder does not dissolve.



6. Place the delivery tube tip into the solution and swirl the flask while titrating with silver nitrate from a yellow to red-brown color. Record the number of digits required.



7. Calculate:

Digits Required x Digit Multiplier = mg/L Chloride

Note: Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.

Note: meq/L Chloride = mg/L Cl^- ÷ 35.45.

Sampling and Storage

Collect at least 100 to 200 mL of sample in a clean glass or polyethylene container. Samples may be stored up to 7 days before analysis.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Chloride Standard Solution Voluette Ampule, 12,500 mg/L Cl^-.
2. Use a TenSette Pipet to add 0.1 mL of standard to the sample after titration in Step 6. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 and 0.3 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 12.5 additional digits of 2.256 N titrant, 25 digits of 1.128 N titrant, or 125 digits of 0.2256 N titrant. If these uniform increases do not occur, refer to *APPENDIX A, ACCURACY CHECK AND STANDARD ADDITIONS.*

Interferences Using the Mercuric Nitrate Method

- Chromate, ferric iron and sulfite in excess of 10 mg/L interfere with this method.
- Eliminate sulfite interference by adding three drops of hydrogen peroxide, 30%, in Step 4.
- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.
- Iodide and bromide interfere directly and titrate as chloride.
- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Interferences Using the Silver Nitrate Method

- Iron in excess of 10 mg/L masks the end point.
- Orthophosphate in excess of 25 mg/L will precipitate the silver.
- Sulfite in excess of 10 mg/L interferes. Eliminate sulfite interference by adding three drops of 30% hydrogen peroxide in Step 4.
- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.
- Cyanide, iodide and bromide interfere directly and titrate as chloride.
- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Summary of the Mercuric Nitrate Method

When using Mercuric Nitrate Standard Solution, the sample is titrated under acid conditions in the presence of diphenylcarbazone indicator. Upon addition of a slight excess of mercuric ion, a pink-purple complex is formed with the indicator, signaling the end point.

Summary of the Silver Nitrate Method

The sample is titrated with Silver Nitrate Standard Solution in the presence of potassium chromate (from the Chloride 2 Indicator Powder). The silver nitrate reacts with the chloride present to produce insoluble white silver chloride. After all the chloride has been precipitated, the silver ions react with the excess chromate present to form a red-brown silver chromate precipitate, marking the end point of the titration.

Request *Hach Water Analysis Handbook,* Publication 8376, to obtain additional information on chloride determinations.

CHLORIDE, continued

REQUIRED REAGENTS for the Mercuric Nitrate Method

Description	Unit	Cat. No.
Mercuric Nitrate Chloride Reagent Set (about 100 tests) Includes: (2) 836-46, (1) 921-01, (1) 14393-01		22726-00
Diphenylcarbazone Reagent Powder Pillows	100/pkg	836-99
Mercuric Nitrate Titration Cartridge, 0.2256 N	each	14393-01
Mercuric Nitrate Titration Cartridge, 2.256 N	each	921-01
Water, deionized	4 L	272-56

REQUIRED REAGENTS for the Silver Nitrate Method

Silver Nitrate Chloride Reagent Set (about 50 tests) Includes: (2) 1057-66, (1) 14396-01, (1) 14397-01		22880-00
Chloride 2 Indicator Powder Pillows	50/pkg	1057-66
Silver Nitrate Titration Cartridge, 0.2256 N	each	14396-01
Silver Nitrate Titration Cartridge, 1.128 N	each	14397-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS for the Mercuric Nitrate Method or Silver Nitrate Method

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46
Select one or more based on sample concentration		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

OPTIONAL REAGENTS

Chloride Standard Solution, 1000 mg/L Cl^-	500 mL	183-49
Chloride Standard Solution, Voluette Ampule, 12,500 mg/L Cl^-, 10 mL	16/pkg	14250-10
Hydrogen Peroxide, 30%, ACS	200 mL	144-45
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfide Inhibitor Powder Pillows	100/pkg	2418-99
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir Stir Plate	5/pkg	41578-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Funnel, poly, 65 mm	each	1083-67
Hach One Combination pH Electrode with Temp	each	48600-22
pH Meter, EC 10, portable	each	50050-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2 mL	each	14515-36
Pipet, volumetric, Class A, 5 mL	each	14515-37
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 25 mL	each	14515-40
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet, volumetric, Class A, 100 mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
Support Ring Stand	each	563-00
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10
Voluette Ampule Breaker Kit	each	21968-00

DR/2000 SPECTROPHOTOMETER

Combines Stored Programs and Advanced Optics

Saving time, saving money. That's the whole idea behind the DR/2000.

When you use the DR/2000, you can forget about constructing calibration curves. And mixing standards. And measuring reagents. Because we've done all that for you.

Hach Company took 40 years of chemistry experience, combined it with microprocessor technology and created a spectrophotometer that gives you fast results, without tedious calculations.

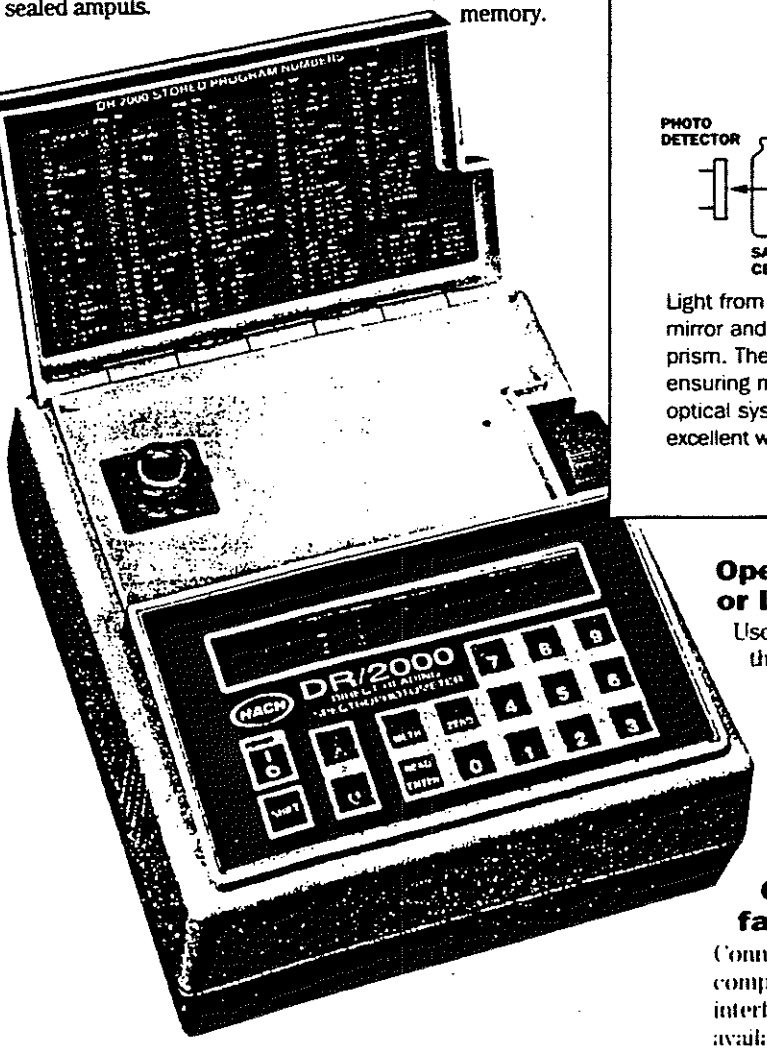
Using our convenient, premeasured reagents will save you more time. And money. You'll appreciate the economy of ready-to-use solutions, PermaChem powder pillows, single-dose polyethylene powder pillows and vacuum-sealed ampuls.

More than 120 Preprogrammed Calibrations

Calibrations for over 120 commonly performed analyses are permanently stored in the DR/2000's ROM (read-only memory). Manual conversion of absorbance data to concentration values are eliminated. That means you won't have to prepare calibration curves. Enter the three-digit program number of the test you want to perform, insert the sample and read the results in concentration units on the digital display.

Store Your Own Calibrations

Customize your DR/2000 by adding up to 50 of your own calibrations to the instrument's permanent memory.



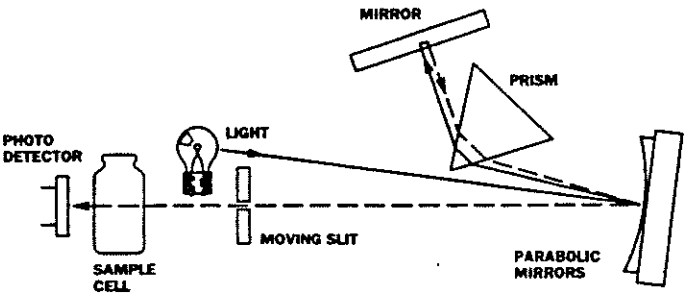
Update Capability

A few simple keystrokes is all it takes to add new Hach methods to your software. As new tests become available, you can add new testing procedures to your DR/2000.

Rugged, High Quality Optics

The DR/2000 is rugged and compact enough to be a field instrument yet accurate and stable enough to satisfy the most exacting analyst. The optical system uses a high-dispersion prism and provides outstanding precision in the 400/900 nm range.

DR/2000 Optical System



Light from a long-life tungsten bulb is reflected off a unique parabolic mirror and dispersed with a double pass through the high-dispersion prism. The selected wavelength is imaged onto a moving slit, ensuring more uniform spectral bandwidth. The factory-calibrated optical system provides accurate readings to 2 absorbance units with excellent wavelength accuracy.

Operates on Battery or Line Power

Use line power when you're in the laboratory. Or switch to battery operation for testing anywhere, anytime. An optional rechargeable battery provides added convenience.

Computer Interface Capability

Connect the DR/2000 to a computer using a RS-232 serial interface. Then use commonly available software to make permanent records of your data and generate written reports of your results.

Multi-language Prompting

Prompting messages in 14 languages (including English, French, German, Spanish and Japanese) guide you step-by-step through stored procedures.

Do-It-Yourself Calibration Adjustment

To help you consistently obtain the best possible analytical answers, a Lamp Recalibration Filter Assembly is included with each new DR/2000 Spectrophotometer. Easy-to-follow instructions permit you to periodically verify the monochromator calibration accuracy and make adjustments if necessary.

New 3.1 Software Improves Operation

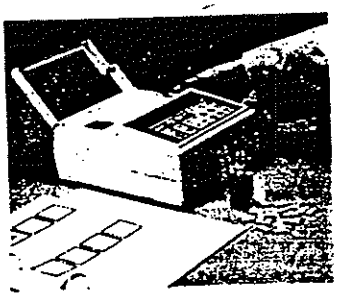
All new DR/2000 Spectrophotometers are now preprogrammed with version 3.1 software, an important update that has made the instrument easier to use without changing its operating methodology.

Outdoor Light Shield

To ensure optimum performance, each DR/2000 Spectrophotometer is supplied with a specially-designed Outdoor Light Shield. The light shield slips over the sample cell and will prevent bright sunlight from interfering with test results.

Selectable Modes

Choose the photometric readout mode that suits your needs: concentration, absorbance or % transmittance.



Complete System for Analysis

A spectrophotometer is only as good as the system that supports it. That's why every DR/2000 is backed by Hach's simplified methods, premeasured reagents, step-by-step instructions and technical support after the sale.

Options Add Speed, Convenience

Pour-Thru Cell

The Pour-Thru Cell (Cat. No. 45215-00) speeds measurement of multiple samples, eliminates errors caused by using different, unmatched sample cells, and contributes to accurate measurement of very low concentrations when high sensitivity is required. Ideal for handling large numbers of samples, the Pour-Thru Cell's low volume design helps prevent contamination or dilution between successive samples. If you're spending too much time handling and washing glassware, supplement a DR/2000 with a Pour-Thru Cell.



Dot Matrix Printer

Record your test results with the economical Citizen Model iDP-560RS L Dot Matrix Printer. Simply connect the DR/2000 to the printer via the RS-232 serial interface. For more details see page 245.

DR/2000 Specifications

See page 30 for complete specifications.

How To Order

44800-00 DR/2000 Spectrophotometer complete with matched pair of sample cells, AccuVac Adapter, 1-inch AccuVac Zeroing Cell, COD Adapter Kit, 13 mm Adapter Kit, 1-inch sample cell, Outdoor Light Shield, Lamp Recalibration Filter Assembly, Battery Holder, Battery Eliminator/Charger $1495.00

Accessories

45215-00 Pour-Thru Cell Kit 225.00
44895-00 1-cm Cell Adapter 10.00
20951-00 1-cm Cells, matched pair 75.00
20950-00 1" Sample Cells, matched pair 55.00
45185-00 Rechargeable Battery 40.00
45192-00 Printer, 120 V ...365.00
45192-02 Printer, 230 V ...365.00
45193-00 Printer Connecting Cable 25.00
16084-00 Phone Jack for RS-232 (out) 3.50
45194-00 Phone Jack for Recorder (out) 5.00
46646-00 Lamp Recalibration Filter Assembly (for use with software versions 2.0 or greater) 50.00
46878-00 DR/2000 Outdoor Light Shield 10.00
25624-00 DR/2000 Dust Cover.10.00

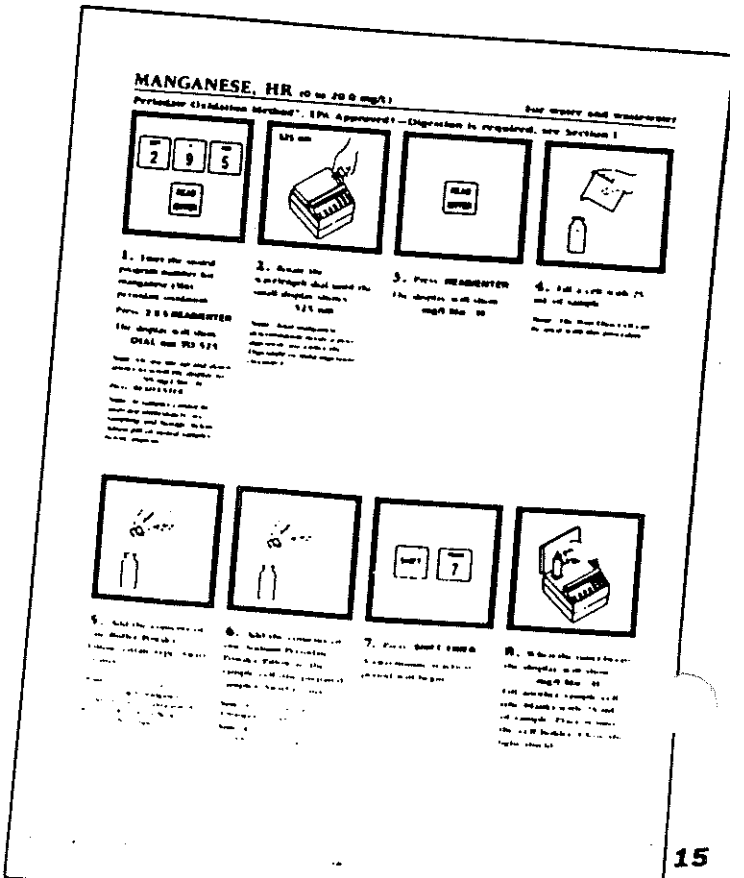
Circle 4178 for more information.

Complete Procedures Manual*

Get accurate answers easily with step-by-step instructions. Each DR/2000 is accompanied by a 400-page procedures manual with step-by-step instructions for performing each test. The easy-to-follow directions are accompanied by over 1500 drawings, illustrating each step. These detailed instructions enable even inexperienced operators to get accurate results.

Each procedure also includes information on sampling and storage, checking accuracy, adjusting for interferences, and a listing of all the reagents and apparatus needed to run the test. Procedures for soil extraction, plant extraction, and other pretreatment procedures are also included.

1. Procedure name
2. Range with units of measure
3. Approval of method by United States EPA if applicable
4. Type of samples analyzed
5. Clarification of EPA approval (if needed)
6. Name of method used
7. Procedure step
8. Keystrokes required
9. Instrument display
10. Additional information that may be applicable
11. Illustration of procedure steps and instrument keystrokes required



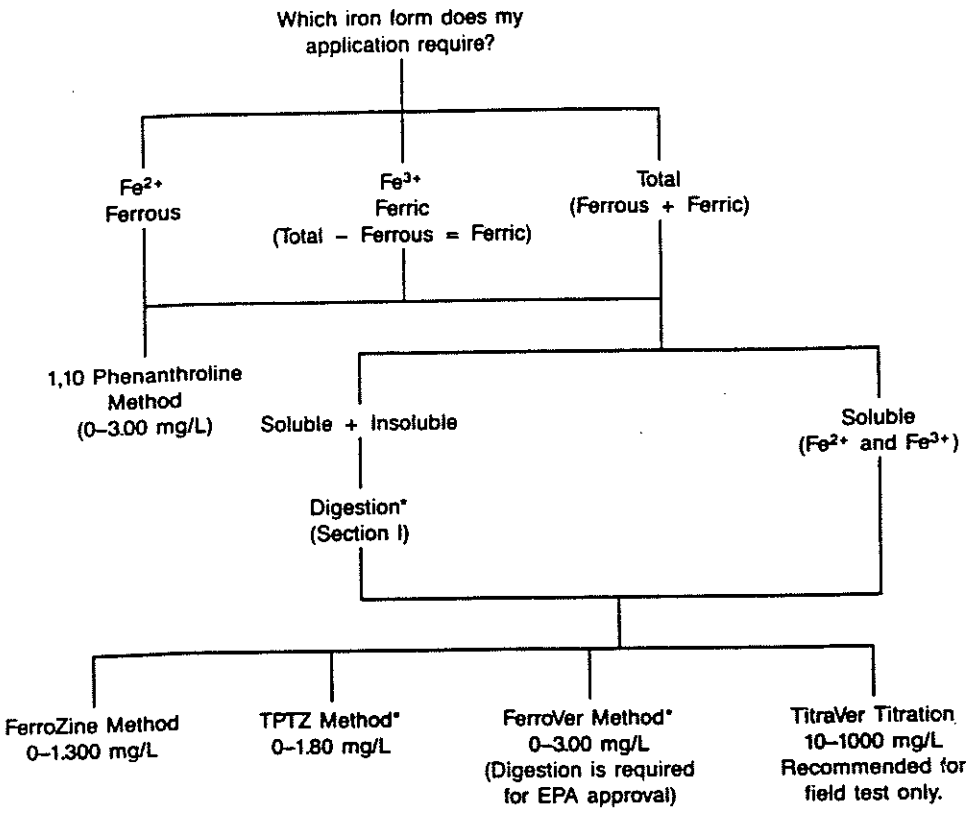
* Available in English, French, Spanish and German

ow to Select the Right Iron Procedure

ATTACHMENT 2
Pg 1

Because there are several iron procedures, the following decision tree will help you select the appropriate procedure for your application.

APPENDIX B-5

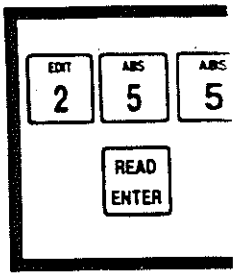


*Note: TPTZ and FerroVer will recover most insoluble iron oxides without digestion.

IRON, FERI

1,10 Phenanthrolii

USING POWDE



1. Enter the stored program number for ferrous iron, (Fe^{2+})– powder pillows.

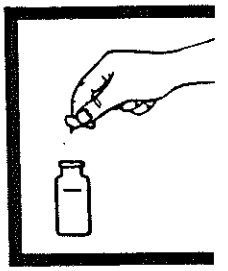
Press: **2 5 5 READ/EN**

The display will sho **DIAL nm TO 51**

Note: DR/2000s with soft versions 3.0 and greater w display "P" and the progr number.

Note: Instruments with sc versions 3.0 and greater w not display "DIAL nm TO message if the wavelength already set correctly. The display will show the me in Step 3. Proceed with S

Note: Analyze samples as as possible to prevent air oxidation of ferrous iron ferric, which is not detect



5. Add the conten one Ferrous Iron Re Powder Pillow to th sample cell (the pre sample). Swirl to m

Note: An orange color v form if ferrous iron is p

Note: Undissolved pow not affect accuracy

*Adapted from Standard Me

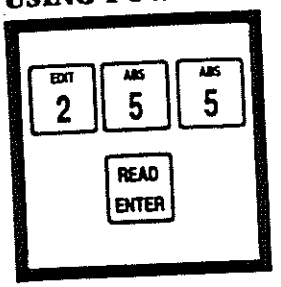
IRON, FERROUS (0 to 3.00 mg/L)

For water, wastewater and seawater

1,10 Phenanthroline Method* (Powder Pillows or AccuVac Ampuls)

ATTACHMENT 2
Pg 1

USING POWDER PILLOWS



1. Enter the stored program number for ferrous iron, (Fe^{2+})– powder pillows.

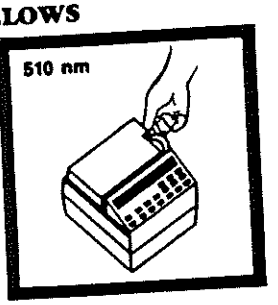
Press: **2 5 5 READ/ENTER**

The display will show:
DIAL nm TO 510

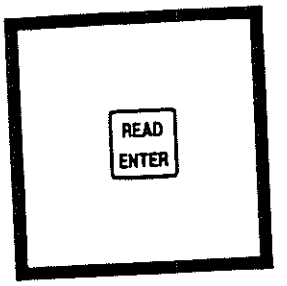
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined

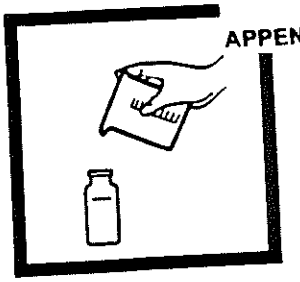


2. Rotate the wavelength dial until the small display shows:
510 nm



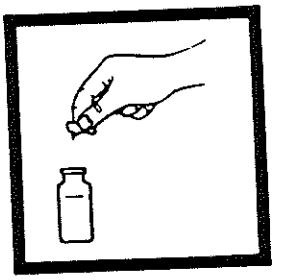
3. Press: **READ/ENTER**

The display will show:
mg/l Fe^{2+}



4. Fill a sample cell with 25 mL of sample.

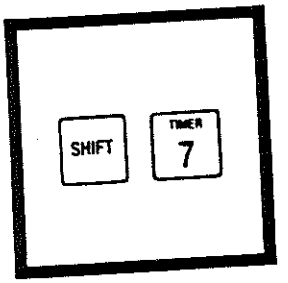
Note: For proof of accuracy, use a 1.0 mg/L ferrous iron standard solution (preparation given in the Accuracy Check) in place of the sample.



5. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix

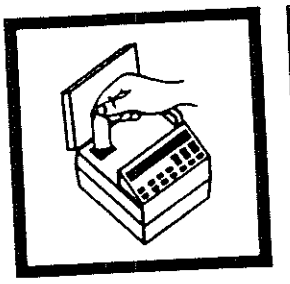
Note: An orange color will form if ferrous iron is present

Note: Undissolved powder does not affect accuracy



6. Press. **SHIFT TIMER**

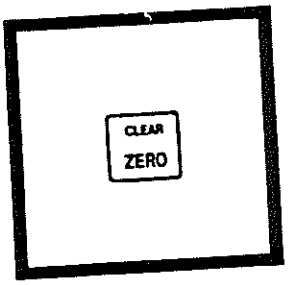
A three-minute reaction period will begin



7. When the timer beeps, the display will show
mg/l Fe^{2+}

Fill a second sample cell (the blank) with 25 mL of sample. Place it into the cell holder

Note: The Four Dram cell can be used with this procedure



8. Press: **ZERO**

The display will show:
WAIT

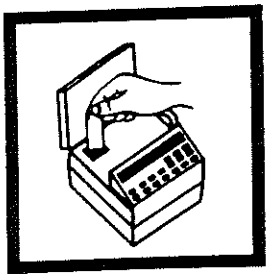
then:
0.00 mg/l Fe^{2+}

*Adapted from Standard Methods for the Examination of Water and Wastewater

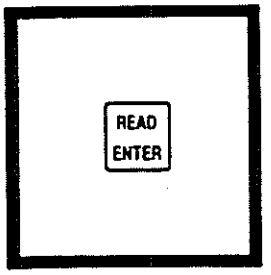
Soluble
(Fe^{2+} and Fe^{3+})

TitraVer Titration
10–1000 mg/L
Recommended for
field test only.

Attachment 2
Pg 3



9. Place the prepared sample into the cell holder. Close the light shield.

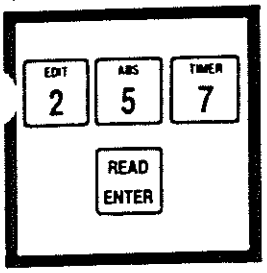


10. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/l. Fe^{2+} will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



1. Enter the stored program number for ferrous iron (Fe^{2+})– AccuVac ampuls.

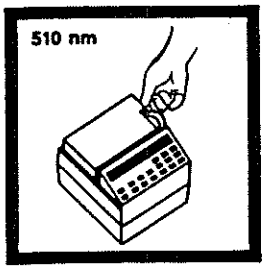
Press: **2 5 7 READ/ENTER**

The display will show:
DIAL nm TO 510

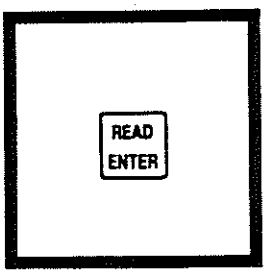
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 4. Proceed with Step 4.

Note: Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined.

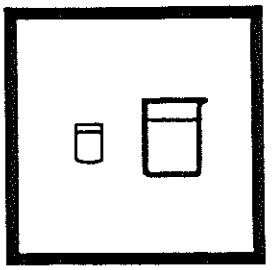


2. Rotate the wavelength dial until the small display shows:
510 nm



3. Press: **READ/ENTER**

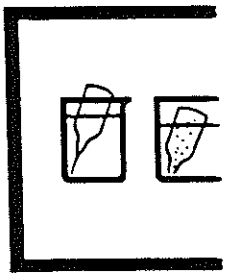
The display will show:
mg/l Fe^{2+} AV



4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

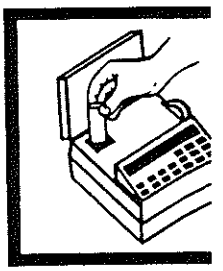
Note: For proof of accuracy, a 1.0 mg/L ferrous iron standard solution (preparation given in the Accuracy Check) can be used in place of the sample.

IRON, FERRO



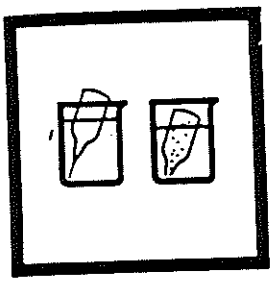
5. Fill a Ferrous Iro AccuVac Ampul with sample.

Note: Keep the tip immer while the ampul fills completely.



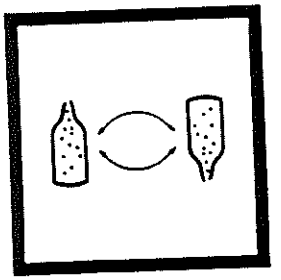
9. When the timer the display will sho
mg/l Fe^{2+} AV
Place the blank into t cell holder. Close th light shield.

IRON, FERROUS, continued



5. Fill a Ferrous Iron AccuVac Ampul with sample.

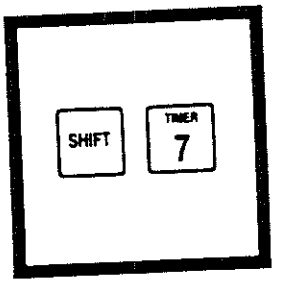
Note: Keep the tip immersed while the ampul fills completely.



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

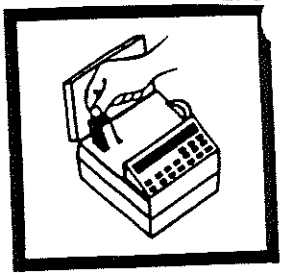
Note: An orange color will form if ferrous iron is present.

Note: Undissolved powder does not affect accuracy.



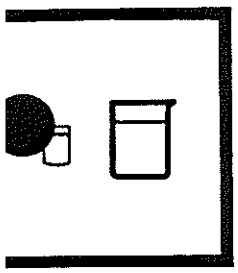
7. Press: **SHIFT TIMER**

A three-minute reaction period will begin.



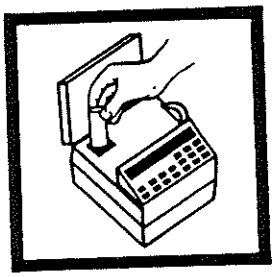
8. Place the AccuVac Vial Adapter into the cell holder.

Note: Place the grip tab at the rear of the cell holder.



. Fill a zeroing vial
e blank) with at least
ml. of sample. Collect
least 40 ml. of sample
a 50-ml. beaker.

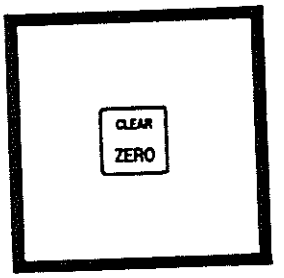
te: For proof of accuracy, a mg/l. ferrous iron standard ution (preparation given in Accuracy Check) can be d in place of the sample.



9. When the timer beeps, the display will show:

mg/l Fe^{2+} AV

Place the blank into the cell holder. Close the light shield.



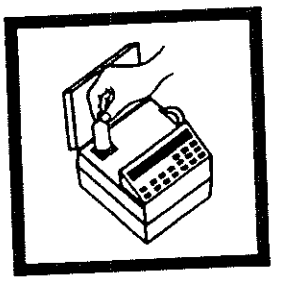
10. Press: **ZERO**

The display will show:

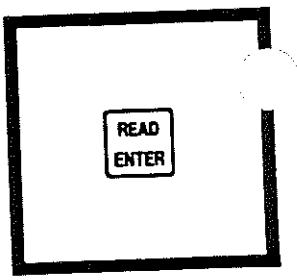
WAIT

then:

0.00 mg/l Fe^{2+} AV



11. Place the AccuVac ampul into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L Fe^{2+} will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result

ATTACHMENT 2
Pg 5

ACCURACY CHECK

Standard Solution Method

Prepare a ferrous iron stock solution (100 mg/L Fe) by dissolving 0.7022 grams of ferrous ammonium sulfate, hexahydrate, in deionized water. Dilute to 1 liter. Prepare immediately before use. Dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.0 mg/L standard solution. Prepare this immediately before use.

PRECISION

In a single laboratory using an iron standard solution of 1.000 mg/L Fe^{2+} and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.006 mg/L Fe^{2+}.

In a single laboratory using a standard solution of 1.000 mg/L Fe^{2+} and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.009 mg/L Fe^{2+}.

SUMMARY OF METHOD

The 1,10 phenanthroline indicator in Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test. See *Chemical Procedures Explained*, Appendix A, for more information.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69

REQUIRED REAGENTS (Using AccuVac Ampuls)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Sample Cell, 10-mL, with cap	1	each	21228-00

OPTIONAL REAGENTS

Ferrous Ammonium Sulfate, hexahydrate		113 g	11256-14
Water, deionized		3.78 L	272-17

OPTIONAL APPARATUS

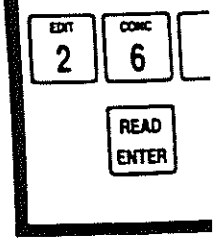
AccuVac Snapper Kit		each	24052-00
Clippers, shears, 7-1/4"		each	23694-00
Flask, volumetric, 100 mL, Class B		each	547-42
Flask, volumetric, 1000 mL, Class B		each	547-53
Pipet, volumetric, 1 mL		each	515-35
Pipet Filler, safety bulb		each	14651-00
Pour-Thru Cell Assembly Kit		each	45215-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224 toll-free for more information
Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON (0 to 1.

FerroZine Metho



1. Enter the store program number fc iron (Fe), FerroZin method.

Press: 2 6 0 READ/I

The display will sh DIAL nm TO

Note: DR/2000s with s versions 3.0 and greate display "P" and the pr number.

Note: Instruments wit versions 3.0 and greate not display "DIAL nm message if the wavelen already set correctly. T display will show the in Step 3. Proceed wit



5. Add the con one FerroZine Ir Reagent Solution to the cell (the p sample). Swirl to

Note: Do not allow to come into contact contents of the pillo

Note: 0.5 mL of Fer Reagent Solution can place of the solution preferred.

Note: If the sample rust, see Interferenc

*Adapted from Stookey

INSTRUCTION MANUAL



WATER QUALITY CHECKER U-10

CODE: 040801000HK-5

WARNING

The DO sensor contains a strong alkaline solution. Should any of this solution come in contact with your clothing or skin, wash it away immediately with plenty of water.

Be especially careful not to allow any of the alkaline liquid in the DO sensor to get in your eyes.

▲CAUTION

Insert the battery with ample care to the polarity. Reverse insertion on the polarity will make damage to the inner PCB.

This device complies with Part 15 of the FCC Rules. Operation is subject to the following two conditions: (1) This device may not cause harmful interference, and (2) this device must accept any interference received, including interference that may cause undesired operation.

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to Part 15 of the FCC Rules. These limits are designed to provede reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference in which case the user will be required to correct the interference at his own expense.

U-10 Water Quality Checker is a state-of-the-art instrument for simultaneous multiparameter measurement of water quality. The HORIBA U-10 measures six different parameters of water samples: *pH, conductivity, turbidity, dissolved oxygen, temperature,* and *salinity.*

The U-10 is compact enough to be held in one hand while taking measurements. It has a large easy-to-read LCD readout. Measurements are taken simply by immersing the probe right into the water sample.

The U-10 is extremely versatile and sophisticated, yet easy to use. You will find it a valuable addition to on-site water control operations, whatever your needs – from testing factory discharges to urban drainage, river water, lake and marsh water, aquatic culture tanks, agricultural water supplies, and sea water.

To get the most out of you Water Quality Checker, pleas this *Instruction Manual* carefull before you begin to take measurements.

Note that Horiba cannot be held responsible for any equipment malfunction or failure should the U-10 Water Quality Checker be operated incorrectly or in a manner other than specified in this *Instruction Manual.*

Horiba's aim is to produce the best possible equipment and documentation for our products. We welcome comments, questions, or suggestions for improvement concerning both our products and the accompanying documentation, such as this *Instruction Manual.*

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Note that the contents of this Instruction Manual are subject to change without prior notice as design changes are made on the instrument.

Second edition: November, 1991
First edition: July, 1991

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Section 1

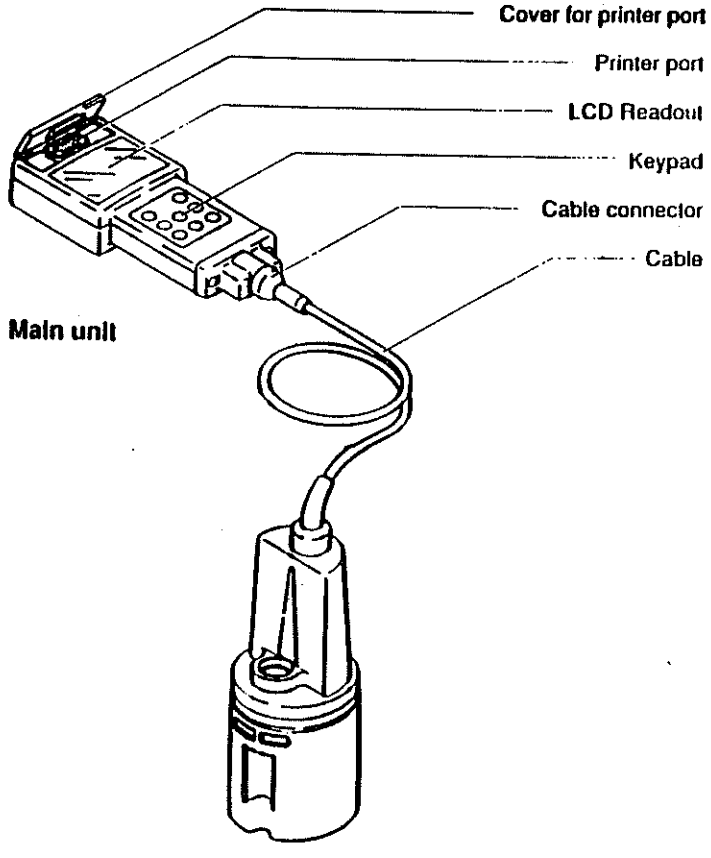
Getting Started

This section first gives an overview of the U-10. It then shows how to set up your U-10 by inserting the DO sensor and the battery.

Configuration of the U-10 2
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Configuration of the U-10

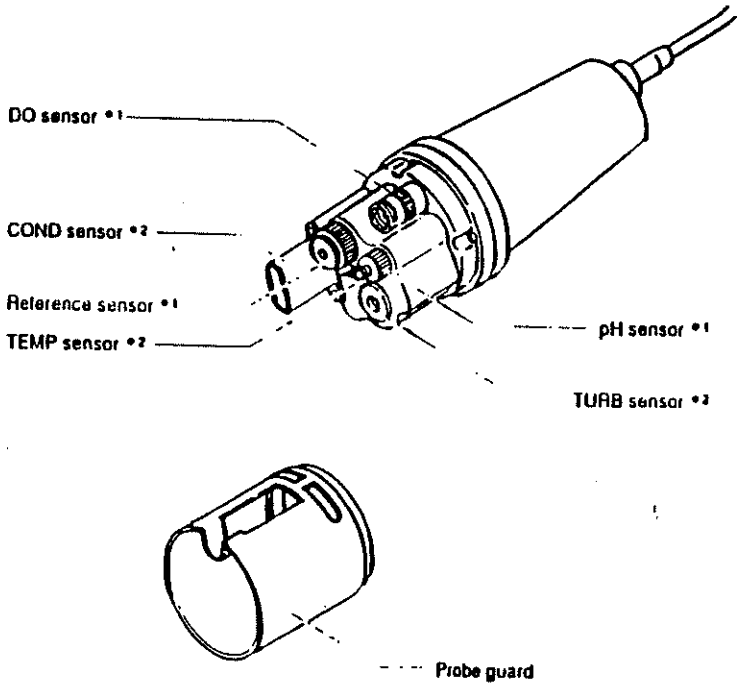
Main unit



Main unit

Probe

Probe

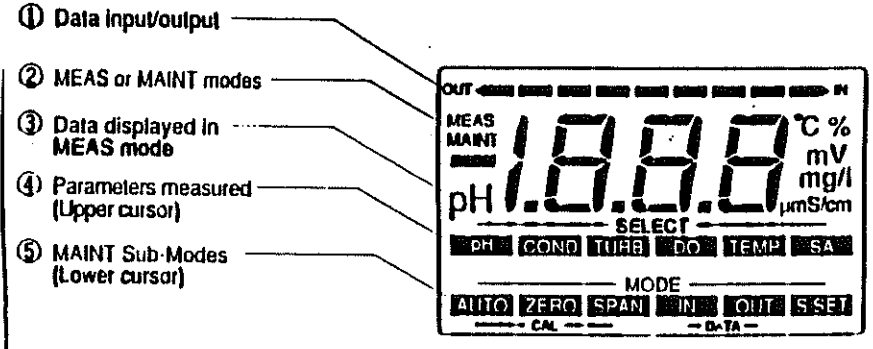


*1. Removable
DO (Dissolved oxygen)
Reference
pH

*2. Non-removable
COND (Conductivity)
TEMP (Temperature)
TURB (Turbidity)

The Readout

The readout has two main functions: (1) it displays the results of measurements, and (2) it serves as a message board to show the operating status of the U-10.



① Data input/output

OUT — Data output

— IN Data input

② MEAS or MAINT modes

The U-10 may be used in one of two modes: Measurement (MEAS) mode or Maintenance mode.

MEAS the U-10 is ready to make 6-parameter measurements

MAINT the U-10 is ready for other operations, e.g., calibration, data input/recall, or salinity setting

③ **Data displayed in MEAS mode**

- 6-parameter results:
  pH, conductivity, turbidity, DO, temperature, and salinity
- Designated value for salinity setting
- Error codes

④ **Parameters measured**

Value displayed on readout is highlighted by upper cursor.

pH	pH
COND	Conductivity
TURB	Turbidity
DO	Dissolved-Oxygen
TEMP	Temperature
SAL	Salinity

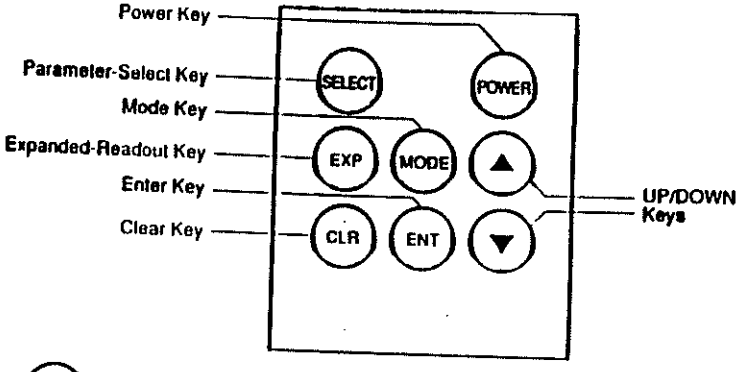
⑤ **MAINT Sub-Modes**

One of six Sub-Modes selected is highlighted by lower cursor.

AUTO	Automatic 1-point calibration
ZERO	Manual zero calibration
SPAN	Manual span calibration
IN	Data input
OUT	Data output (recall)
S SET	Salinity setting correction

The Keypad

The U-10 is operated by the keypad on the main unit, which has eight surface-sealed keys, as illustrated.



POWER

Power Key (POWER)
Turns the main unit ON/OFF.
When this key is pressed to turn the U-10 ON, the readout comes in the MEAS mode, showing the parameter last displayed in the previous measurement. If the U-10 is left with the power ON for 30 minutes without any of the keys being activated, the power will be turned OFF automatically.

SELECT

Parameter-Select Key (SELECT)
Use this key to move the upper cursor to the measured parameter you want to show on the readout. It toggles through the six parameters in order:

pH → COND → TURB → DO → TEMP → SAL

MODE

Mode Key (MODE)
Toggles back and forth between MEAS and MAINT modes. When in the MAINT mode, this key toggles the lower cursor through the six maintenance Sub-Modes.

AUTO → ZERO → SPAN → IN → OUT → S SET

EXP

Expanded-Readout Key (EXP)
Toggles between (1) standard readout value and (2) expanded readout, for greater resolution, with decimal point moved one digit to the left.

ENT

Enter Key (ENT)
This acts like the RETURN Key or Enter Key on a computer keyboard. The U-10 Enter Key has four main functions, depending on which mode the unit is in.

1. In the AUTO Sub-Mode: Press this key to start automatic calibration.
2. In either the ZERO or SPAN Sub-Modes: Used in manual calibration to set the value for the standard solution being used.
3. In the IN Sub-Mode: Inputs data being measured to memory.
4. In the OUT Sub-Mode: Recalls values from one of the 20 Data-Set Nos. that is now shown on the readout. Prints data when a printer is connected.

CLR

Clear Key (CLR)
This acts like the ESCAPE Key on a computer keyboard. It has three main functions, depending on which mode the unit is in.

1. In the AUTO Sub-Mode: Aborts the auto-calibration now in progress.
2. In the IN Sub-Mode: Deletes data in memory from all 20 Data-Sets.
3. When the readout shows an error code: Clears the error code from the readout.

▲ ▼

UP/DOWN keys
Use these keys to select values when in one of the MAINT Sub-Modes. They have two main functions.

1. In either the ZERO or SPAN Sub-Modes: Use these keys to select value for the standard solution.
2. In the OUT mode: Used to toggle through the 20 Data-Set Nos. to select the one you wish to recall.

Setting up the U-10

Preparations of the pH sensor and the reference sensor

1. Remove the protective rubber cap from the pH sensor.
2. Remove the sealing tape from the reference sensor.

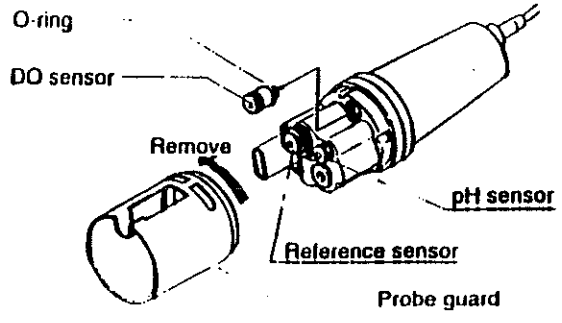
Inserting the DO sensor

WARNING

The DO sensor contains a strong alkaline solution. Should any of this solution come in contact with your clothing or skin, wash it away immediately with plenty of water. Be especially careful not to allow any of the liquid in the DO sensor to get in your eyes.

The Dissolved-Oxygen (DO) sensor has a delicate membrane that can easily be ruptured. For safety's sake, the U-10 is shipped to you with the DO sensor packed separately. You should insert the DO sensor when you unpack your U-10 unit.

1. Make sure that the DO sensor has the correct O-ring, as shown.
2. First, fit the DO sensor lightly into its socket, and then put on the probe guard to align it correctly.
3. Then, tighten the DO sensor securely to the probe body. When doing this, be especially careful not to damage the membrane, which is located in the front of the DO sensor.



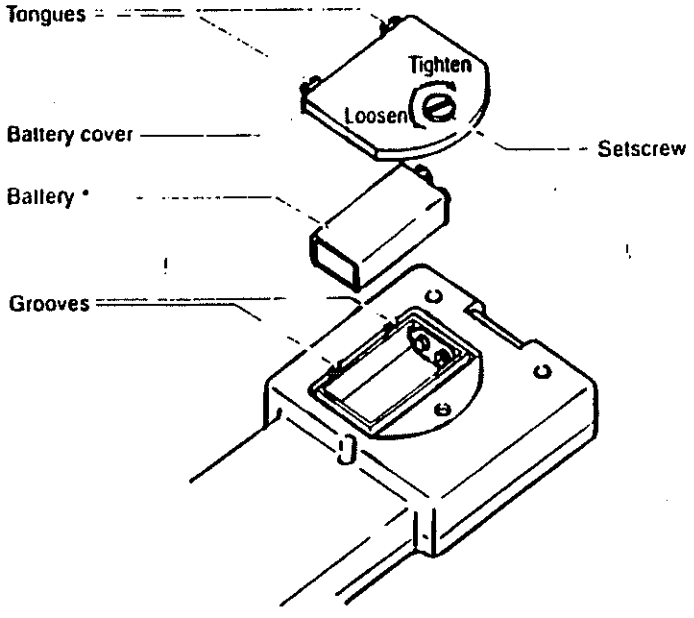
Inserting the battery

The U-10 is shipped from the factory with the battery packed separately.

The battery may be inserted by loosening the set-screw on the battery cover and pulling up the cover. Make sure that the plus and minus poles of the battery match the terminals correctly.

If the readout shows the message Er 1, it means that the battery is defective or exhausted and should be replaced.

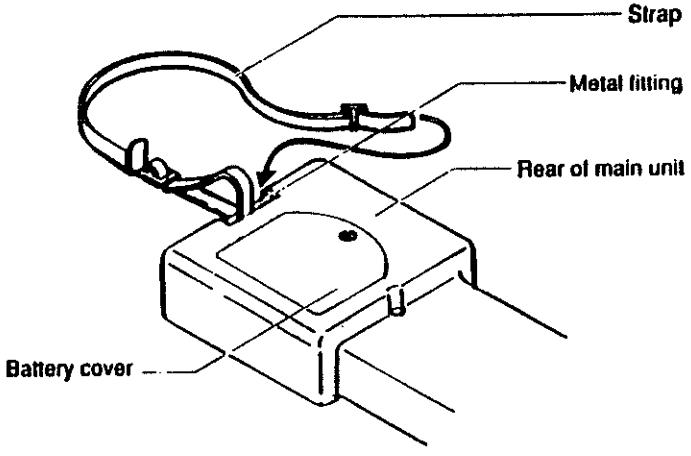
If you are replacing the battery and already have data stored in the U-10 memory that you wish to save, be sure to turn OFF the POWER Key before you remove the old battery. This will assure that data stored in memory will be maintained by the internal backup battery.



* Use a 9V battery

Attaching the carrying strap

Hook both ends of the strap through the metal fitting on back of the main unit, as illustrated.



Section 2

Making Measurements

Making a measurement with the U-10 Water Checker is extremely simple. Just turn on the power and place the probe in the sample of water you wish to measure.

All six parameters are measured simultaneously. These parameters may be stored in memory, printed out, or viewed one-by-one on the LCD readout. For printing and data storage, see the appropriate sections following this one. To view the parameters one-by-one on the readout, use the SELECT Key to toggle the upper cursor through them.

While the U-10 is both rugged and precise, the key to accurate measurements is cleanliness and frequent calibration. It is essential to clean the U-10 thoroughly after each measurement, and it is recommended that you re-calibrate your U-10 as frequently as possible. For best results, you should recalibrate it before each measurement session. Cleaning and calibration procedures are described below in this section and in the following one.

How to make a measurement 12
Initial readout 13
Select the parameter you want shown on the readout ... 14
Expanded readout 15
Measuring fresh water 16
Measuring salt water 17
After measurement: Cleaning and storing the U-10 18

How to make a measurement

POWER **1** Turn the power on.

2 Gently place the probe into the water sample.

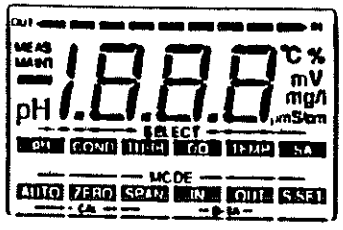
Basically, that's all there is to it: just turn it on and put the probe in the sample. Of course, the U-10 can do many sophisticated things with the sample data, and for best results, you should be careful about calibrating the unit and maintaining it in good condition. This is explained in detail below and in the next section.

Be careful!
Never drop or throw the probe into the water. It is a precision instrument containing five delicate sensors and five pre-amps; you can damage it beyond repair by unnecessary rough handling.

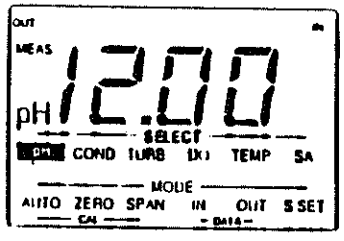
Initial readout

POWER

When you first turn the power on, the U-10 will be in the MEAS mode, the readout will look like this, with all the LCD segments activated.



After about two seconds, the readout will change to show that a new measurement is being made. The readout will show the last parameter that the upper cursor was on when the previous measurement was made, i.e., pH as illustrated here.



(Expanded readout shown)

The display of the decimal point in the readout mode will also be in the same format as was selected with the EXP Key in the previous measurement, i.e., standard or expanded (as illustrated here).

Select the parameter you want shown on the readout of the measured data

SELECT

All six parameters are automatically measured at once. Use the SELECT Key to toggle the upper cursor to the parameter you want.

pH	: pH
COND	: Conductivity
TURB	: Turbidity
DO	: Dissolved oxygen
TEMP	: Temperature
SAL	: Salinity

To get a uniform reading, slowly move the probe up and down to circulate the water through it. (Move it 1 foot (30 cm) per sec.) Then wait for the readout to stabilize while doing this.

Expanded readout

EXP

Use the EXP readout mode when you wish to see the results with one additional decimal place of accuracy. The EXP Key toggles the readout back and forth between standard to expanded display. The table below shows the result of using the EXP readout mode for each of the six parameters.

Table 1. Accuracy of expanded readout

Parameter	Range of measurement	Accuracy	
		Standard readout	Expanded readout
pH	0-14 pH	0.1 pH	0.01 pH
COND	0-1 mS/cm	0.01 mS/cm	0.001 mS/cm
	1-10 mS/cm	0.1 mS/cm	0.01 mS/cm
	10-100 mS/cm	1 mS/cm	0.1 mS/cm
TURB	0-800 NTU	10 NTU	1 NTU
DO	0-19.9 mg/l	0.1 mg/l	0.01 mg/l
TEMP	0-50°C	1°C	0.1°C
SAL	0-4%	0.1%	0.01%

Note that the salinity parameter is the only value not measured directly with its own sensor. The U-10 obtains salinity by converting the conductivity value. If large amounts of conductive ions other than salt-water components are present in the sample, an error may occur. Be cautious when interpreting the salinity results.

Measuring fresh water or salt water?

The U-10 can be set to the salinity for either fresh water or salt water when measuring DO. This is done by using the S.SET Sub-Mode.

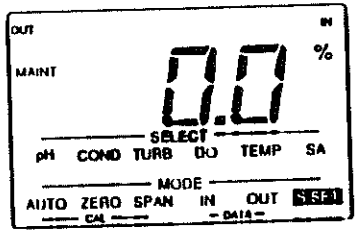
Measuring fresh water

MODE

1. First, use the MODE Key to put the U-10 in the MAINT mode. Keep pressing the MODE Key to toggle the lower cursor to the S.SET Sub-Mode.

▲ ▼

2. Once you are in the S.SET Sub-Mode, use the UP/DOWN Keys to select the salinity value. For fresh water, set the salinity to 0.0%.



ENT

3. Finally, press the ENT Key to complete the salinity setting while in the S.SET Sub-Mode.

MODE

4. When the salinity setting has been made, switch back to the MEAS mode by pressing the the MODE Key.

Measuring salt water

1. First, use the MODE Key to put the U-10 in the MAINT mode. Keep pressing the MODE Key to toggle the lower cursor to the S.SET Sub-Mode.

2. For salt water, set it to *A* (*i.e.*, for auto-salinity.
   The *A* setting should be sufficient for measurements of normal sea water with a salinity value close to 3.3%. For sea water of an unusual salinity, however, and where the value is otherwise known, you may wish set the value manually to any salinity within the range of 0.0%-4.0%. (You may also possibly want to use a manual setting if, for example, the COND sensor is malfunctioning but it is still desirable to take readings of the other parameters.)

3. Finally, press the ENT Key to complete the salinity setting while in the S.SET Sub-Mode.

4. When the salinity setting has been made, switch back to the MEAS mode by pressing the the MODE Key.

After measurement: Cleaning and storing the U-10

1. Turn OFF the power.

2. Wash the probe thoroughly with tap water. Be sure to flush off all of sample solution from the probe.

Storing the U-10 for brief periods, *i.e.*, about 1 week or less:
Fill the calibration beaker with tap water and fit the probe over it.

For longer storage
The pH sensor must always be kept moist. Fill the small rubber cap with water and use it to cover the pH sensor.
The KCl internal solution in the reference sensor may seep out over time. Place vinyl tape around the O-ring portion to prevent this.
If you are going to store the U-10 for a prolonged period without using it, remove the battery from the main unit.

Section 3

Calibrating the U-10

The U-10 Water Checker may be calibrated either manually or automatically. The 4-parameter auto-calibration procedure is quite handy and should be sufficient for most measurement operations.

Manual calibration for each of the four parameters is more accurate but, of course, also more time-consuming. This method should be used for more precise measurement. The manual calibration procedure is explained below in detail, following the description of the auto-calibration procedure.

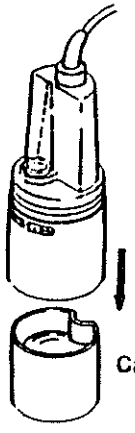
The auto-calibration procedure is extremely simple. The U-10 Water Checker uses just a single solution to do a simultaneous calibration of four parameters: *pH, COND, TURB,* and *DO*. Your U-10 comes with a bottle of standard phthalate pH solution and a calibration beaker for this purpose.

Auto-calibration procedure 20
Manual (2-point) calibration procedures 23
pH Calibration 24
1.Zero calibration 24
2.Span calibration 25
COND Calibration 26
1.Zero calibration 28
2.Span calibration 29
TURB Calibration 30
1.Zero calibration 31
2.Span calibration 31
DO Calibration 32
1.Zero calibration 33
2.Span calibration 33

Auto-calibration procedure

Fill the calibration beaker to about 2/3 with the standard solution. Note the line on the beaker.

Fit the probe over the beaker, as illustrated. Note that the beaker is specially shaped to prevent the DO sensor from being immersed in the standard solution. This is because the DO auto-calibration is done using atmospheric air.

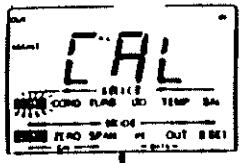


Calibration beaker

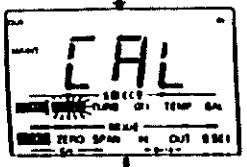
MODE — With the power on, press the MODE Key to put the unit into the MAINT mode. The lower cursor should be on the AUTO Sub-Mode; if it is not, use the MODE Key to move the lower cursor to AUTO.

ENT — With the lower cursor on AUTO, press the ENT Key. The readout will show CAL. Wait a moment, and the upper cursor will gradually move across the four auto-calibration parameters one-by-one: *pH, COND, TURB,* and *DO*. When the calibration is complete, the readout will briefly show End and then will switch to the MEAS mode.

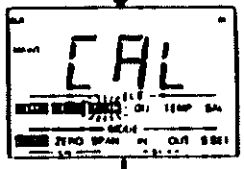
The upper cursor will blink while the auto-calibration is being made. When the auto-calibration has stabilized, the upper cursor will stop blinking.



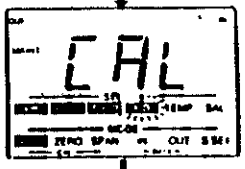
First, pH is being auto-calibrated



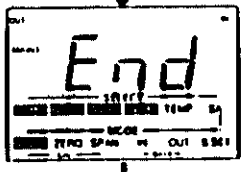
Then, COND is being auto-calibrated



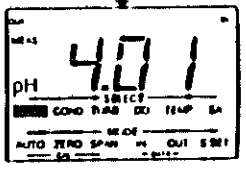
Next, TURB is being auto-calibrated



Finally, DO is being auto-calibrated



Auto-calibration now ends

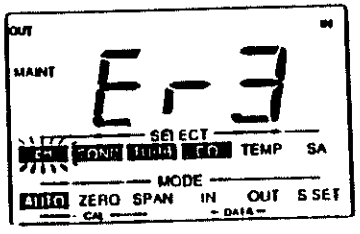


And the readout switches to the MEAS mode

Note: If you wish to abort the auto-calibration for any reason, press the CLR Key. The parameters auto-calibrated so far will be stored in memory.

Auto-calibration error

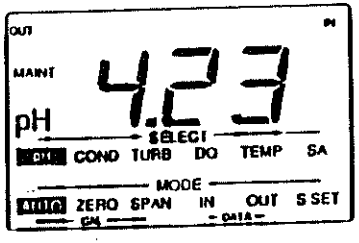
After the DO auto-calibration, if the unit does not switch to the MEAS mode as it should, and the readout shows either E-3 or E-4, an auto-calibration error has occurred. Parameters will blink where an error occurred.



pH auto-calibration error

CLR

If this happens, re-do the auto-calibration. First, press the CLR Key to cancel the error code.



ENT

Then press the ENT Key to re-start the auto-calibration. Restart the auto-calibration beginning again with pH.

Manual (2-point) calibration procedures

For normal measurements, the 4-parameter auto-calibration described above is sufficiently accurate. However, you may wish to do a parameter-by-parameter, 2-point manual calibration of one or more of the four parameters. This is recommended either for high-accuracy measurements, especially when using the expanded readout mode. It is necessary if a new probe is being used for the *first time*.

Parameters to be calibrated manually.

pH	• Zero	(see page 24.)
	• Span	(see page 25.)
COND	• Zero	(see page 28.)
	• Span	(see page 29.)
TURB	• Zero	(see page 31.)
	• Span	(see page 31.)
DO	• Zero	(see page 32.)
	• Span	(see page 33.)

Parameters not to be calibrated.

Sample temperature
Salinity

pH calibration

pH calibration on the U-10 is done using two commercially-available standard solutions of different pH values, one for the zero calibration, the other for the span calibration. Note that the temperature characteristics of the various standard solutions that are available may differ; therefore, before using these two solutions to make the pH calibration, carefully measure the temperature and determine the temperature characteristics of each.

Preparation

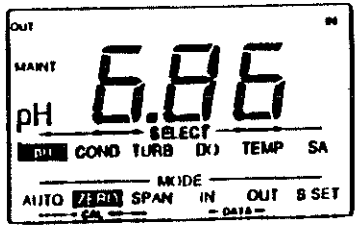
Wash the probe 2-3 times, using de-ionized or distilled water. Place it in a beaker of each standard solution.

1. Zero calibration

Use a pH7 standard solution for the zero calibration.

Operation

1. With the power on, press the MODE Key to put the unit into the MAINT mode.
2. Press the MODE Key again to move the lower cursor to ZERO.
3. Use the SELECT Key to move the upper cursor to pH.
4. When the readout has stabilized, use the UP/DOWN Keys to select the value of the pH 7 standard solution at the temperature of the sample. Refer to Table 2 for pH values of standard solutions at various temperatures.



5. Press the ENT Key to complete the zero calibration for pH.

2. Span calibration

Use either a pH4 or a pH9(10) standard solution for the span calibration.

Operation

MODE

1. Use the MODE Key to move the lower cursor to SPAN.

▲ ▼

2. As in Step 4. above in zero calibration, when the readout has stabilized, use the UP/DOWN Keys to select the value of the standard solution (i.e., either pH4 or pH9) at the temperature of the sample. Again, refer to Table 2 for pH values of standard solutions at various temperatures.

ENT

3. Press the ENT Key to complete the span calibration for pH.

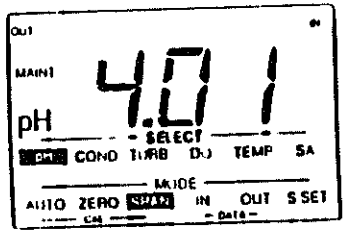


Table 2 pH values of standard solutions at various temperatures*

Temperature °C / °F	pH2[a]	pH4[b]	pH7[c]	pH9[d]	pH10[e]	pH12[f]
0 / 32	1.67	4.01	6.98	9.46	10.32	13.43
5 / 41	1.67	4.01	6.95	9.39	10.25	13.21
10 / 50	1.67	4.00	6.92	9.33	10.18	13.00
15 / 59	1.67	4.00	6.90	9.27	10.12	12.81
20 / 68	1.68	4.00	6.88	9.22	10.06	12.63
25 / 77	1.68	4.01	6.86	9.18	10.01	12.45
30 / 86	1.69	4.01	6.85	9.14	9.97	12.30
35 / 95	1.69	4.02	6.84	9.10	9.93	12.14
40 / 104	1.70	4.03	6.84	9.07	9.89	11.99
45 / 113	1.70	4.04	6.83	9.04	9.86	11.84
	1.71	4.06	6.83	9.01	9.83	11.70

a : oxalate, b : phthalate, c : neutral phosphate, d : borax,
e : carbonate, f : Sat.calcium hydroxide solution

* These pH valves are for Japanese standard solutions. Should you prefer to use different standard solutions, be sure to make the proper adjustments in calibration

COND calibration

The U-10 can measure conductivity in the range of 0-100 mS/cm. Depending on the sample concentration, however, the U-10 automatically selects the proper range out of its three possible ranges of 0-1 mS/cm, 1-10 mS/cm, and 10-100 mS/cm.

Therefore, if you are doing a manual calibration for COND, this must be done for each of the three ranges. However, since the zero point is common for all three ranges, only the three one-point span calibrations need be done separately.

Preparing the standard solution for COND span calibration

This solution uses a potassium chloride as a reagent. For greater accuracy, the solution should be freshly prepared each time. If it is unavoidable to use a stored solution, be sure to keep it tightly capped in a polyethylene or hard glass bottle. The shelf life of this solution is six months. Date-stamp the bottle for reference. Never use a KCl standard solution that has been stored for more than six months: the calibration accuracy may be adversely affected.

Use potassium chloride powder of the best quality commercially available. Dry the powder for two hours at 105°C, and cool it down, in a desiccator. Weigh out an appropriate amount of dried and cooled potassium chloride powder according to the table below. Make the potassium chloride standard solution as shown.

Table 3 Making the potassium chloride standard solution

KCl standard solution	KCl weight g	Conductivity* mS/cm	Range to be calibrated mS/cm
0.005N	0.373	0.718	0-1
0.05N	3.73	6.67	1-10
0.5N	37.28	58.7	10-100

* Value at the temperature, 25°C

To prepare the standard solution, use a 1-liter volumetric flask. First, dissolve the KCl in a small amount of de-ionized or distilled water. Then fill the flask with de-ionized or distilled water up to the 1-liter line. Finally, shake the solution to mix it thoroughly.

1. Zero calibration

This calibration is carried out in atmospheric air; no solution is needed.

Preparation

Wash the probe 2-3 times, using de-ionized or distilled water. Shake the probe to remove any water droplets from the COND sensor. Then allow it to dry by exposing it to fresh air.

Operation



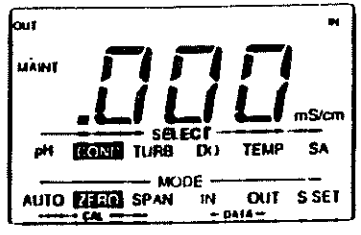
1. Use the MODE Key to move the lower cursor to ZERO.



2. Use the SELECT Key to move the upper cursor to COND.



3. Use the UP/DOWN Keys to set the readout to zero.





4. Press the ENT Key. This completes the zero calibration for COND.

2. Span calibration

This procedure uses a standard solution of potassium chloride. **For best results, a fresh batch of the solution should be prepared each time.** See page 27 for details.

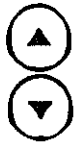
Preparation

Wash the probe 2-3 times using de-ionized or distilled water. **Following this, wash it 2-3 times in the KCl standard solution you have prepared. Then place the probe in a beaker of the KCl solution maintained at a temperature of 25±5°C.**

Operation



1. Use the MODE Key to move the lower cursor to SPAN.



2. After the readout stabilizes, as you did for the pH calibration, use the UP/DOWN Keys to select set the value of the KCl standard solution, referring to the KCl table.



3. Press the ENT Key to complete the span calibration for this COND range.

4. Repeat this procedure for the three ranges, using each of three values of KCl standard solutions.

TURB calibration

Use good-quality de-ionized water, which may be considered as having a turbidity of zero. If that is not readily available, distilled water may be used instead. When doing the turbidity zero calibration, it is particularly crucial that you clean the probe thoroughly. Never use a dirty probe; otherwise the calibration will be unreliable.

Preparing the standard solution for TURB span calibration

1. Weigh out 5.0 g of hydrazine sulfate.
2. Dissolve this in 400 m*l* of de-ionized or distilled water.
3. Then weigh out 50 g of hexamethylenetetramine, and dissolve it in 400 m*l* of de-ionized or distilled water.
4. Mix these two solutions, add enough de-ionized or distilled water to make 1,000 m*l*, and stir the mixed solution thoroughly.
5. Allow this solution to stand for 24 hours at a temperature of 25 ±3°C.

   The turbidity of this solution is equivalent to 4000 NTUs. The shelf-life of this solution is six months; i.e., this 4,000-NTU value will remain accurate for a maximum of six months.

   Each time you carry out this calibration, it is necessary to dilute the 4,000-NTU standard solution to prepare an 800-NTU standard solution for calibration. To do this, measure out 50 m*l* of the 4,000-NTU solution into a 250-m*l* measuring flask.

   It is recommended that you use a rubber pipette aspirator for this. Then add de-ionized or distilled water up to the 250-m*l* line.

   The standard solution used here for the turbidity calibration will precipitate easily. Therefore, be sure to stir the solution thoroughly before use.

1. Zero calibration

Preparation

Wash the probe thoroughly 2-3 times using de-ionized or distilled water. Shake off excess water droplets, and then place it in a beaker of de-ionized or distilled water.

Operation



1. Use the MODE Key to move the lower cursor to ZERO.



2. Use the SELECT Key to move the upper cursor to TURB.



3. After the readout has stabilized, set it to 0.0, using the UP/DOWN Keys.



4. Press the ENT Key to complete the zero calibration for TURB.

2. Span calibration

Preparation

Wash the probe thoroughly, using de-ionized or distilled water. Shake off excess water droplets. Then place it in a beaker of the 800-NTU solution you have prepared for this purpose.

Operation

1. Stir this 800-NTU span standard solution thoroughly.



2. Use the MODE Key to move the lower cursor to SPAN.

3. After readout has stabilized, i.e., about 60 to 90 seconds, set the readout to "800" NTU, which is the value for this standard solution.



4. Press the ENT Key to complete the span calibration for TURB.

DO calibration

Unlike the other calibration procedures, the solution for the DO calibration cannot be stored for use; because the amount of dissolved oxygen in the solution is crucial, a fresh batch must be prepared each time, just before it is used in the DO calibration.

1. Zero calibration

Use a solution of sodium sulfite dissolved in either de-ionized water or tap water.

Preparation

1. Add about 50g of sodium sulfite to 1,000 ml of water (either de-ionized water or tap water will do). Stir this mixtuer to dissolve.

2. Wash the probe 2-3 times in tap water, and place it in the zero standard solution.

Operation



1. Use the MODE Key to move the lower cursor to ZERO.



2. Use the SELECT Key to move the upper cursor to DO.



3. After the readout has stabilized, set it to 0.0, using the UP/DOWN Keys.



4. Press the ENT Key. This completes the zero calibration for DO.

2. Span calibration

Use either de-ionized water or tap water that has been saturated with oxygen in air.

Preparation

1. Put 1 or 2 liters of water in a container (either de-ionized water or tap water will do). Use an air pump to bubble air through the solution until it is oxygen-saturated.

2. Wash the probe 2-3 times in tap water, and put it in the span calibration solution.

Operation

1. First, be sure the U-10 is set for fresh water readings. To do this, set the S.SET Sub-Mode to 0.0%.

MODE

2. Then, use the MODE Key to move the lower cursor to SPAN.

3. After the readout has stabilized, while slowly moving the probe up and down in the solution, set the readout value to the appropriate DO value for the temperature of this solution. For DO values at various temperatures, refer to Table 4.

ENT

4. Press the ENT Key to complete the span calibration for DO.

Table 4 Amounts of saturated dissolved oxygen in water at various temperatures, salinity = 0.0%

Temperature	DO	Temperature	DO
0 °C	14.16 mg/l	21 °C	8.68 mg/l
1	13.77	22	8.53
2	13.40	23	8.39
3	13.04	24	8.25
4	12.70	25	8.11
5	12.37	26	7.99
6	12.06	27	7.87
7	11.75	28	7.75
8	11.47	29	7.64
9	11.19	30	7.53
10	10.92	31	7.42
11	10.67	32	7.32
12	10.43	33	7.22
13	10.20	34	7.13
14	9.97	35	7.04
15	9.76	36	6.94
16	9.56	37	6.86
17	9.37	38	6.76
18	9.18	39	6.68
19	9.01	40	6.59
20	8.84		

Section 4

Data Storage and Printout

The U-10 can store up to 20 sets of data, 120 data points, of the values measured for each of the six parameters: pH, COND, TURB, DO, TEMP, and SALINITY. Values stored in memory can be recalled to the readout as desired.

If a printer is connected to the U-10 printer port, whenever a Data-Set is either stored in memory or recalled to the readout, it can also be simultaneously output to the printer.

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Storing data

MODE

1. Press the MODE Key to put the U-10 in the MAINT mode.

MODE

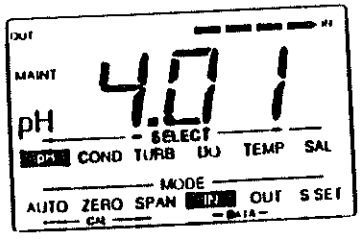
2. Continue to press the MODE Key to move the lower cursor to IN, the *Input* Sub-Mode.

SELECT

3. Use the SELECT Key to move the upper cursor to the parameter you wish to see on the readout.

ENT

4. When the readout stabilizes on a value, press the ENT Key. This will automatically input the set of six parameters for this measurement into memory.



The readout will first show the Data-Set No. for about two seconds. At the top right-hand corner, a dashed arrow points to IN, showing that data is being input. Then each parameter is automatically read into memory, one-by-one from pH to salinity. The upper cursor skips along to show this. If a printer is connected, these six values will also be printed out at the same time.

The upper cursor then returns to pH, with the U-10 still in the IN Sub-Mode.

ENT

5. You may now continue and input another set of data: simply press the ENT Key again.

The Data-Set No. will automatically advance one digit, and the next set of six parameters will be read into memory in the same manner. This procedure can be repeated for up to a total of 20 Data-Sets.

If 20 Data-Sets have been read into memory, the storage capacity is full and no more data may be input. The U-10 will beep three times to indicate the memory is full.

MODE

6. To return the readout to the previous setting in the MEAS mode, press the MODE Key again.

alling data

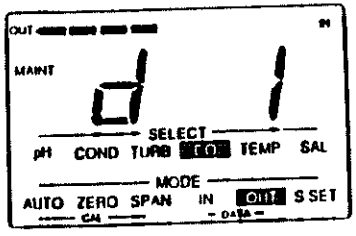
MODE

1. Press the MODE Key to put the U-10 in the MAINT mode.

MODE

2. Continue to press the MODE Key to move the lower cursor to OUT, the *Output* Sub-Mode. The readout will show d.1, meaning Data-Set No. 1.

At the top left-hand corner, a dashed arrow points to OUT, showing that data can be output now to the readout.



▲ ▼

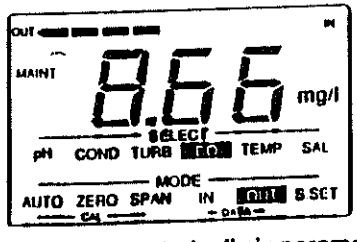
3. Use the UP/DOWN Keys to display the Data-Set No. of the values you wish to recall.

SELECT

4. Use the SELECT Key to move the upper cursor to the parameter you wish to view.

ENT

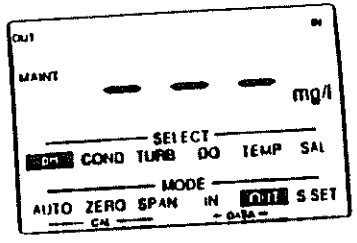
5. Press the ENT Key to display the data on the readout.



If a printer is connected, all six parameters in this Data-Set will also be printed out at the same time.

ENT

6. When the ENT Key is pressed again, the next Data-Set No. is displayed in order, i.e., *d2*, if two data sets are in memory. At this point, you can either press the ENT Key again to view the contents of this Data-Set, or you can use the UP/DOWN Keys to go up or down to another Data-Set No.
   If a particular Data-Set is empty, three dashes appear on the readout.



MODE

7. To return the readout to the previous setting in the MEAS mode, press the MODE Key again.

Deleting data

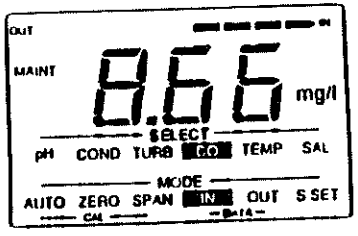
Set the U-10 as if you were going to input data:

MODE

1. Press the MODE Key to put the U-10 in the MAINT mode.

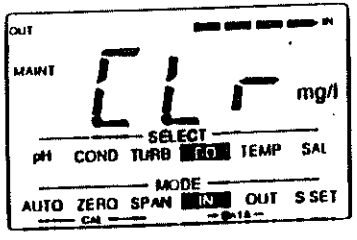
MODE

2. Continue to press the MODE Key to move the lower cursor to IN, the Input Sub-Mode.



CLR

3. Then, to erase all the data from all the Data-Sets in memory, press the CLR Key. The readout will show the message CLr for about two seconds.

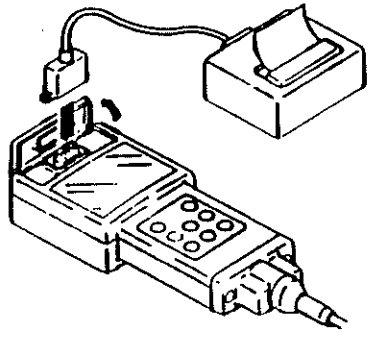


Be careful!
You cannot delete individual Data-Sets. The CLR Key always erases all data from memory.

Printing out data

If a printer is connected to the U-10 printer port, whenever a Data-Set is either stored in memory or recalled to the readout, it is also simultaneously output to the printer.

The U-10 printer port is a standard Centronics parallel port. To connect a parallel printer to the U-10: Open the rubber printer-port cover, located directly over the readout on the main unit, and connect the printer cable.



Note:
When a printer is not being used, disconnect the cable from the U-10 printer port, and close the cover tightly.

- Sample printout

```
NO. 1 DATE  /  /
 pH      5.0
 COND    1.5    mS/cm
 TURB  390      NTU
 DO      0.5    mg/l
 TEMP   23      °C
 SAL     1.0    %
NO. 2 DATE  /  /
 pH      3.1
 COND    1.3    mS/cm
 TURB  270      NTU
 DO      0.7    mg/l
 TEMP   25      °C
 SAL     0.1    %
NO. 3 DATE  /  /
 pH      3.1
```


Section **5**

Daily Maintenance and Troubleshooting

For accurate measurements and prevention of malfunction, routine careful maintenance of the U-10 is important. In particular, failure to maintain the sensors properly can lead to serious trouble or incorrect measurements. The U-10 is provided with error-code functions for the ready detection of potential problems.

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Error Codes

The U-10 has an easy-to-understand error message function so you can spot trouble readily. Error codes are displayed on the readout and the unit will beep if an error occurs.
(Note that if you press an incorrect sequence of keys, the unit will beep three times to indicate you have pushed the wrong key.)

Error Code	Cause	Action
Bad battery Er 1	• Defective or low battery	• Replace battery
Failure in main unit Er 2	• Malfunction of memory backup IC	• Push POWER Key to turn the U-10 ON again. If this error code is still displayed, contact your Horiba dealer for repair or replacement.
Zero-calibration error Er 3	*for all parameters*	
	• Poor connection in probe-to-main unit cable	• Connect the cable securely.
	• Water in one of the sensor sockets	• Dry out the sensor sockets.
	• Temperature of sample exceeds maximum scale of U-10	• Replace the probe.
	for pH	
	• Contaminated pH sensor.	• Clean the pH sensor.
	• Improper concentration of reference solution in reference sensor	• Replace the reference solution.
	for COND	
	• Contaminated COND sensor	• Clean the sensor, using tooth brush and neutral detergent.

Error Code	Cause	Action
	for TURB	
	• Contaminated or defective LED sensor	• Clean out the tube containing the LED turbidity sensor, using test tube brush and neutral detergent. Never use an abrasives or cleansers for this.
	for DO	
	• Broken DO sensor membrane.	• Check the LED turbidity sensor. If it defective, the entire probe must be replaced. Check DO sensor. If defective, replace.
Span-calibration error Er 4	*for all parameters*	
	• Poor connection in probe-to-main unit cable	• Connect the cable securely.
	• Water in one of the sensor sockets	• Dry out the sensor sockets.
	• Temperature of sample exceeds maximum scale of U-10	• Replace the probe.
	for pH	
	• Contaminated pH sensor.	• Clean the pH sensor.
	• Improper concentration of reference solution in reference sensor	• Replace the reference solution.
	for COND	
	• Contaminated COND sensor	• Clean the sensor, using tooth brush and neutral detergent.
	for TURB	
	• Contaminated or defective LED sensor	• Clean out the tube containing the LED turbidity sensor, using test tube brush and neutral detergent. Never use an abrasives or cleansers for this. • Check the LED turbidity sensor. If it defective, the entire probe must be replaced.

Error Code	Cause	Action
Span-calibration error E-4	*DO Auto-calibration* • Broken DO sensor membrane. • Excessive difference between DO sensor temperature and atmospheric temperature. *DO aqueous solution calibration* • Broken DO sensor membrane. • Contaminated electrode. • Insufficient agitation of solution.	• Check DO sensor membrane. If defective, replace. • Leave DO sensor in atmosphere for 30-60 min. • Check DO sensor membrane. If defective, replace. • Clean the electrode using a soft brush, taking care not to scratch membrane. • Agitate solution thoroughly.
Memory full E-5	• Data-sets for 20 samples are already in memory.	• To delete all data from memory, put the U-10 in the IN Sub-Mode mode and press the CLR Key.
Printer error E-6	• Jammed printer paper. • Poor cable connection. • Wrong printer. • Defective printer.	• Eliminate jamming of printer paper. • Replace the cable. • Use proper parallel Centronics printer. • Replace the printer as necessary.

...inal probe maintenance

Washing the turbidity sensor

The sensor is a glass tube. Wash out the tube and remove stains carefully, using tap water and a test tube brush.

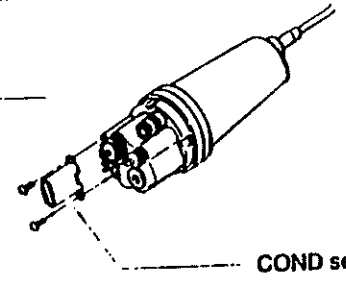
Be careful not to scratch the inside of the glass tube. Never use abrasives or cleansers.



Cleaning the conductivity sensor

Remove COND sensor guard, and carefully use a soft brush to clean off any dust from the sensor unit.

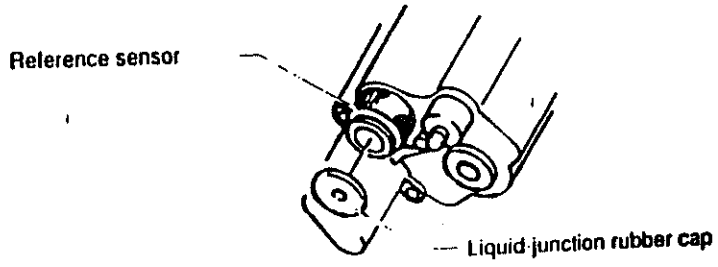
Be sure to replace the COND sensor guard before taking measurements.



Recharging the reference sensor with reference solution

Recharge the reference sensor with reference solution about once every two months, as follows.

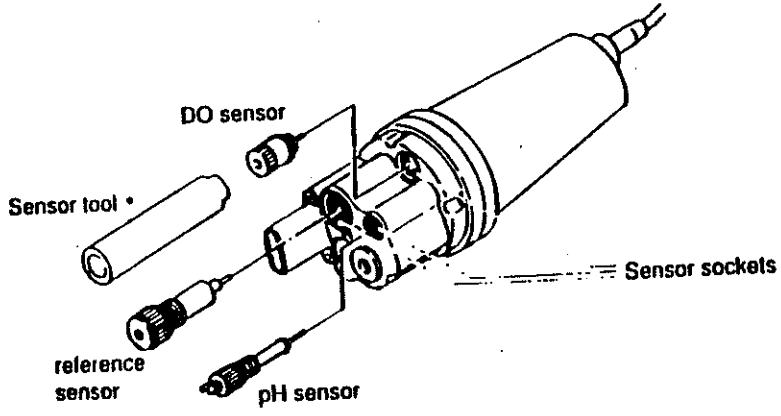
1. Remove the liquid-junction rubber cap from the reference sensor, and pour out the old solution.
2. Fill the reference sensor completely with new reference solution. Make sure there are no air bubbles.
3. Replace the liquid-junction rubber cap.
4. Carefully wash off all excess reference solution from the probe.



Replacing faulty sensors

Three of the U-10's sensors are replaceable: the *pH sensor*, the *reference sensor*, and the *DO sensor*.
These may be replaced as follows.

1. Wipe off any water droplets from the probe.
2. Remove faulty sensor.
3. Insert the new sensor carefully with your fingers.
4. Be careful not to let the sensor sockets get wet.

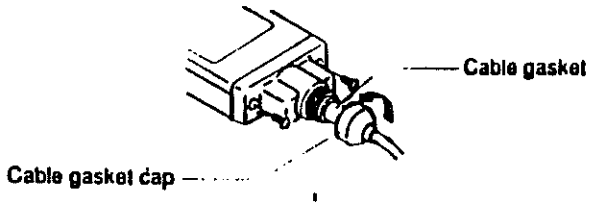


• When replacing the DO sensor, use the sensor tool provided as an accessory.

Replacing a faulty probe

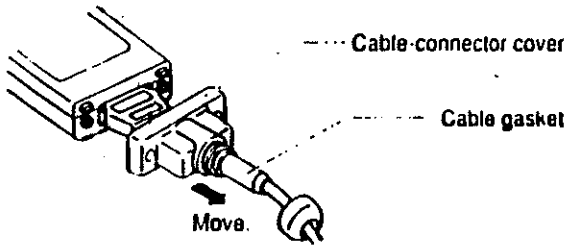
Disconnect the cable from the main unit

1. Loosen the cable gasket cap, and remove cap from gasket.



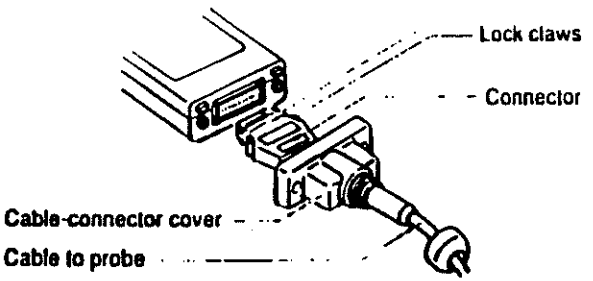
2. Slide back the gasket.

3. Back off the two screws on the cable-connector cover.



4. Slide off the cable-connector cover to expose the connector lock claws.

5. Press lock claws on both sides with your fingers to release the connector. Pull out the connector from the main unit.



Connect the new probe

1. Insert the connector until it clicks.

2. Re-attach the cable-connector cover to the main unit.

3. Slide the cable gasket toward the cable-connector cover, and screw on the cable gasket cap.

Before you use a new probe for the first time, it is necessary to calibrate it manually for all four parameters. Refer to Section 3, "Calibrating the U-10," for instructions on manual calibration.

WELL WIZARD®

Dedicated sampling systems

Installation, Operation, and Maintenance User's Guide

Part No. 34999

QED
Ground Water Specialists™

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A QuickStart Guide to This Book

This book contains a lot of information about the Well Wizard components, what they do, and how to install them. You probably won't need all of that information every time you pick up the book. Feel free to read only what you need—the information is structured so you can do that. The following table shows where to go to find the types of information you want.

Where to Go to Find What You Want

For Information About...	Look Here...
The Well Wizard components and what they do	Chapter 1: "Introducing Well Wizard"
How to install the Well Wizard components	If you received *pre-assembled* components, Chapter 2: "Installing the Components;" if you received *unassembled* components and bulk tubing, Chapter 5: "Installing a Pump Using Bulk Tubing"
How to purge excess water from a well	Chapter 3: "Purging the Well"
How to collect a sample	Chapter 4: "Collecting a Sample"
How to maintain (sometimes replace) some components of your system	Chapter 6: "Maintaining Your Well Wizard System"
What your pump configuration looks like	Appendix A: "Specifications"
How to help QED troubleshoot your system	Appendix B: "My Well Wizard is Broken: What to Do"
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1

INTRODUCING WELL WIZARD

To monitor the quality of ground water, you need an efficient way to collect unbiased samples. Well Wizard is a total system for meeting all your ground water monitoring needs–with the flexibility to meet your special requirements. This chapter describes the components of the Well Wizard system.

The Well Wizard system includes both *dedicated* and *portable* components. The water-contacting components are dedicated; you permanently install them in each well. The control elements are portable; you transport them from well to well.

Dedicated Components

Dedicated Well Wizard components include:

- A sampling pump.
- Pump tubing.
- An optional inlet screen.
- A well cap.
- An optional pneumatic static water-level probe.
- An optional packer.
- An optional purge pump.

The following sections describe these components.

Sampling Pump

A Well Wizard sampling pump is an air-actuated bladder pump that you permanently position in the well.

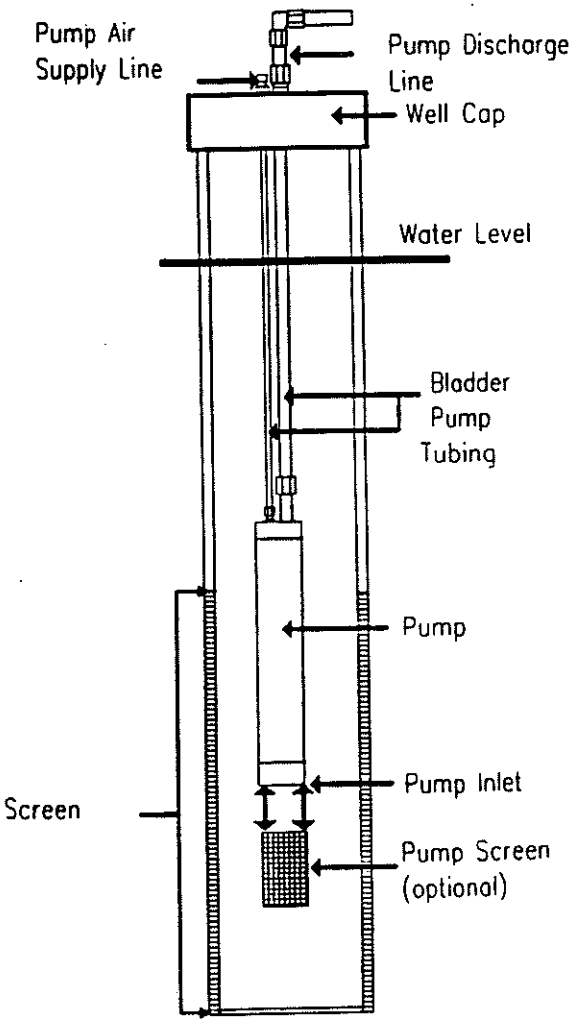


Figure 1-1: Well Wizard Pump Installed in a Well

As Figure 1-1 shows, you normally position the pump inlet midway in the screen section of the well, suspending it by two tubes that supply air to the pump and convey the water sample to the well cap. Whenever possible, pumps are shipped already preassembled to the tubing and the well cap assembly.

Several types of Well Wizard bladder pumps are available.

1100 Series Pumps

The 1100 series pumps include four major components:

- Upper-end check valve assembly (polyvinyl chloride (PVC) or Teflon™).
- Lower-end check valve assembly (PVC or Teflon).
- Bladder cartridge (Teflon).
- Pump body (PVC or Teflon).

You can totally disassemble this pump without tools by unscrewing each end cap and pushing the bladder cartridge out of the pump body (for more information, refer to the instructions included with the field-replaceable bladder kit). The weep hole on the water-discharge fitting aids cold-weather operation by allowing the water discharge line to drain after use.

1200 Series Pumps

The 1200 series pumps include two major components:

- Bladder cartridge assembly (either Teflon and stainless steel or PVC and stainless steel).
- Pump body (stainless steel).

You can partially disassemble this pump (for more information, refer to the instructions included with the field-replaceable bladder kit). The pump body covers the weep hole on the upper portion of the bladder cartridge to aid cold-weather operation, so you may sometimes see water dribble from the pump body.

1500 Series Pumps

The 1500 series pumps are the same as the 1200 series Well Wizard pumps except that they are much longer. They're available in stainless steel with PVC or stainless steel with Teflon. Also known as *Power Pumps*, these pumps save you from needing both a purge pump and a sampling pump in deep wells with moderate purge volumes, by delivering higher flow rates.

How Bladder Pumps Work

The bladder pump has two alternating cycles (refer to Figure 1-2):

- **During the discharge cycle,** air forced into the space between the pump body and the pump bladder squeezes the water inside the bladder into the exit/entrance holes of the fill rod. As air pressure increases, liquid–having no place else to go–is forced up the discharge line and to the surface. The bottom check ball is forced down by the air pressure in the pump; this seals the inlet so that no water can enter the bladder chamber.
- **During the refill cycle,** with no air pressure holding it down, the water pressure pushes the bottom check ball up, allowing the water to reenter the bladder chamber. The bladder expands as it refills with water. The top check ball seals because of the force of the water pressure in the discharge tubing.

Caution: Although you can operate a Well Wizard pump *dry* without damaging it, the bladder can be punctured if you pump sand. So be sure to use an inlet screen in wells with high sand and sediment content, or when the inlet of the pump is placed within 2 feet of the bottom of the well. Remember, the Well Wizard 10-year warranty is void if you don't use an inlet screen.

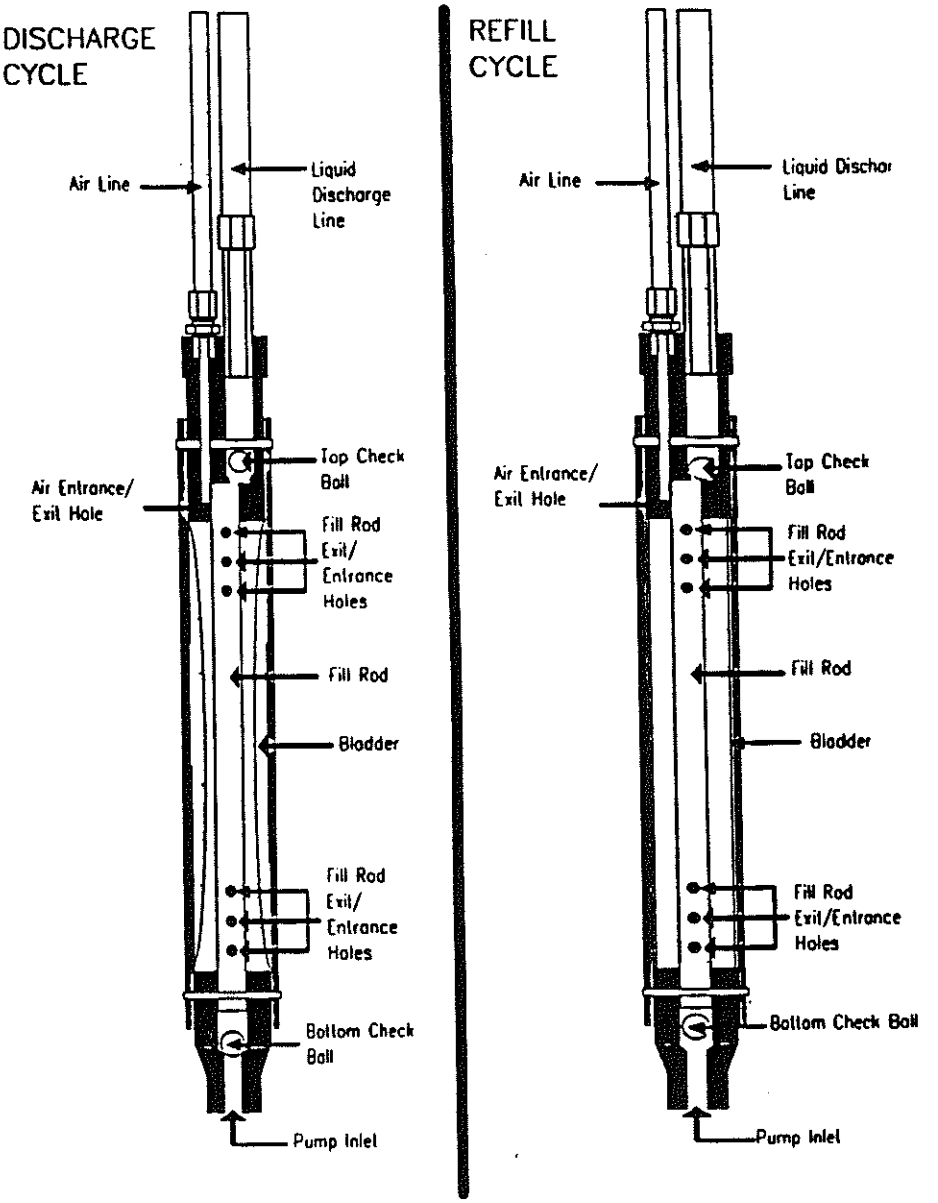


Figure 1-2: Bladder Pump Cycles

Pump Tubing

A ground water sample is only as good as the tubing it runs through. Your Well Wizard was shipped with one of the following types of superior-quality tubing:

- Polyethylene.
- Teflon-lined polyethylene.
- Teflon.

Most tubing is supplied as a bonded pair (air supply and discharge), to save time and avoid tube entanglement.

Unless your order specified that you wanted *bulk* tubing, the tubing for your Well Wizard bladder pump is pre-cut to the correct length for your well. If you also have a Purge Mizer, you'll need to fit and trim its tubing; if you have a Purge Master, that tubing is pre-cut but not connected to the pump or cap. Instructions for these procedures are in Chapter 2, "Installing the Components."

Inlet Screen

An inlet screen can protect the bladder in your Well Wizard pump by preventing sand from contacting the bladder. If you install a screen on your dedicated Well Wizard bladder pump, QED warrantees the pump for a full 10 years.

Well Cap

You fit a well cap to the top of the well casing to suspend the pump and tubing. There are two terminal fittings inside the basic well cap (see Figure 1-3):

- A compression *through fitting* for the discharge line.

- A short brass *quick-connect nipple* for the pump air-supply line.

The *protected* well cap has a lid with a lock pin. You can record well identification and reference date information on the cap label. The *unprotected* well cap is meant for wells located within a user-supplied protected standpipe.

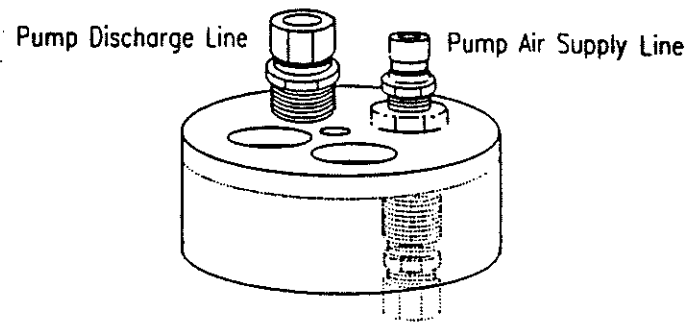


Figure 1-3: Well Cap

Pneumatic Static Water-Level Probe

You can permanently mount an *optional* static water-level probe inside the well. Then you can use a portable instrument to pneumatically measure the submergence of the probe.

Packer & Purge Pump

In conjunction with dedicated Well Wizard sampling pumps, you can install an *optional* packer (Purge Mizer) or purge pump (Purge Master) to shorten well purge times in any size well over 2 inches in diameter:

- **A Purge Mizer** packer inflates to seal off the sampling zone from the remainder of the water column. A *tandem* Purge Mizer combined with a standard Purge Mizer and a sampling pump lets you seal off both *above* and *below* the sampling zone.

- **A Purge Master** purge pump saves purge time in wells that contain a large volume of water to be purged before ground water sampling. This pump operates on a gas-displacement principal that results in high flow rates. However, because drive air contacts the well water, you don't also use this pump for sampling–you use the Well Wizard bladder pump instead.

Portable Components

Portable Well Wizard components include a cycle controller, water-level meter, disposable sample filters, and a flow-through cell.

Cycle Controller

A cycle controller controls operation of the Well Wizard pump by regulating the air flow from a compressed-gas source to the pump. Figure 1-4 shows the control panel from a typical Well Wizard cycle controller. Several controllers are available.

Model 3013 Automatic Controller

When connected to an appropriate compressed-gas source, the Model 3013 Automatic Controller alternately pressurizes then vents the air-supply line to the pump, allowing the pump to discharge, then fill with water. Using two timers, you can separately adjust the duration of the discharge pumping and venting cycles to maximize the pumping rate. The timers have a range of a fraction of 1 second to 2 minutes. A separate control lets you reduce the flow rate for sample collection.

Because this controller is pneumatically operated, it requires no electrical power supply. QED recommends that the compressed-gas sources be of high quality, such as breathing air or air from an oil-less compressor like the one offered in the Well Wizard product line.

WARNING! Do not apply pressure greater than 120 psi to the standard controller. Higher pressures may create hazardous conditions and will void your Well Wizard system warranties. However, higher air-flow-rate and higher pressure versions are available.

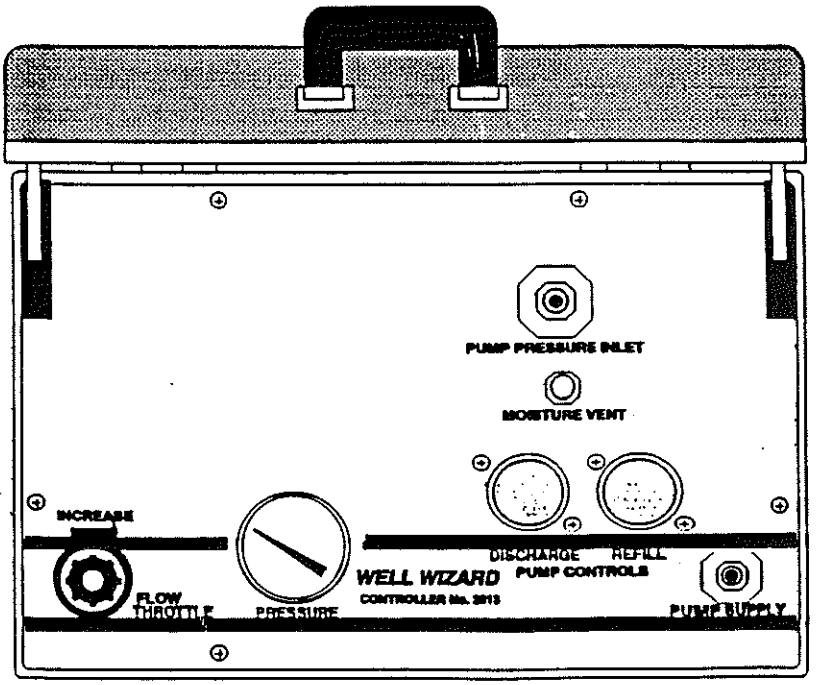


Figure 1-4: Typical Well Wizard Cycle Controller Control Panel

Model 3111 Automatic Controller/Compressor

The Model 3111 Automatic Controller/Compressor is a self-contained, cart-mounted unit that combines a compressor with a 3013 Automatic Controller. Its air-cooled gasoline engine drives a 100 psi oil-less compressor. This is a convenient, easily transportable compressed-air source.

WARNING! Do not apply pressure greater than 120 psi to the controller. Higher pressures may create hazardous conditions and will void your Well Wizard system warranties. However, higher air-flow-rate and higher pressure versions are available.

Model 350 Electronic Controller

Because the Model 350 Electronic Controller is electronic, it's also lightweight. Beyond that, this controller works essentially the same as the 3013 Automatic Controller, except that its timers have a narrower range.

Water-Level Meter

QED offers two approaches to portable static water-level measurement:

- **The pneumatic water-level approach** uses a portable battery-operated meter to measure the submergence of the dedicated probe. You calibrate the meter when you install it, and periodically after that. Batteries and a refillable compressed-gas charge from the pump controller output power the meter.
- **The electronic water-level approach** uses a portable conductivity probe attached to a calibrated tape. A light shines and a buzzer sounds when the probe touches the water surface. You lower this probe into each successive well.

Flow-Through Cell

Purge Saver is QED's *optional* flow-through cell. It simultaneously uses four probes to measure the pH balance, conductivity, temperature, and dissolved oxygen content of purge water. Purge Saver lets you know when it's okay to sample—generally saving you from spending a lot of time and from removing large volumes of water. If you have Purge Saver, for information about how to operate and maintain it, refer to the separate Purge Saver documentation.

QuickFilter

To ensure accurate samples of dissolved metals, you can use an *optional* QED QuickFilter. It removes solids larger than 0.45 micron. Because QuickFilters are disposable—you use one for each sampling event—there's no need to try to clean or decontaminate the filter from well to well.

2

INSTALLING THE COMPONENTS

If you've received a set of preassembled dedicated components, you'll find that unpacking them and installing them is easy when you follow the instructions in this chapter. Because not everyone needs to read the whole chapter, the first section helps you decide which of the other sections you need to read.

If, instead of preassembled components, you've received unassembled components and bulk tubing, read Chapter 5, "Installing a Pump Using Bulk Tubing."

Before You Begin...

How many of the installation procedures in this chapter you need to follow depends entirely on which components you have. But *everyone* needs to refer to these sections:

- "Unpack the Components."
- "Install the Basic Sampling Pump."

To find out which of the other sections to read, take stock of what you have by referring to the stapled sheets titled "Downwell Equipment Build/Specifications Sheet(s)." These sheets–and any other instructions–are inside a box labelled "Instructions Enclosed," which is inside Box 1.

When you know what you have, refer to Table 2-1 to find out which sections of this chapter you need to read to install your specific set of components—and in what order:

Table 2-1: What to Read & In What Order

If you have	Read this	In this sequence
A sampling pump	"Unpack the Components"	First
Inlet screen	"Install the Inlet Screen"	*After* unpacking the components
Packer (Purge Mizer)	"Install an Optional Packer–Purge Mizer"	*Before* installing the basic pump
Purge pump (Purge Master)	"Install an Optional Packer–Purge Pump"	*Before* or *after* installing the basic sampling pump–refer to the "Downwell Equipment Build/Specifications Sheet(s)"
Water-level meter	"Install an Optional Water-Level Meter Probe"	*After* installing the basic pump and any packer or purge pump

Unpack the Components

Here's how to unpack the Well Wizard dedicated components.

1. If you need to install a Well Wizard system in more than one well, decide which well you want to do first. Then find the box of components with the correct well-identification number written on the outside of the box.

2. If you *don't* have a Purge Mizer, skip to Step 3; if you *do* have a Purge Mizer, get the following tools ready:

   2 8" adjustable crescent wrenches.

   2 12" adjustable crescent wrenches.

   1 Tubing cutter (supplied by QED).

3. Carry the box to the well site, then open the box, but don't touch anything yet.

4. Open the box, then, before unpacking the rest of the box, put on a pair of the latex gloves you find inside the box.

> **Caution:** Touching well components with your bare hands can contaminate the components and degrade the quality of the samples obtained using the Well Wizard system. Always wear clean latex gloves when unpacking and installing a Well Wizard system, and at any other time when your hands might touch a water-contacting component.

5. Taking care to *not kink the tubing*, gently remove the plastic-wrapped pump and tubing from the box. A label on the package provides the well ID, cap, and tubing length. You may need this information later, so save the label.

> **Note:** The plastic bag also contains the lab-clean certificate on which is recorded the pump batch serial number. Keep this tag *for each pump* you install. It's your proof that the pump is contaminant free–if you need to, you can call QED with the serial number to find out which lab certified the pump.

6. Open the plastic wrapping, then gently slide the pump out of the bag.

Install the Inlet Screen

Well Wizard bladder pumps have a 10-year warranty that is valid *only* if you use the appropriate inlet screen.

There are two types of inlet screen: one that you *thread* onto the pump inlet for 1100 series pumps, and one that you secure with *set screws* for 1200, 1300, and 1500 series pumps. The correct screen for each pump is usually included with the other components for the well–the box label tells you where to find the screen. The following sections describe how to install the two types of inlet screen.

Screens for 1100 Series Pumps

To install a screen on an 1100 series pump, follow these steps:

1. Still wearing the latex gloves, open the plastic wrapping, then remove the screen.
2. Thread the screen onto the male-threaded pump inlet, making sure the screen is firmly tight.

Screens for 1200, 1300, & 1500 Series Pumps

To install a screen on a 1200, 1300, or 1500 series pump, follow these steps:

1. Still wearing the latex gloves, open the plastic wrapping, then remove from the bag both the screen and the small plastic bag that contains spare set screws and a small Allen wrench.
2. Find the groove around the inlet end of the stainless steel pump body (the end opposite the air and water connectors), then slide the screen onto the bottom of the pump assembly, aligning the top rim of the screen with the top groove.

Note: If you have difficulty installing the screen, use the Allen wrench to loosen the set screws a little.

3. Using the Allen wrench, *lightly* tighten each of the set screws, then make sure the screws have engaged the groove.
4. Using the Allen wrench, *firmly* tighten each of the set screws.
5. Check to make sure the screen is secure.

Install an Optional Packer–Purge Mizer

If you have a Well Wizard sampling system with Purge Mizer, it was shipped with the Purge Mizer *support cable* and *three tubing connections* loose at the cap, to allow you to adjust the length of the various tubes to exactly fit your well. To finish installing these, complete the steps in the following sections **before** completing the steps in "Install the Basic Sampling Pump," later in this chapter. As a guideline, at the end of Purge Mizer installation, you want to have the Purge Mizer cable *taut* and the tubing just slightly *slack*–so the cable bears the weight of the pump. Note that there are always several inches of inflation tubing left that must later be trimmed, but still left slack, to avoid kinking.

Note: If you don't understand how to use the compression style fittings described in the following sections, refer to the instructions in "Install or Replace Pump Connectors" in Chapter 6, "Maintaining Your Well Wizard System."

Attach the Purge Mizer Cable to the Well Cap

How you attach the Purge Mizer support cable to the well cap depends on whether you have a standard cap or a 2120A 2-inch cap. The following sections describe both procedures.

Standard Cap

If you have a Purge Mizer and a standard cap (with support bar), follow these steps to attach the support cable to the cap.

1. Push the threaded terminal through the cap far enough that the support bar can spin freely on it.
2. Spin the bar down to the bottom threads of the terminal.
3. Lower the bar onto the cap, between the cap fittings.

The result should resemble Figure 2-1.

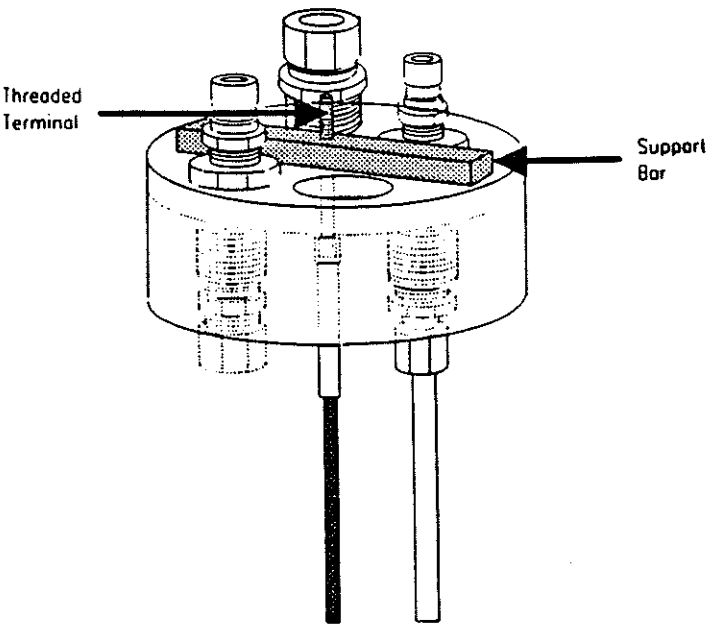


Figure 2-1: Installing Cable on a Standard Cap

2120A 2-Inch Cap

If you have a Purge Mizer and a 2120A 2-inch cap, follow these steps to attach the Purge Mizer support cable to the cap.

1. With the support bracket between the sides of the strap fork, slide the clevis pin through the holes.
2. Slide the cotter pin through the clevis pin.
3. Secure the cotter pin by bending the ends.

The result should resemble Figure 2-2.

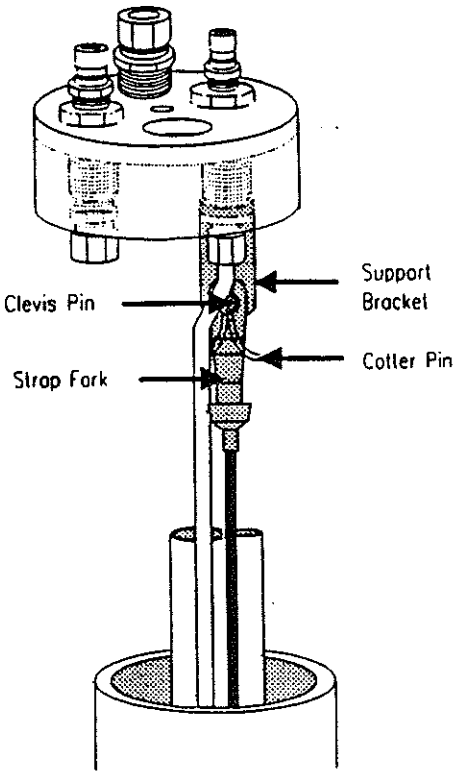


Figure 2-2: Installing Cable on a 2120A 2-Inch Cap

Install the Discharge Tubing

To install the discharge tubing, follow these steps.

1. Pull or push the 1/2-inch discharge tubing through its fitting, adjusting it until it's slightly *less* taut than the Purge Mizer support cable–leaving about *1-1/2 feet* extending above the well cap.

> **Caution:** For now, don't cut off the approximately 1-1/2 feet of excess tubing that extends above the well cap. Wait until Step 3 in "Install the Well Cap," later.

2. With a wrench, hold the base of the through fitting and, with another wrench, tighten the fitting nut until firm.

Install the Inflation Tubing

To install the Purge Mizer inflation tubing, follow these steps.

1. Determine the length of 1/8-inch Purge Mizer inflation tubing needed to extend completely into the compression style fitting on the underside of the cap or cap plate while leaving the tubing *less* taut than the Purge Mizer support cable.

> **Caution:** Measure with care. It's better to leave a little extra tubing prior to cutting than to cut off too much.

2. Use the tubing cutter to cut off the excess tubing.
3. Push the tubing fully into the fitting until it contacts the shoulder inside the fitting.
4. On the top of the cap or cap plate, with a wrench, hold the brass anchor fitting in which the 1/8-inch Purge Mizer inflation tube fitting is installed.
5. Tighten the tubing fitting with the wrench until it's firm.

6. Turn the tubing fitting about three-quarters of a turn past hand tight—but don't tighten it enough to crush the Purge Mizer tubing.

Install the Air-Supply Tubing

To install the air-supply tubing, follow these steps.

1. Determine the length of 1/4-inch air-supply tubing needed to extend completely into the brass 1/4-inch compression fitting on the underside of the cap or cap plate while leaving the tubing *less* taut than the Purge Mizer support cable.

   Caution: Measure with care. It's better to leave a little extra tubing prior to cutting than to cut off too much.

2. Use the tubing cutter to cut off the excess tubing.
3. Push the tubing into the fitting until it contacts the shoulder inside the fitting.
4. On the top of the cap or cap plate, with a wrench, hold the brass anchor fitting in which the 1/4-inch air-supply tubing is installed.
5. Tighten the tubing fitting with another wrench until it's hand tight.
6. Turn the tubing fitting one and one-quarter turns *past* hand tight.

Install the Basic Sampling Pump

Depending on the length of the tubing and whether your pump includes a Purge Mizer or a Purge Master, it may be easiest for two people to install the pump–but one person often can do it. To install the pump, follow these steps.

Caution: Make sure that you don' bring the tubing or other pump components in contact with the ground or any other surface. It's often helpful to spread out a polypropylene tarp next to the well during installation.

1. Still wearing the latex gloves, if you have a protected well cap, mark any necessary information–such as well ID and depth–on the label inside the well cap.
2. Slowly lower the pump into the well while uncoiling the tubing bundle, until the entire length of tubing is in the well.

   Note: If you don't have a Purge Mizer, skip Step 3.

3. What you do in this step depends on which components you have:
   - **If you have just the basic sampling pump,** either anchor the well cap in position or leave it loosely attached.
   - **If you have a *Purge Mizer*,** lower the cap on the well. Then, leaving 1 inch or a little more, cut off the remaining tubing (about 1-1/2 feet) and attach it to the sample elbow. You can store the elbow and tubing in one of the unused holes in the cap plate.
   - **If you have a *Purge Master that you haven't yet installed*,** proceed with the instructions in "Install an Optional Purge Pump–Purge Master."

Install an Optional Purge Pump–Purge Master

If you have a Well Wizard sampling system with Purge Master, although the tubing is cut to the correct length for your well, you need to install the tubing when you install the pump. Refer to the "Downwell Equipment Build/ Specifications Sheet(s)" to see whether to install your sampling pump or your purge pump first.

The following sections tell you how to install Purge Master.

Attach the Tubing Bundle to the Pump

Follow these steps to install the Purge Master tubing bundle.

1. Get the following tools ready:
   2 12"/300 mm adjustable crescent wrenches
   1 Tubing cutter (supplied by QED)
2. Make sure that both the 3/4-inch and the 1/2-inch fitting nuts on the top of the pump are loose.
3. Holding one end of the tubing bundle, press a 1/2-inch and a 3/4-inch tubing insert into the corresponding tubing.
4. Loosening the nuts as necessary, push the tubing into the 3/4-inch and 1/2-inch fittings on the top of the pump, as follows:
   - Push the larger tubing into the 3/4-inch fitting until it contacts the shoulder inside the fitting.
   - Push the smaller tubing into the 1/2-inch fitting until it contacts the shoulder inside the fitting.
5. With a wrench, tighten the 3/4-inch fitting nut hand tight.
6. With a wrench, hold the fitting base, then turn the 3/4-inch fitting nut one additional turn *past* hand tight.

7. With a wrench, tighten the 1/2-inch fitting nut hand tight.
8. With a wrench, hold the fitting base, then turn the 1/2-inch fitting nut one additional turn *past* hand tight.

Lower Purge Master into the Well

To lower the Purge Master into the well, follow these steps.

1. Lift the cap plate or unprotected cap out of the well and let it hang off to one side.
2. Lower the pump into the well slowly while uncoiling the tubing bundle–until there's about 3 feet of tubing left.

Attach the Discharge Tubing to the Well Cap

To attach the discharge tubing to the well cap, follow these steps.

1. With the large fitting nut on the *top* of the cap plate or unprotected cap loose, push the discharge tubing through its fitting–leaving about 1-1/2 feet extending above the cap.

> **Caution:** For now, don't cut off the approximately 1-1/2 feet of excess tubing that extends above the fitting. Wait until Step 3 in "Install the Well Cap," later.

2. If you have a cap that has a fitting nut on the underside, with a wrench, tighten the fitting nut on the underside hand tight.
3. With a wrench, hold the fitting base.
4. Turn the fitting nut one additional turn *past* hand tight.

Attach the Air-Supply Tubing to the Well Cap

To attach the air-supply tubing to the well cap, follow these steps.

1. Loosen the 1/2-inch fitting nut on the top of the cap or cap plate.
2. Referring to Figure 2-3, estimate where to cut the air-supply tubing so that it contacts the shoulder inside the 1/4-inch air fitting on the underside of the cap or plate—leaving a little bit of slack (the 3/4-inch tubing should provide the main support for the pump).

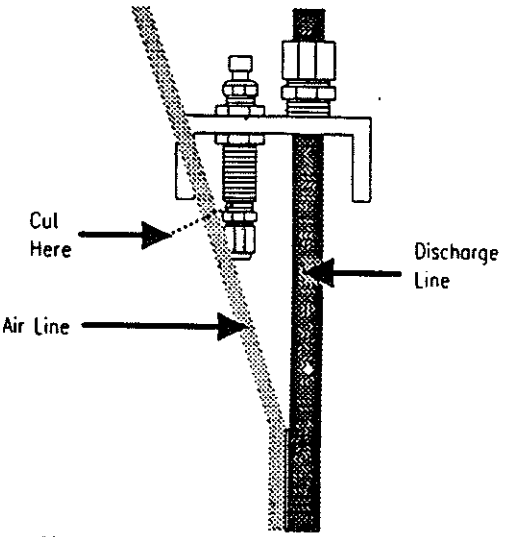


Figure 2-3: Where to Cut the Tubing

3. Cut the air-supply tubing according to your calculation in Step 2.
4. Push the air-supply tubing into the fitting until it contacts the shoulder inside the fitting.
5. With a wrench, tighten the fitting nut hand tight.
6. With a wrench, hold the fitting base.
7. Turn the fitting nut one additional turn *past* hand tight.

Install the Well Cap

To install the well cap, follow these steps.

1. If you want to prevent debris (such as rust from the protective casing) from getting on the well cap and into the well, fit a plastic bag over the well cap.
2. Lower the cap or cap plate on the well.
3. Making sure that you allow room to install the discharge elbow so that the elbow clears the top edge of any unprotected cap or protective casing, trim off the excess 1-1/2 feet of discharge tubing using the tubing cutter.
4. Store the sample elbow and tubing in the spare hole in the cap, if you want to.

Install the Optional Water-Level Meter Probes

If your Well Wizard system includes the Model 6010E Electronic/Pneumatic Water-Level meter, the following steps describe how to install the probe. Refer to Figure 2-4 as you follow the steps.

Caution: Ensure that the static water level in the well has returned to its natural level after any recent purging or sampling or displacement due to equipment installation. In wells that recover very slowly, water displacement during new-equipment installation may temporarily alter the true static water level of the well.

1. Measure the current static water level in the well (C in Figure 2-4), then record it using your traditional method.

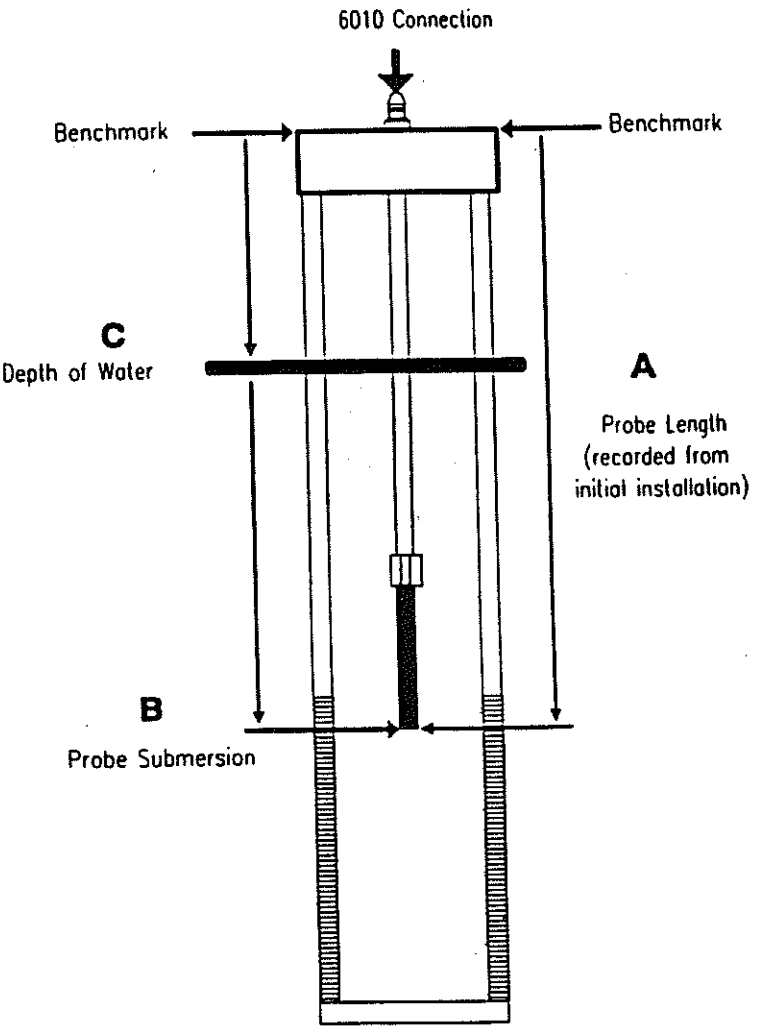


Figure 2-4: Measurements for Probe Installation

2. Review the historic static water-level fluctuations to determine whether the current reading reflects a good starting point for water-level probe location. Ideally, the probe should be submerged about 10 to 12 feet below the *mean static level*.
3. Decide where you want to locate the water-level probe.

> **Caution:** Although 10 to 12 feet below the mean static level is an *ideal* submergence for the probe, you *must* submerge the probe at least 1 foot but not more than 25 feet, because the meter can't display depths outside this range.

4. Measure and cut the 1/4-inch probe tubing to the length you calculated.
5. Attach the tubing to the probe assembly, then, to avoid an air leak and false readings, tighten it carefully using two wrenches.
6. Lift up the cap or plate, then lower the probe and tubing into the well.
7. Attach the probe tubing to the 1/4-inch compression fitting under the cap or plate, then tighten it using two wrenches.
8. Lower the cap or plate back into position on the well casing.
9. Determine the probe submergence. To find out how to do that, refer to Chapter 3, "Purging the Well," and read the section about measuring the water level with a dedicated water-level meter.
10. Add the static water level depth you measured in Step 1 to the submergence reading you determined in Step 9 (A in the drawing), to determine the probe location.
11. Record the probe length (A) and the measured calibration static water level determined in Step 1, for use in all future water-level depth calculations.
12. Apply the new probe submergence readings to the calibration to determine the new static water level.

3

PURGING THE WELL

Before sampling, you need to purge the well according to your approved sampling plan. This chapter tells you how to:

- Measure the water level using either a dedicated or a portable water-level meter.
- Purge the well using:
  - Just the sampling pump.
  - The sampling pump *and* Purge Mizer (packer).
  - Just Purge Master (purge pump).
- Maximize the pumping rate for both a sampling pump and Purge Master.

Measure the Water Level

Before you purge the well, you normally check the static water level. You can do that with either a dedicated or a portable water-level meter, as described in the following sections.

With a Dedicated Water-Level Meter

If you have a Model 6010E Electronic/Pneumatic Water-Level meter, to measure the water level, first you charge the air tank, then you use the water-level meter to measure the water level. The following sections tell you how.

Note: Rapid temperature changes adversely affect water-level meter operation. The best approach is to store the meter at the temperature in which you will use it. If this isn't possible, move the unit to the appropriate temperature at least 45 minutes before you want to use it to allow the temperature to stabilize. Then you can expect the accuracy to be as follows:

- 40 to 120° F ambient air temperatures: +/-0.01 feet.
- -20 to 40° F ambient air temperatures: +/-0.02 feet.

Charge the Tank

1. As shown in Figure 3-1, attach the black driver-controller hose to the controller.
2. As also shown in the figure, attach the red air-supply line from the **PUMP SUPPLY** connector on the controller to the **TANK RECHARGE** fitting, to charge the internal air tank to 100 psi.
3. Set the controller **DISCHARGE** timer for the maximum discharge time (**F** on the Model 3013 and **5 O'CLOCK** on the Model 350).
4. Set the **REFILL** timer for the minimum refill time (**A** on the Model 3013 and about **9 O'CLOCK** for the Model 350).
5. Start the compressed-air source.
6. Let the controller cycle until the 6010E pressure gage reads 80 to 100 psi.

Caution: Do not apply pressure greater than 120 psi to the controller. Higher pressures may create hazardous conditions and will void your Well Wizard system warranties.

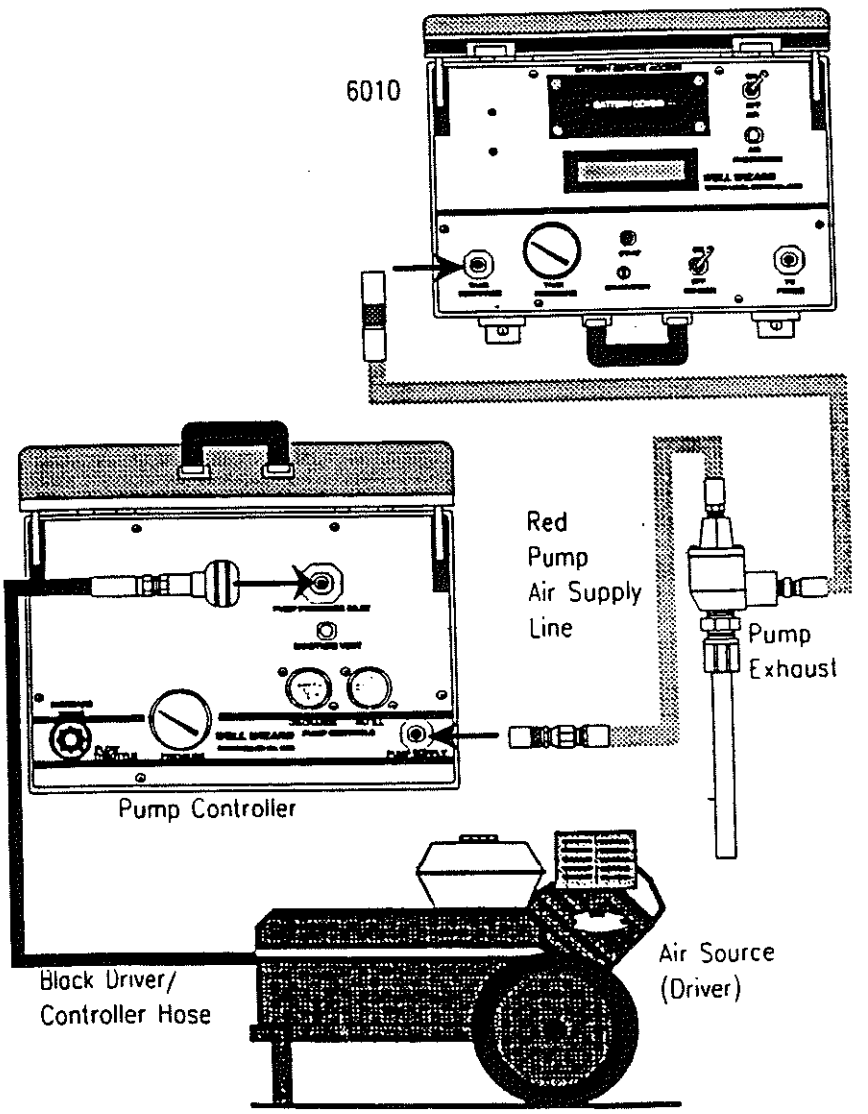


Figure 3-1: Attaching the Hoses

Operate the Meter to Measure Water Levels

1. Set the **SENSOR** switch to **ON**.
2. When the message reads **Attach to Well**, attach the clear air tubing from the **TO PROBE** fitting to the mating well cap connection.
3. Set the **AIR** switch to **ON**.
4. Press **START** once.
5. Press **AIR PRE-CHARGE** until the display shows the highest reading–you see the numbers increase, then stabilize at the highest reading.
6. Wait for the message to read **Probe Submersion Depth** (this is "B" in the diagram on the face of the meter), then record the reading when the depth stabilizes.
7. Move the **AIR** and the **SENSOR** switches to **OFF**.
8. Subtract the reading for Probe Submersion Depth ("B" in the diagram on the meter) from the known Probe Submergence ("A" in the diagram on the meter), established during probe installation (read about installing an optional water-level meter probe in Chapter 2, "Installing the Components"). The result is the depth of the static water-level probe.

With a Portable Water-Level Meter

If you have a portable water-level meter, follow these steps to measure the water level.

1. Still wearing the latex gloves, remove the black 1/2-inch square-head hole plug from the well cap.

   Note: If you don't see the black square-head screw, the sample tube may be stored in the opening. If so, remove it instead.

2. Insert the probe of the water-level meter through the opening, then unreel the probe tape into the well.

3. When the light shines and the buzzer sounds, the probe has contacted water. Write down or remember the depth to the static water level by reading the length shown on the tape, so you can refer to it when you're purging the well.
4. Remove the probe from the well, then replace the black square-head screw (or the sample tube and elbow).

Purge Using the Sampling Pump

To purge the well using just a Well Wizard sampling pump, you can follow either the general procedure described in the next section, *or* the steps in the more-detailed sections that follow.

Note: If you have a Purge Mizer (packer) as well as a sampling pump, follow the steps in "Purge Using Purge Mizer (packer)," before proceeding with these steps. If you have a Purge Master (purge pump), follow the steps in "Purge Using Purge Master (purge pump);" you don't need the steps in this section.

General Procedure for Purging

Here are the general steps to follow for purging.

1. Start the compressor.
2. Hook up the hoses.
3. Set both timers on C for the Model 3013 or about 9 O'CLOCK for the Model 350.
4. Turn the yellow FLOW THROTTLE control knob completely clockwise, to make sure the pressure is as high as it will go.

If Steps 1 through 4 don't give you enough information, you may want to follow the steps in the following section *instead*, because they provide much more detail.

Detailed Procedure for Purging

The following sections provide the detailed steps for purging.

Get Purging Started

1. Considering the depth and size (diameter) of the well, calculate the number of gallons to be purged to comply with your approved sampling plan.
2. Start the compressor engine.

   But don't connect the red air-supply line to the Well Wizard controller yet. Instead, follow Steps 3 and 4 carefully.

3. As shown in Figure 3-2, connect the short end of the red pump air-supply line to the pump connector on the well cap.
4. Connect the long end of the red pump air-supply line to the **PUMP SUPPLY** connector on the Well Wizard controller.
5. Point the pump discharge line away from you.
6. Set both timers on **C** on the Model 3013 or at about **9 O'CLOCK** on the Model 350.
7. Connect the black driver/controller hose to the **PUMP PRESSURE INLET** connector on the Well Wizard controller.

   You'll notice **loud hissing and honking sounds** as air releases through the side of the Well Wizard controller housing and as air releases through the exhaust valve. This is *normal*.

   Note: If the controller doesn't sound as though it is alternating between cycles (pressurizing then venting), shorten the cycle times by setting the **REFILL** and **DISCHARGE** timer knobs to **A** on the Model 3013 or at about **9 O'CLOCK** on the Model 350.

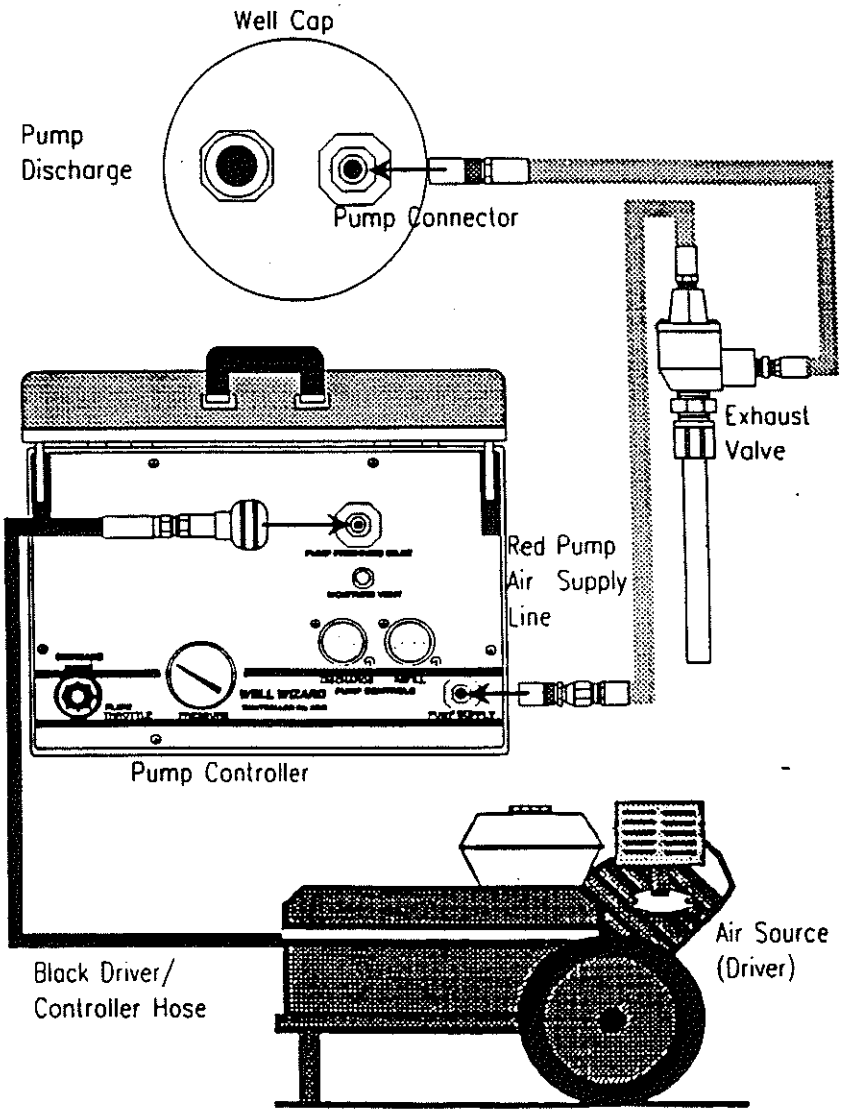


Figure 3-2: Connecting the Red Pump Air-Supply Line

After the venting noises stop, water flows from the pump discharge line as you begin to purge the well. The time required to actually begin discharge of water depends on the depth to the water–it may take several *seconds* or several *minutes*.

8. Check the air pressure on the **PRESSURE** gage on the Well Wizard controller. The pressure–which controls the flow rate–should be between 60 and 120 psi. If necessary, adjust the pressure using the **FLOW THROTTLE** control knob. Pull up on the yellow outer ring to unlock the throttle, adjust the setting, then push down to lock the throttle.

   Turning the **FLOW THROTTLE** knob clockwise increases pressure; turning it counterclockwise decreases pressure.

9. To make well purging as efficient as possible, refer to the steps in "Maximize the Pumping Rate," next.

10. Every 15 minutes, press down (and hold down for 5 seconds) the silver **MOISTURE VENT** button on the Well Wizard controller. This expels accumulated moisture from the side of the controller. It's especially important to vent the moisture during humid conditions and very cold conditions.

Maximize the Pumping Rate

Purging a well can be a time-consuming process. By adjusting the **REFILL** and **DISCHARGE** timers, you can make well purging as efficient as possible–so that as soon as the venting cycle ends, the pump is completely full and the discharge begins, and vice versa.

To do that, as detailed in the following steps, you first make both cycle times *long*, to ensure that the pump will completely fill then completely empty. Then you shorten one time until you see an effect on volume; then you shorten the second time the same way.

1. Lift the yellow outer ring of the **FLOW THROTTLE** control, turn the knob fully clockwise, then push down to lock the control.

2. Turn the **DISCHARGE** and the **REFILL** timer knobs to **D** on the Model 3013 or **12 O'CLOCK** for the Model 350–a *long cycle time*.
3. Using a 1,000 ml graduated cylinder for measuring (1,500 ml for Model 1500 pumps), measure the volume of water discharged in one cycle. This is the maximum pump volume–remember what it is.

> **Note:** For 1100 Series pumps, discharge volume should be 250 - 350 ml; for 1200 Series pumps it should be 350 - 450 ml. If your discharge volume is less than this, try increasing the refill cycle time. If that doesn't work, try shortening the refill cycle time, especially in deeper wells. (In deeper wells with very little water, if the cycle is too long, the water may actually have time to bleed through the weep hole before it can be discharged.)

4. To achieve as short a refill time as possible *without losing any refill volume*, slightly decrease the **REFILL** timer setting (turn the knob *counter*clockwise about half a setting). Then measure the volume of water discharged in the next three cycles. Repeat this step until you notice a decrease in discharge water volume.
5. Increase the **REFILL** timer setting (turn the knob *clock*wise) enough to regain full discharge volume. Refill is now set for maximum flow.
6. To achieve as short a discharge time as possible *without losing any discharge volume*, slightly decrease the **DISCHARGE** timer setting (turn the knob *counter*clockwise). Then measure the volume of water discharged in the next three cycles. Repeat this step until you notice a decrease in discharge water volume.
7. Increase the **DISCHARGE** timer setting (turn the knob *clock*wise) enough to regain full discharge volume. Discharge is now set for maximum flow.

Now you're purging efficiently.

Purge Using Purge Mizer (packer)

If you have a Purge Mizer, after you measure the water in the well, you inflate Purge Mizer, purge the well, then prepare for sampling.

Warning! *Never* inflate Purge Mizer outside of the well. Inflate Purge Mizer *only* when positioned at full depth in the well casing. Always deflate Purge Mizer after use.

To purge using Purge Mizer, follow these steps.

1. Couple the Purge Mizer control unit to the Purge Mizer air tubing fitting on the well cap (see Figure 3-3).
2. Couple the control unit to the short end of the red pump air-supply line connected to the Well Wizard controller.
3. Turn the PRESSURE REGULATOR knob fully counterclockwise.
4. Activate the compressed-gas source.

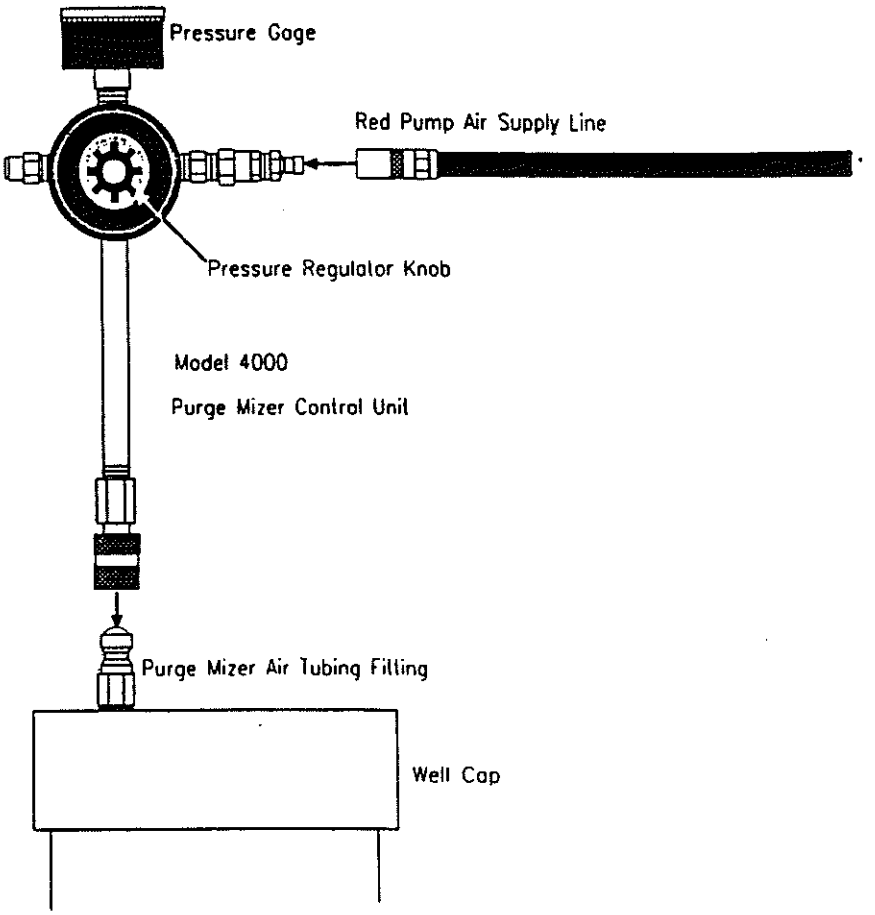


Figure 3-3: Coupling the Purge Mizer Control Unit

5. To fully inflate the Purge Mizer, slowly turn the **PRESSURE REGULATOR** knob on the Purge Mizer control unit clockwise to increase the pressure to the level recommended in Table 3-1.

Table 3-1: Recommended Pressure Levels

Purge Mizer Submergence (feet)	Inflation pressure (psi)
20	50
40	60
60	70
80	80
100	90

Note: The Purge Mizer inflates during the controller discharge cycle. To speed inflation, you can lengthen that cycle.

6. When you reach the correct pressure, disconnect the red air-supply hose. The Purge Mizer control unit check valve maintains the pressure.
7. Purge the well with the sampling pump as described in "Purge Using the Sampling Pump." If the pressure reading on the Purge Mizer control unit pressure gage remains steady, you know that Purge Mizer is operating correctly.

Purge Using Purge Master (purge pump)

If you have a Purge Master (purge pump), follow the steps in the following sections for high-rate purging.

Connect the Discharge Tubing Elbow

1. Connect the discharge tubing elbow to the 3/4-inch tubing protruding from the cap or cap plate.
2. Tighten the fitting nut with a wrench.
3. Direct the end of the tubing on the discharge elbow into the collection vessel.

Connect Purge Master

1. If you have a locking well cap, make sure the cap pin is engaged.
2. To achieve a short discharge cycle to start with, set the **DISCHARGE** timer knob at **A** on the Model 3013 or at about **9 O'CLOCK** on the Model 350.
3. Connect the short end of the red pump air-supply line to the quick-connect nipple on the cap or cap plate nearest to the white high-rate discharge fitting (see Figure 3-4).

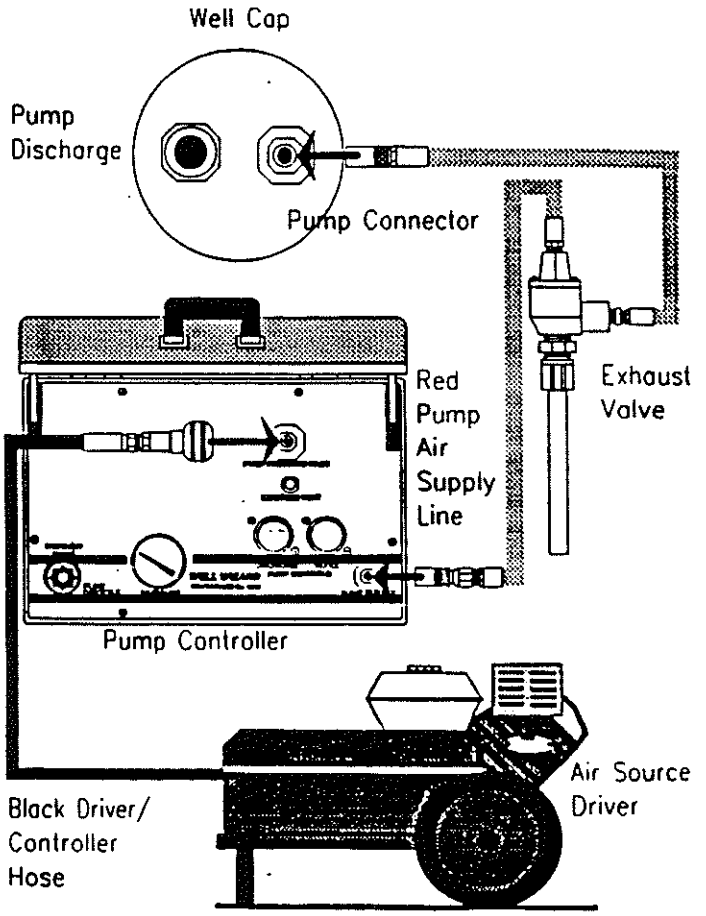


Figure 3-4: Connecting Purge Master

4. Connect the other end of the red pump air-supply line to the **PUMP SUPPLY** connector on the controller.
5. Not exceeding 125 psi, connect the black driver/controller hose to the **PUMP PRESSURE INLET** connector on the controller.

As purging begins, you'll notice **loud hissing and honking sounds** as air releases through the side of the Well Wizard controller housing and as air releases through the exhaust valve. This is *normal*. After the venting noises stop–from several seconds to several minutes–water flows from the pump discharge line as you begin to purge the well.

Note: If the controller doesn't sound as though it's alternating between cycles (pressurizing then venting), turn the **REFILL** and **DISCHARGE** timer knobs to shorten the cycles.

Set the Cycles

1. Use Tables 3-2 and 3-3 as guides to setting the **REFILL** and **DISCHARGE** timers, depending on the depth and submergence of the Purge Master in the well.

Table 3-2: Recommended Discharge Times

Pump Depth (ft.)	Discharge Time (sec.)
50	2.5
75	3.5
100	4.5

Table 3-3: Recommended Refill Times

Pump Depth (ft.)	Pump Submergence (ft)	Refill Time (sec.)
50	25	5.5
75	25	6.0
100	25	7.5
50	50	5.0
75	50	5.5
100	50	7.0

2. Turn the **FLOW THROTTLE** knob on the controller fully clockwise.

Maximize the Pumping Rate

Even with Purge Master, purging a well can be a time-consuming process. By adjusting the discharge and refill cycles, you can make well purging as efficient as possible.

1. With the pump operating, set the refill time *long* (about **11 O'CLOCK** for Model 350 or **C** for Model 3013 in most cases—a higher setting if the well is shallow).
2. Referring to Table 3-4, set the discharge time *short* (1 second for wells shallower than 50 feet; 3 seconds for wells 50 to 100 feet, and 5 seconds for wells deeper than 100 feet). Water should begin to flow through the discharge line after 5 to 15 pumping cycles, depending on the depth of the well.

Table 3-4: Approximate Settings Versus Times

Model 350 Setting	Seconds	Model 3013 Setting
7 o'clock	1	A
-	3	B
8 o'clock	3.5	-
9 o'clock	7	-
-	9	C
10 o'clock	13	-
11 o'clock	16.5	-
12 o'clock	19.5	-
-	20	D
1 o'clock	22.5	-
2 o'clock	26.5	-
-	31	E
3 o'clock	32	-
4 o'clock	35.5	-
5 o'clock	37	-
-	42	F

3. Measure the liquid discharged during one cycle. The volume of the liquid is less than the internal volume capacity of the pump.
4. Increase the discharge time *gradually* (turning the knob less than a full setting), letting the pump go through its cycle three to five times after each adjustment.
5. Repeat Step 4 until you see air bubbles coming through the discharge line.
6. Decrease the discharge time slightly to eliminate the air bubbles. The amount discharged per cycle is now close to the internal volume capacity of the pump—the *discharge* cycle is maximized.

> **Note:** If air and water begin to shoot out *hard*, the discharge cycle time is too long. Set the discharge time short again, then repeat Step 4 using even smaller timer adjustments.

7. Decrease the refill time *gradually*, letting the pump cycle three to five times after each adjustment.
8. Repeat Step 6 until you see air bubbles coming through the discharge line.
9. Increase the refill time slightly to eliminate the bubbles. The amount of water discharged per cycle should still be close to the internal volume capacity of the pump—the *refill* cycle is maximized.

> **Note:** If air and water begin to shoot out *hard*, the refill cycle time is too short. Set the discharge time long again, then repeat Step 4 using very small timer adjustments.

Clear the Discharge Line

During the winter in northern climates, to prevent the discharge tubing of your Purge Master from *freezing*, you need to clear the discharge line of standing water above the static water level.

1. Before disconnecting the air supply from Purge Master, set the discharge cycle time on the controller long enough to cause air to exit from the Purge Master discharge line.
2. Wait until all the water is blown out of the discharge tubing.

4

COLLECTING A SAMPLE

After you've purged the well, you're ready to sample. A slow flow rate is recommended in most sampling protocols. When you *slow* the flow from the pump, you also avoid spurts, sprays, and drips.

The following sections tell you how to adjust the rate of flow for sampling and how to collect the sample.

Adjust the Rate of Flow

When you collect a sample, you want a smooth, non-aerated flow. To get that kind of flow, follow these steps.

1. Turn the FLOW THROTTLE knob on the controller *counter-*clockwise to slow the flow.
2. If you want to use a QuickFilter to filter your sample, disconnect the air supply on the controller to stop the pump, attach the QuickFilter to the tubing following the instructions on the box, then re-connect the air-supply on the controller to re-start the pump.

> **Caution:** To avoid housing or membrane failure and sample contamination, make sure the pressure does **not** exceed 60 psi.

3. If you purged the well using a Purge Master purge pump, reconnect the red pump air-supply line to the sampling pump, then make sure that you purge 1/2 to 1 gallon of water through the sampling pump. This ensures that you sample fresh well water.
4. Turn the **DISCHARGE** timer knob to **D** for the Model 3013 or to **12 o'clock** for the Model 350, to lengthen the cycle (because it will take longer to get the full volume of the pump at the slower flow).
5. Continue adjusting the **FLOW THROTTLE** knob until the flow is completely smooth.

Collect the Sample

To collect the sample, follow these steps.

1. If you're using a QuickFilter, discard the initial volume of filtered sample (500 ml for Model FF8100; 1,000 ml for Model FF8200).
2. Direct the flow into the sample vessel.
3. Turn off the driver engine, then disconnect the hoses from the well cap.
4. If you have a Purge Mizer, turn down the regulator to relieve the pressure, then remove the Purge Mizer control unit. The Purge Mizer deflates automatically.

Install or Replace Well-Cap Tubing Ferrules in a Typical Well Cap

The following sections describe how to replace or install well-cap tubing ferrules. Most people never need to perform either of these procedures. You may need them, however, if you want to re-position the pump or replace kinked tubing.

Unscrew Fitting Caps & Expose Ferrules

Refer to Figure 6-1 as you follow these steps.

1. Using a wrench, loosen the pump discharge fitting cap by turning it counterclockwise.

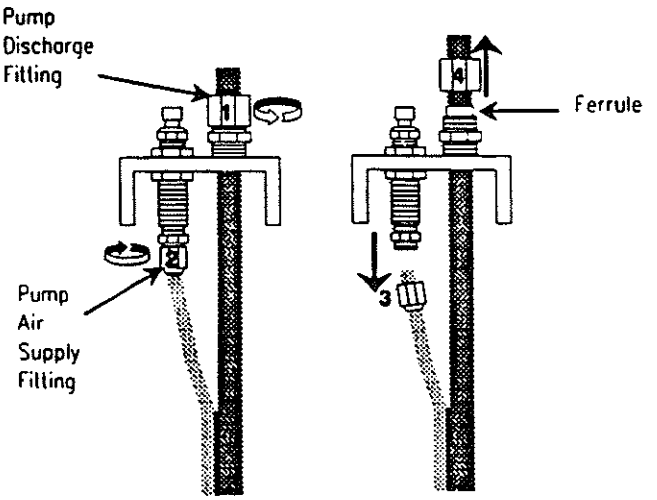


Figure 6-1: Unscrew Fitting Caps & Expose Ferrules

2. Using a wrench, loosen the pump air-supply fitting cap by turning it counterclockwise.
3. Pull the pump air-supply tubing down and out of the fitting.

4. Slide the pump discharge fitting cap up the tube to expose the ferrule.

Discard Tubing & Ferrule, Save Cap for Re-Use

Refer to Figure 6-2 as you follow these steps.

1. Pull the pump discharge tubing up through the cap to allow access to the ferrule.

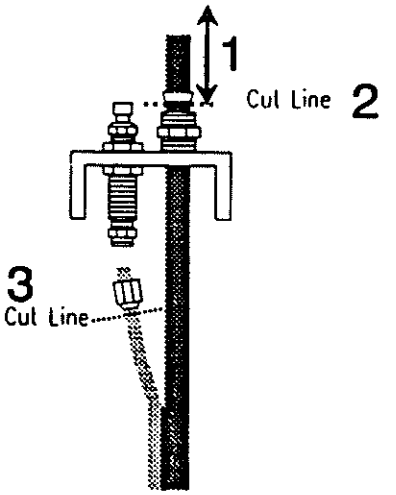


Figure 6-2: Discard Tubing & Ferrule

2. Cut the pump discharge tubing just behind the ferrule.
3. Cut the pump air-supply tubing just behind the fitting cap.
4. Discard the portions you just cut off, saving the fitting caps for re-use.

Re-Attach the Fitting Caps

Refer to Figure 6-3 as you follow these steps.

1. Re-attach the pump discharge fitting cap with the new ferrule (smaller end down)—leaving it slightly loose to allow the tube to pass through.
2. Attach a new nut to the pump air-supply tubing—leaving it slightly loose to allow tubing to pass through.

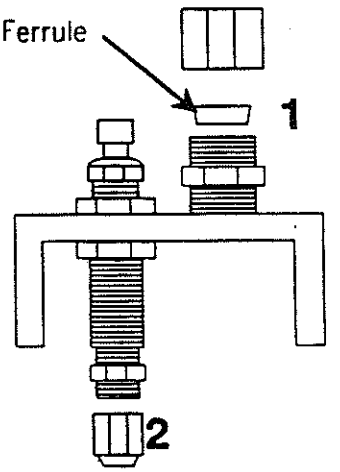


Figure 6-3: Re-Attach the Fitting Caps

Re-Connect the Tubing

Refer to Figure 6-4 as you follow these steps.

1. Separate the tubing for about 6 to 12 inches.

Caution: Don't pull tubing apart *side*ways—it may tear. Instead, hold the larger tube stationary with one hand. Then, with the smaller tube in the other hand, either push or pull directly toward or away from you.

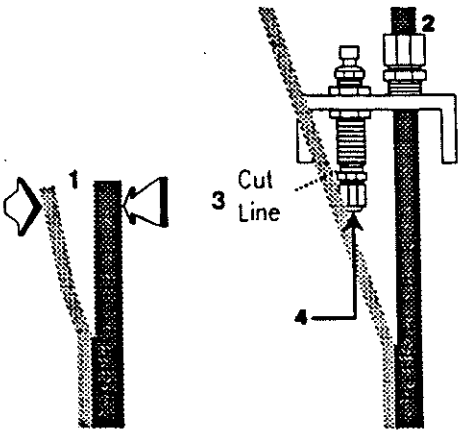


Figure 6-4: Re-Connect the Tubing

2. Push the pump discharge tubing through the pump discharge fitting to the desired length, then tighten the nut.

> **Note:** The length you want depends on the clearance required for any protective casing. You typically need about 1-1/2 feet.

3. Cut the air-supply tubing to size, to allow it to reach *all* the way into the fitting.
4. Push the air-supply tubing all the way into the fitting until it contacts the shoulder inside the fitting, then tighten the nut.

Install or Replace Pump Connectors

The following sections described how to install or replace the three types of connectors that may be included in your Well Wizard system.

Stainless Steel Connectors

Swagelok™ tube fittings, which include four pieces (see Figure 6-5), come to you completely assembled, finger tight.

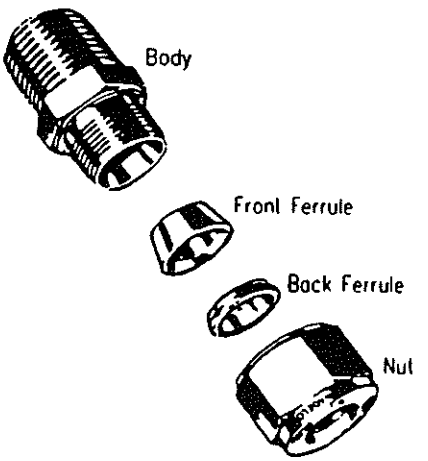


Figure 6-5: Parts of the Swagelok Tube Fitting

Caution: If you disassemble a connector before you use it, dirt or foreign material can get into the fitting and later cause a leak.

To install a stainless steel connector, follow these steps.

1. If you're working with a 1/2- or a 3/4-inch connector, wrap the male threads under the nut with Teflon tape.

2. Insert the tubing into the Swagelok tube fitting as follows:
   - **For 1/4-inch tubing,** insert it approximately 5/8 inch.
   - **For 3/4-inch tubing,** insert it up to 7/8 inch.

   Make sure that the tubing firmly contacts the shoulder of the fitting and that the nut is finger tight.

> **Note:** If the tubing is 3/8 inch or larger, you must use a tubing insert. Just push the stainless steel insert into the tubing before inserting the tubing into the tube fitting.

3. Referring to Figure 6-6, scribe or mark the nut at the 6 o'clock position.

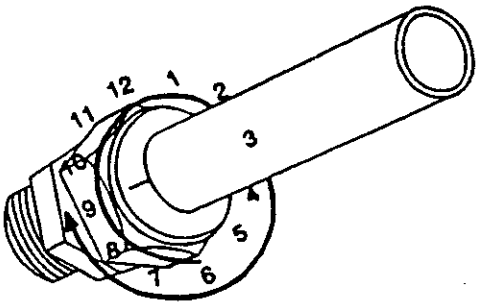


Figure 6-6: Clock Positions

4. While holding the fitting body steady with a backup wrench or vise, tighten the nut as follows, depending on the size of the tube fitting:
   - **For fittings larger than 3/16 inch,** turn the fitting one and one-quarter turns (watch the scribe mark make one complete turn, then continue to 3-o'clock).
   - **For fitting sizes 1/6, 1/8, and 3/16 inch,** turn the fitting three-quarters of a turn (watch the scribe mark turn to 9 o'clock).

> **Note:** These are guidelines, you may need to further tighten the nut.

Purge Master Barb-and-Clamp Connectors

To install Purge Master barb-and-clamp connectors, follow these steps, referring to Figure 6-7. Have handy the 2-inch purge pump clamp tool (Part Number 35188) that's available from QED.

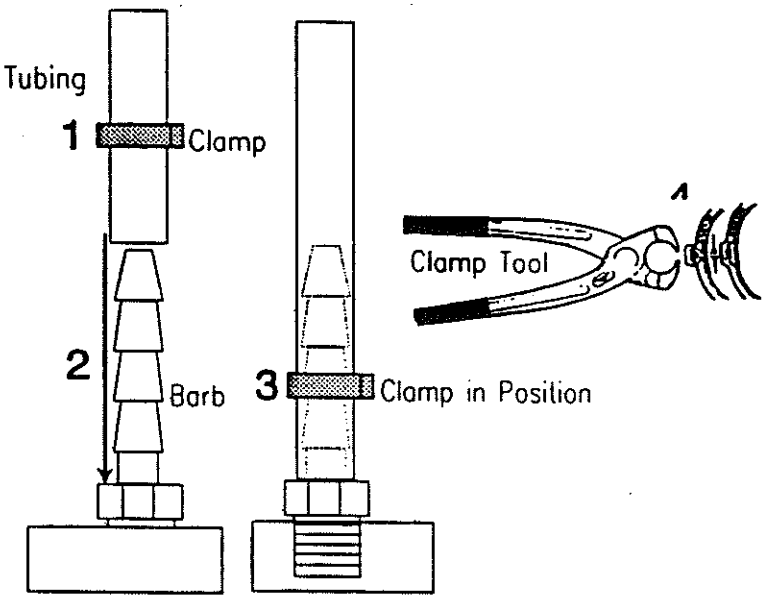


Figure 6-7: Barb & Clamp Connector

1. If you're replacing an old connection, remove the old clamp by cutting through its ear with the clamp tool; otherwise, skip to Step 2.
2. Cut the tubing cleanly and squarely to length.
3. Slide the clamp onto the tubing, then push the tubing onto the barb fitting until the tube contacts the body hex.
4. Position the clamp on the tubing outside of where the barb is positioned in the tube, making sure the hooks on the clamp band are engaged.
5. Squeeze the ear closed with the clamp tool.

Polypropylene Connectors

To install a polypropylene connector, follow these steps.

1. Cut the tubing cleanly and squarely to length.
2. If the tubing is larger than 1/2 inch, push an insert into the tube.
3. Push the tubing into the completely assembled connector until it contacts the shoulder inside the fitting (see the illustration on the left in Figure 6-8).
4. Tighten the nut with a wrench, but be careful to not over tighten it; the nut should **not** come in contact with the shoulder of the body (see the illustration on the right in Figure 6-8).

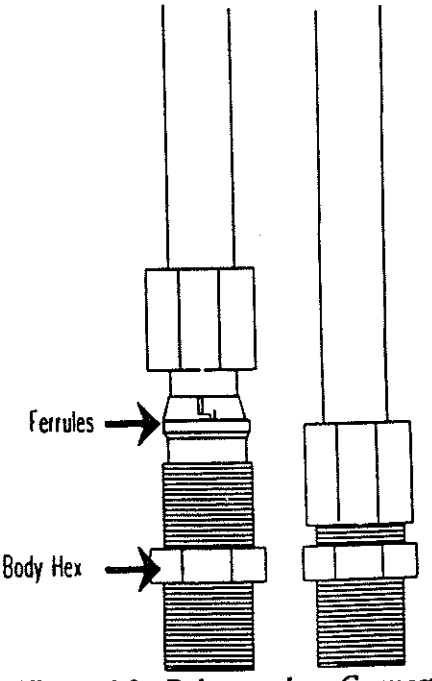


Figure 6-8: Polypropylene Connector

APPENDIX A
SPECIFICATIONS

The following sections provide specifications for Well Wizard controllers and the various Well Wizard sampling system types.

Standard Controller/Compressor

Table A-1 shows compressor performance for the standard controller/compressor cart, Model 3111HR/LR.

Table A-1: Model 3111HR/LR Performance

Air Flow (scfm)	Pressure (psig)
6.0	0
5.5	25
4.7	50
4.3	100

Other specifications are as follows:

- 200 feet maximum lift with *compressor* air source.
- 250 feet maximum lift with *compressed-gas cylinder* air source (regulator set at 125 psi).
- 2.5 hours of operation on a full tank of gasoline.

High-Pressure Controller/Compressor

Table A-2 shows compressor performance for the high-pressure controller/compressor cart, Model 3111HP/LH.

Table A-2: Model 3111HP/LH Performance

Compression (scfm)	Pressure (psig)
2.4	0
2.27	70
2.2	125
2.1	165

Other specifications are as follows:

- 320 feet maximum lift with the supplied *compressor* air source.
- 600 feet maximum lift with *compressed-gas cylinder* air source (regulator set at 300 psi).
- 2.5 hours of operation on a full tank of gasoline.

Well Wizard Equipment Configurations

Well Wizard sampling systems are available in Types A through L, as shown in the following figures. Type A is the basic sampling pump; the other types include options using Purge Mizer and Purge Master in various positions relative to the sampling pump. The diagram letters appear on the "Downwell Equipment Build/Specification Sheet(s)" supplied with your Well Wizard system.

Sampling System Type A

Figure A-1 shows the Type A sampling system, the basic bladder pump.

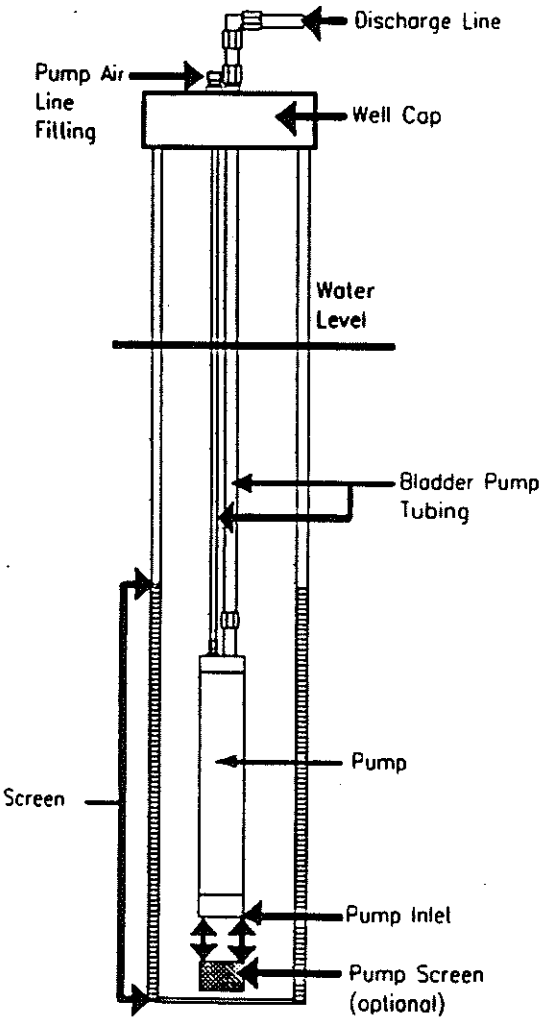


Figure A-1: Type A—Bladder Pump Only

Sampling System Type B

Figure A-2 shows the Type B sampling system, the bladder pump *below* a Purge Master.

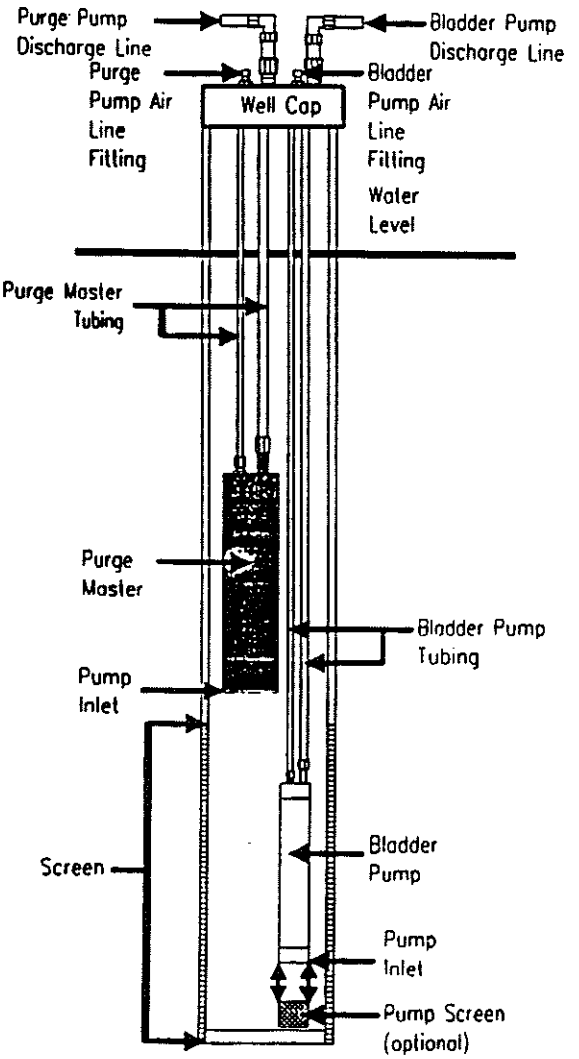


Figure A-2: Type B—Bladder Pump Below a Purge Master

Sampling System Type C

Figure A-3 shows the Type C sampling system, a bladder pump *above* a Purge Master.

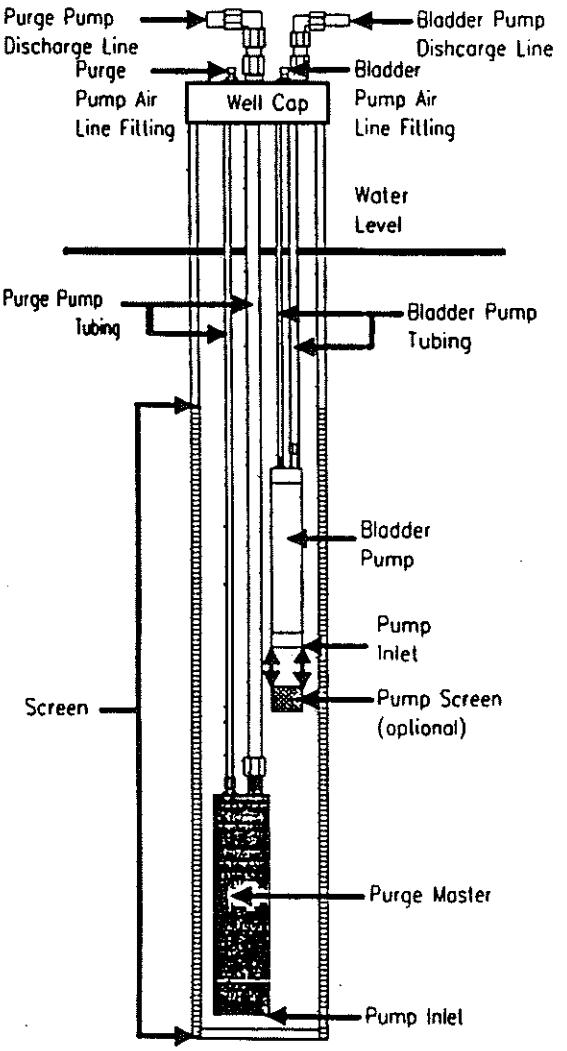


Figure A-3: Type C—Bladder Pump Above a Purge Master

Sampling System Type D

Figure A-4 shows the Type D sampling system, a bladder pump above a Purge Mizer with an inlet extension.

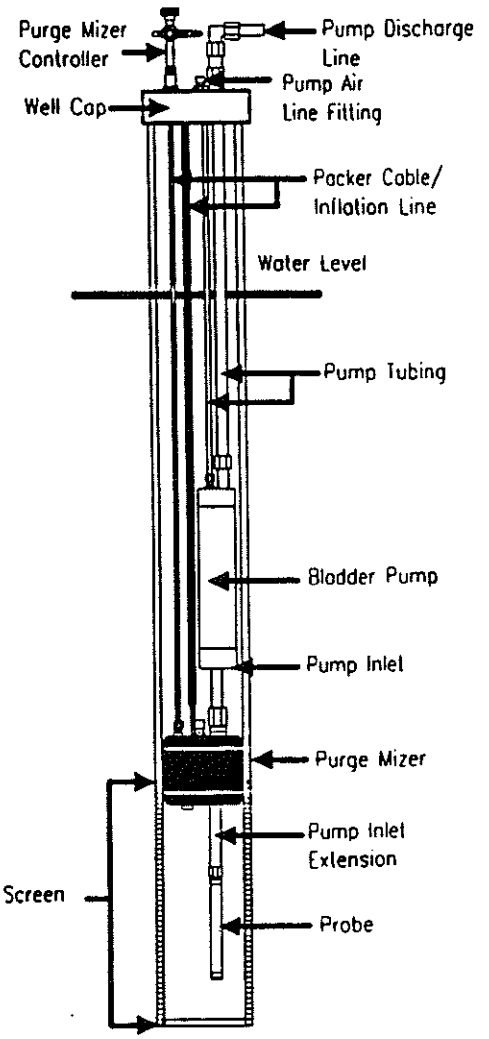


Figure A-4: Type D—Bladder Pump Above Purge Mizer with Extension

Sampling System Type E

Figure A-5 shows the Type E sampling system, a bladder pump *below* a Purge Mizer.

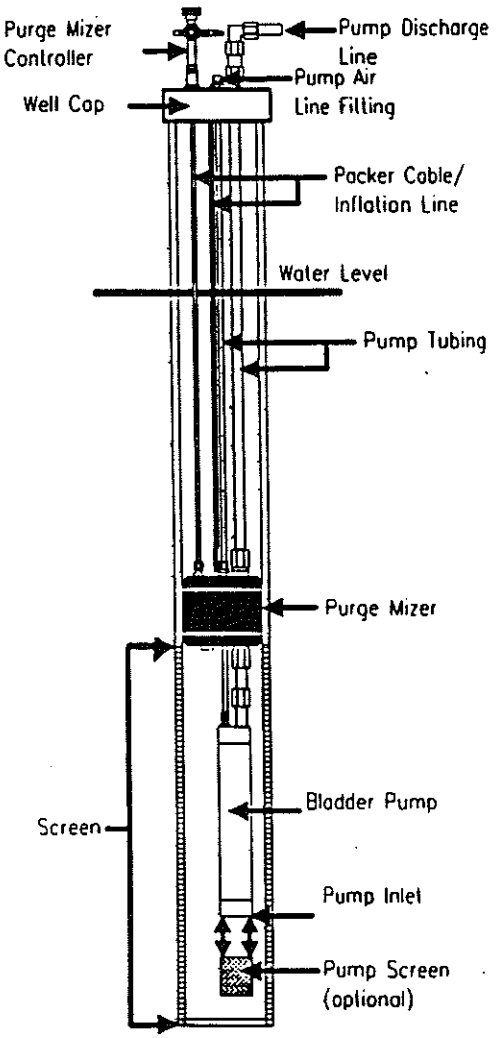


Figure A-5: Type E—Bladder Pump Below a Purge Mizer

Sampling System Type F

Figure A-6 shows the Type F sampling system, a bladder pump with electric submersible *above*.

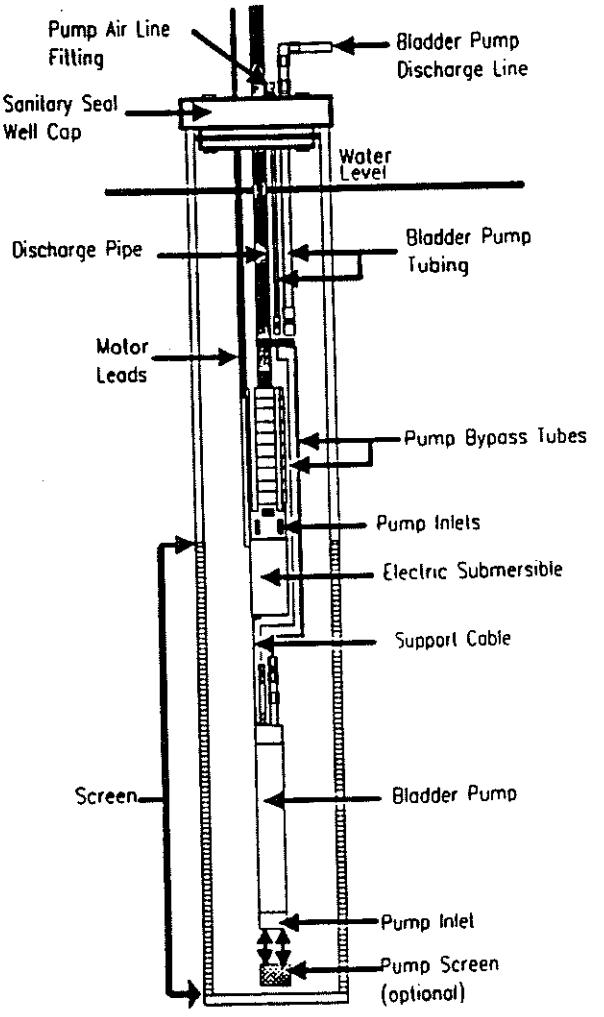


Figure A-6: Type F—Bladder Pump with Electric Submersible Above

Sampling System Type G

Figure A-7 shows the Type G sampling system, a bladder pump with electric submersible *below*.

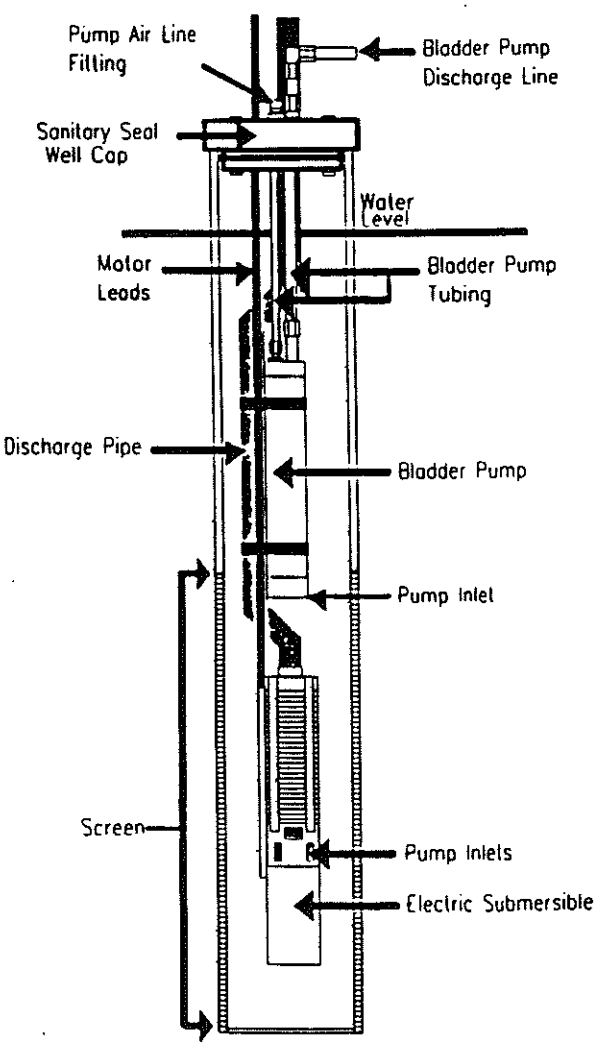


Figure A-7: Type G—Bladder Pump with Electric Submersible Below

Sampling System Type H

Figure A-8 shows the Type H sampling system, a bladder pump with Purge Master and Purge Mizer.

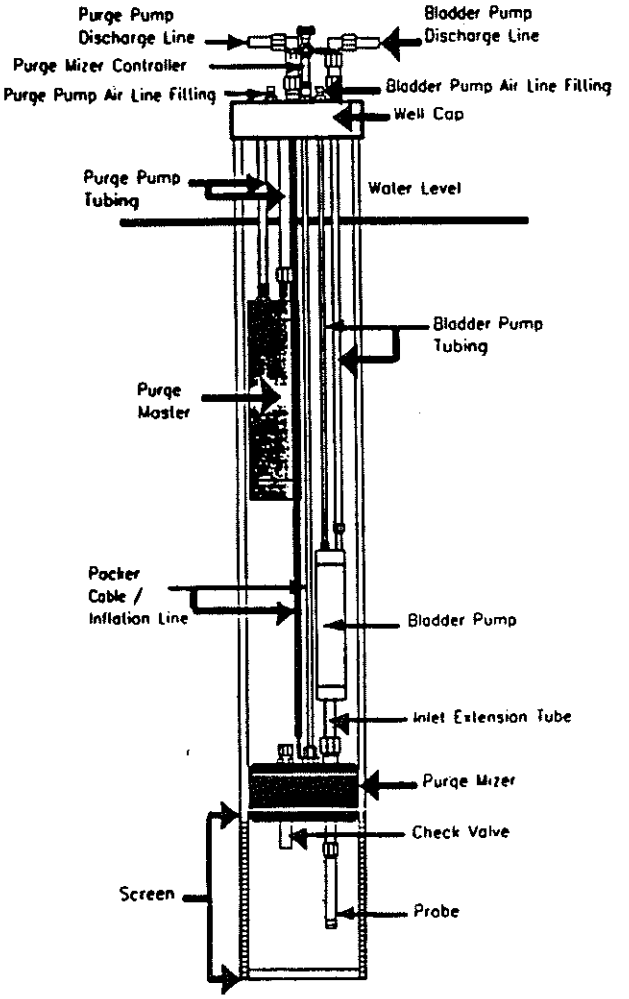


Figure A-8: Type H—Bladder Pump with Purge Master and Purge Mizer

Sampling System Type I

Figure A-9 shows the Type I sampling system, a bladder pump with tandem Purge Mizers.

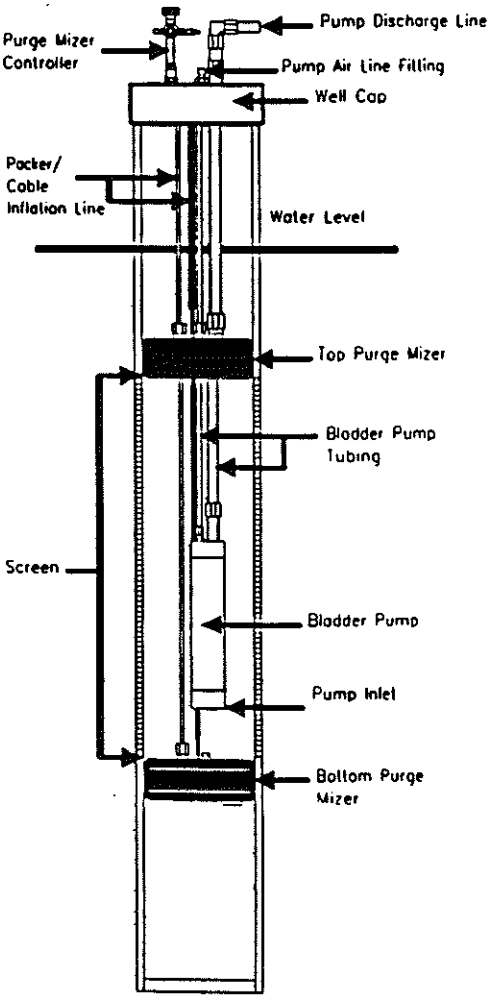


Figure A-9: Type I—Bladder Pump with Tandem Purge Mizers

Sampling System Type J

Figure A-10 shows the Type J sampling system, a bladder pump with Purge Master and Purge Mizer.

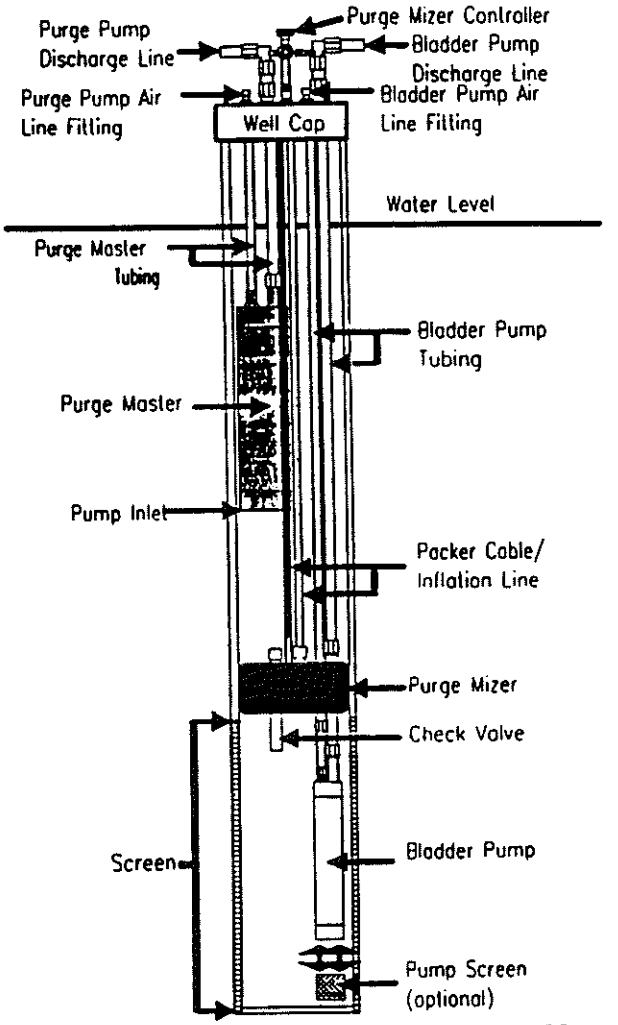


Figure A-10: Type J—Bladder Pump with Purge Master and Purge Mizer

Sampling System Type K

Figure A-11 shows the Type K sampling system, a bladder pump below a Purge Mizer with a vent line.

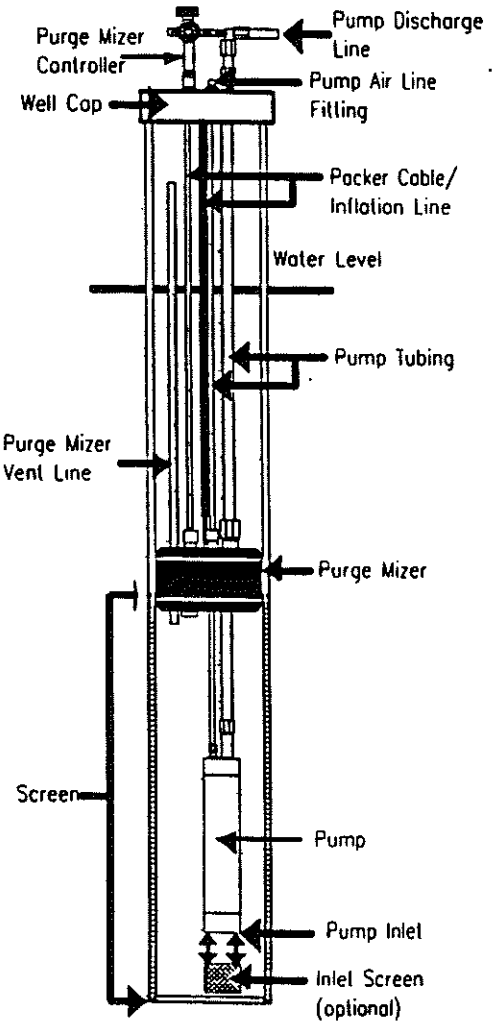


Figure A-11: Type K—Bladder Pump Below a Purge Mizer with a Vent Line

Sampling System Type L

Figure A-12 shows the Type L sampling system, a bladder pump with an inlet extension.

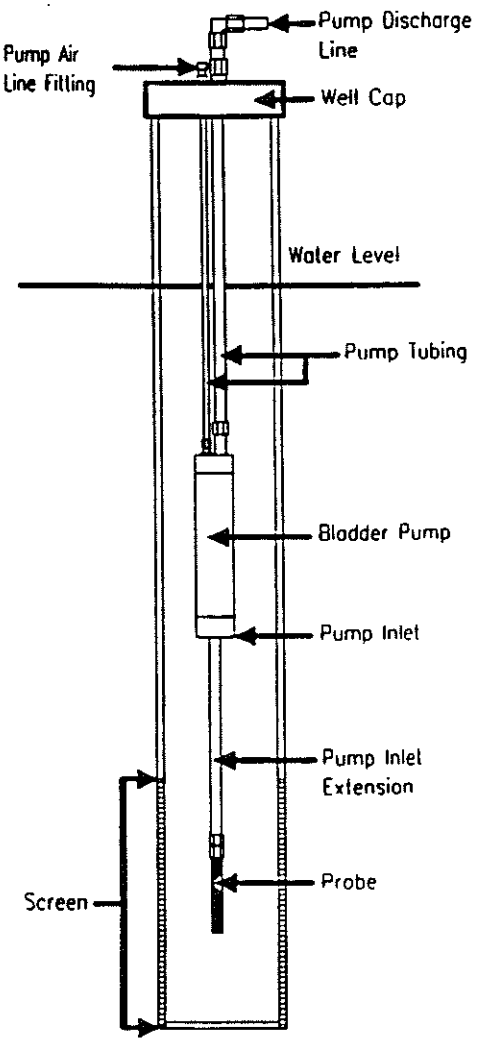


Figure A-12: Type L—Bladder Pump with an Inlet Extension

APPENDIX B
MY WELL WIZARD IS BROKEN: WHAT TO DO

QED sometimes gets calls from customers who say, "My Well Wizard is broken. What should I do?" We *want* to help–and we *will* help–but first we need to know the symptoms. As described in this book, your Well Wizard is a *system* that includes many components. Together we can discover the problem, solve it, and have your system up and running again before long. The following sections provide the trouble-shooting information you need to get a solution started.

Warning! Don't disassemble any component of your Well Wizard system. Doing that could void your warranty coverage.

Perform These Three Checks

If you have a problem, the following three checks will help to either locate the problem or assist in our diagnosis and repair. In case you later have to call QED, write down your findings as you perform these checks–so you can tell us what happened when you performed them.

Note: The components of your Well Wizard system and the correct ways to use them are described earlier in this book. If you're new to Well Wizard, before you decide that you have a problem, please take a few minutes to become familiar with the system and how to operate it.

Check Controller Cycling and Pressure

Make sure the controller is cycling and attaining a pressure of at least 80 psi in 60 seconds. You *may* have to turn the **FLOW THROTTLE** control knob fully clockwise and set the **DISCHARGE** timer knob on **F** for the Model 3013 or **5 O'CLOCK** for the Model 350 to achieve this pressure.

Check Cycle Length Adjustment

Make sure that you can change the cycle length by adjusting the **REFILL** and **DISCHARGE** timer knob positions.

Check for Sufficient Discharge Volume

Make sure that the discharge volume is as high as it should be. To do that, follow these steps.

1. Set the **REFILL** and **DISCHARGE** timer knobs to **F** for the Model 3013 or **5 O'CLOCK** for the Model 350.
2. Measure the volume of one discharge cycle. The volume should be as follows:
   - **For 1100 series pumps,** the volume should be greater than 300 ml.
   - **For 1200 series pumps,** the volume should be greater than 400 ml.
3. If the volume is low, check for the following:
   - Insufficient submergence of the pump.
   - A well-water recovery rate that's too slow.
   - A leaky discharge fitting or leaky tubing.

Call QED, if Necessary

If the three checks didn't reveal a minor problem that you can easily fix–such as a loose fitting–please call our Customer Service department at one of the following numbers for assistance.

- **Monday through Friday, 8:00 a.m. to 5:00 p.m. EST:** (313) 995-2547.
- **After hours and weekends:** 1-800-272-9559 (*or* 1-313-746-8045 if you're outside the U.S.).

The person you talk to may ask you to look at a schematic drawing or to refer to a parts list. The schematic drawings and parts lists are in Appendix C.

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THIS DEVICE IS NOT INTENDED TO DETECT COMBUSTIBLE LEVELS OF GASES. THIS DEVICE IS CLASSIFIED FOR USE IN ATMOSPHERES CONTAINING COMBUSTIBLE LEVELS OF GASES.

CET APPAREIL CEST NE PAS INTENDER POUR DETECTER DES NIVEAUX DE COMBUSTION DES GAZ. CET APPAREIL EST CLASSIFIE POUR USAGE DANS DES ATMOSPHERES CONTENANT DES NIVEAUX DE COMBUSTION DES GAZ.

! WARNING !

-DO NOT PROCEED BEFORE READING-

THIS MANUAL MUST BE CAREFULLY READ BY ALL INDIVIDUALS WHO HAVE OR WILL HAVE THE RESPONSIBILITY FOR USING, MAINTAINING, OR SERVICING THIS PRODUCT. The product will perform as designed only if it is used, maintained, and serviced in accordance with the manufacturer's instructions.

CAUTION!!
TO REDUCE THE RISK OF ELECTRIC SHOCK, TURN OFF POWER BEFORE REMOVING THE SENSOR CAP FOR SERVICE. THE SENSOR CAP PROVIDES AN ELECTROSTATIC SHIELD. NEVER OPERATE THE UNIT WHILE THE CAP IS REMOVED.

TO REDUCE THE RISK OF IGNITION OF HAZARDOUS ATMOSPHERES, RECHARGE BATTERY ONLY IN AN AREA KNOWN TO BE NON HAZARDOUS.

NE CHARGER LES BATTERIES QUE DANS EMPLACEMENTS DESIGNES NON DANGEREUX

THE MODEL PGM-76 EQUIPMENT IS SUITABLE FOR USE IN CLASS I, DIVISION 2, GROUPS A,B,C,D OR NON-HAZARDOUS LOCATIONS ONLY.

THE MODEL PGM-76IS EQUIPMENT IS CLASSIFIED AS TO INTRINSIC SAFETY FOR USE IN CLASS I, DIVISION 1, GROUPS A,B,C,D OR NON-HAZARDOUS LOCATIONS ONLY.

WARNING

EXPLOSION HAZARD - SUBSTITUTION OF COMPONENTS MAY IMPAIR SUITABILITY FOR CLASS I , DIV 2 AND CLASS I, DIV 1

AVERTISSEMENT

RISQUE D'EXPLOSION - LA SUBSTITUTION DE COMPOSANTS PEUT RENDRE CE MATERIEL INACCEPTABLE POUR LES EMPLACEMENTS DE CLASSE I, DIVISION 2 / CLASSE I, DIVISION 1

Special Note

-1-

When the MiniRAE Plus (PGM-76) Professional PID is taken out from the transport case and turned on for the first time, there may be some residual organic vapor trapped inside the ionization chamber. The reading may therefore show a few ppm. Connect the zero gas adapter supplied with the unit will clear the residual vapor and reduce the reading to zero quickly.

-2-

The battery of the MiniRAE Plus unit drains slowly even when turned off. If the unit has not been charged for 4-5 days, the battery voltage will be low. Therefore, it is a good practice to leave the unit in the charger so that it is fully charged and ready for immediate use. It is also recommended to fully charge the unit FOR AT LEAST 24 HOURS before using it. If the unit is going to be put on the shelf for more than 4-5 days, it is highly recommended to turn off the battery switch at the back of the unit. This will prevent the battery from being deeply discharged.

-3-

The battery switch also serves as a reset switch for the microprocessor inside the MiniRAE Plus Professional PID unit. If for some reasons, the unit is hang up (foe example, no response to key press or display funny characters on LCD display), turn off the switch and then turn it on again should reset the microprocessor.

1.0 GENERAL INFORMATION

MiniRAE Plus is a Programmable Professional Photo-Ionization Detector (PID) to measure organic vapors in hazardous or industrial environments. It incorporates a sampling pump and data download capabilities for continuous toxic monitoring, site survey and leak detection applications. It can measure two classes of toxic gases: (1) organic vapors with the supplied 10.6 eV gas discharge lamp, and (2) chlorinated compounds with the interchangeable 11.7 eV lamp available as in optional accessory. Features are:

- **Lightweight and Compact**
  - 18 oz , cellular phone size
- **Dependable and Accurate**
  - rugged design, microprocessor control
- **User Friendly**
  - menu driven, intuitive end-use operation
- **Programmable Alarm Thresholds**
  - audio buzzer & flashing display alarm

MiniRAE Plus (PGM 76K) consists of : a Professional PID unit, AC charging adapter, interface cable, user manual, calibration accessories and a hard transport case.

1.1 General Specifications

Table 1.1

Professional PID Unit Specification	
Size	7.1"L x 2.7"W x 1.8"H (18.0 cm x 6.9 cm x 4.6 cm)
Weight	18 oz with battery (0.510 kg)
Detector	Interchangeable 10.6eV or 11.7eV electrodeless ultraviolet discharge lamp with Teflon/stainless steel chamber
Operating Hours	10 hours continuous operation
Battery	Two rechargeable, 6V, 500 mAh, sealed, lead-acid. Field replaceable.
Gas Sampling:	Piston pump with >400 ml/min intake flow rate
Gas Inlet Probe:	6" flexible 5/32" tube
Gas Outlet :	5/32" diameter barb fitting
Attachment:	wrist strap
Display	7 digit LCD with LED back light
Analog Output:	0 to 1 V
Range	0 - 999.0 ppm with 0.1 ppm resolution, 1000-1999 ppm with 1 ppm resolution (continued)

(continued)

Accuracy	+/- 2 ppm or +/- 10% of reading, calibrated to 100 ppm Isobutylene
Response Time	< 3 seconds to reach 90% of exposed concentration
Key-pads	2 operation keys, 2 programming keys, and an ON/OFF key
Alarm Setting	Separate alarm limit settings for TWA, STEL, and Peak in Hygiene Mode; low and high alarm limits for Survey Mode
Alarm	95 dB buzzer and flashing red LED to indicate exceeded preset limits, low battery, or lamp failure
Calibration	Two points field calibration for zero gas and standard gas
Protection	Password protected calibration settings, alarm limits, and data in Hygiene Mode
Data Storage	48 STEL readings (15 minutes interval) in Hygiene Mode; 50 site readings in Survey Mode
Temperature	-10° to 40°C (14° to 104° F)
Humidity	0 % to 100% relative humidity (non-condensing)

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2.0 OPERATION OF MINIRAE PLUS

The MiniRAE Plus Professional PID Unit is a portable organic vapor monitor/sampler. It gives the real time measurements and activates alarm signals whenever the exposure exceeds preset limits. Prior to factory shipment the MiniRAE Plus is preset with default alarm limits and the sensor is pre-calibrated with 100 ppm Isobutylene gas. After receiving the unit, first turn on the battery switch on the back of the unit. Then charge the unit for at least 24 hours to fully charge the battery. The unit is ready for immediate operation.

2.1 Physical Description

Figure 2.1 shows the main components of the MiniRAE Plus Professional PID Unit which includes :

- 5 keys for user to interact with the unit : power key and 2 operation keys for normal operation; two programming keys for setting up the unit
- LCD display with back light to show real time and calculated measurements
- Buzzer and red LED for alarm signal whenever the exposures exceed preset limits
- Probe assembly (including gas inlet tube and sensor cap) to draw air sample
- Battery charging jack for connection to AC or DC charging adapter and a battery switch to disconnect battery from the unit
- Gas outlet port for connection to sample collection bag
- Multi-interface jack for connection to PC, audio interface or analog output

The operation details are explained in the following sections.

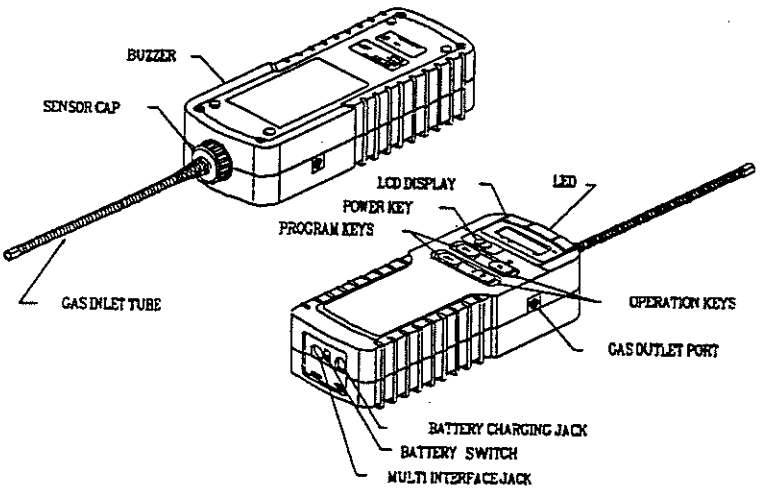


Figure 2.1 Major parts of the MiniRAE Plus

2.2 Two Modes of Operation

The MiniRAE Plus PGM-76 Profession PID unit offers two different operating modes:

1) Industrial Hygiene Mode (simplified as Hygiene Mode) : In this mode of operation, the unit measures the air sample once each second and compares it with a preset peak alarm limit. These same measurements are also averaged over one minute interval with the result value used to compute Time Weighted Average (TWA) and Short Term Exposure Level (STEL) values which are themselves compared to preset alarm limits.

In addition, the STEL values are captured and recorded every 15 minutes for up to 12 hours. A time stamp indicates when the unit was last turned on and off.

2) Site Survey / Leak Detection Mode (simplified as Survey Mode): In this mode of operation, the unit measures air sample once each second and compares it with a preset low alarm limit. A variable frequency alarm signal is generated in proportion to the magnitude of the measurement. When datalog is enabled, the average value or the peak value over a sampling period which can be programmed from 1 second to 9999 seconds (166 hours) is stored.

The datalogging can be initiated manually (event driven) or the unit can perform continuous sampling (automatic). Up to 50 sets of sample readings with 24 hour time stamps can be recorded in this mode.

Selection of Operation Mode:

Users can configure the instrument to be in either one of the two operating modes using a software package - "ProRAE -76" which is supplied with the Basic Kit of MiniRAE Plus. This software runs on any Personal Computer (PC) under Window™ 3.1 or DOS environment. Please refer to section 6 on how to install this software package , how to interface MiniRAE Plus instrument to PC and how to configure the instrument for either Hygiene or Survey Mode.

After the configuration is downloaded to the instrument as described in section 6, the instrument will be setup to operate in the appropriate mode.

Indication of Current Operation Mode:

When the MiniRAE Plus Professional Unit is first turned on, a software version message will appear in the LCD display. If the unit is configured for Hygiene Mode, the message will be " HG - x.xx". If it is configured for Survey Mode, the message will be "Su - x.xx" where x.xx is the version number of each operating software.

2.3 Keys and Display

Figure 2.2 shows the LCD display and the keypad on the front panel of the unit. The function of the 5 keys during normal operation are summarized bellow:

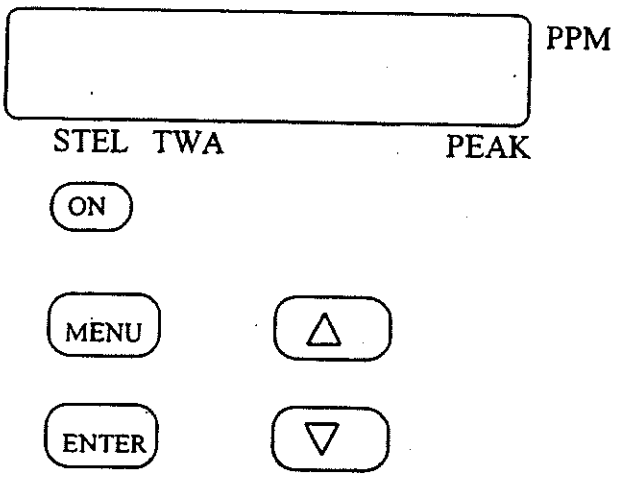


Figure 2.2 Key-pad and display of MiniRAE Plus

Table 2.1

Key	Function in Normal Operation
[on]	-Toggle on/off the power;
[up]	-Toggle on/off the back light
[down]	-Choose display readings
[enter]	-Confirm to turn off the power*
[menu]	-Enter into programming task** **Caution: entering programming task will interrupt normal gas monitoring operation of the unit.**

Note:

* - **[enter]** key is also used to turn off buzzer during Hygiene Mode operation, and to start /stop datalogging operation in Survey Mode. (see section 2.8 and 2.9 for details)

** - **[menu]** key is also used in conjunction with the **[on]** key to clear previously saved data in Hygiene Mode during a special power on sequence (see section 2.11 for details)

The MiniRAE Plus Professional PID includes a 7-digit LCD display with 4 labels of STEL, TWA, PEAK, and PPM marked on the window, as shown in Figure 2.2. The display will show the following five types of readings:

- Real time gas concentration in ppm
- Short term exposure level (STEL) of the gas concentration in ppm*
- Time weighted average (TWA) value of the gas concentration in ppm **
- Peak gas concentration in ppm
- Battery voltage in volt (from 5.3 to 6.4 V)

Note:

* - the 15 minute STEL reading is only available in Hygiene Mode operation.

** - the TWA reading is based on fixed 8 hours average value define by OSHA in Hygiene Mode operation. In Survey Mode, the TWA reading is the average value over each sampling period.

2.4 Power On/Off

To turn on the MiniRAE Plus Professional PID Unit, press **[on]** key. The audio buzzer will beep once and the display will show "HG- x.xx" or "Su- x.xx" to indicate the operating mode and software version number. The unit will then go through a self-diagnostic routine to check the key components of the unit. A ".dIAG.." message will be displayed with red back light turned on while the self-diagnostic routine is executing. The red LED and back light will flash once and buzzer beep once to ensure that they are functional. The sampling pump will be turned on and start to draw air sample.

After about 30 seconds, the display will change to instantaneous reading of the gas concentration in ppm if the unit passes diagnostics tests. If there is any problem with the unit, an error message will be displayed (Refer to section 9 for troubleshooting of the particular error condition).

To turn off the MiniRAE Plus Professional PID Unit, press **[on]** key. The message "Off" will flash on the LCD display. If users really want to turn off the unit, press **[enter]** key to confirm and the unit will be turned off. Press any other key will return the unit to normal operation.

2.5 Display Readings

The MiniRAE Plus Professional PID Unit can display five different readings : instantaneous gas concentration , STEL*, TWA, peak and battery voltage. Here is a brief explanation of each reading:

1) The **instantaneous** reading is the gas concentration in parts per million (ppm). The reading is updated once a second and is shown as " xxx.x" in the LCD display without any arrow cursor or character display. Note: in Survey Mode, a two digit site number will also be displayed together with the instantaneous reading as "00 xxx.x". The site number starts from 00 and ends at 49.

2) The **STEL*** reading is the last 15 minute average reading of the gas concentration. The reading is updated once a minute and is shown as "xxx.x" with a small arrow cursor pointing to the "STEL" label on the LCD window.

3) The **TWA** reading in Hygiene mode is the accumulated reading of the gas concentration divided by 8 hours since the data was cleared last time. The reading is updated once a minute and is shown as "xxx.x" with a small arrow cursor pointing to the "TWA" label on the LCD window. In Survey mode,

the **TWA** reading is the average gas reading during the previous sampling period.

4) The **peak** reading in Hygiene mode is the maximum reading of the gas concentration since the data was cleared last time. The reading is updated at one second interval and is shown as "xxx.x" with a small arrow cursor pointing to the "PEAK" label on the LCD window. In Survey mode, the **peak** reading is the peak gas reading druing the previous sampling period.

5) The **battery voltage** reading is the current battery voltage in volt. The reading is updated once a minute and is shown as "bAt xxx.x" in the LCD window.

Choose a reading :
The five readings are arranged in a "round robin" order:

instantaneous => STEL* => TWA => Peak => battery voltage => instantaneous

To choose a specific reading, press the **[down]** key one or more times in normal operation mode until the desired reading shows. For example, to display STEL reading, press **[down]** once. To display TWA reading. press **[down]** key twice, and so on.

* - the STEL value is not displayed in Survey Mode.

2.6 Alarm Signal

The built-in microcomputer constantly updates and monitors real time gas concentration and compares it with the programmed alarm limits (TWA, STEL, and peak limits for Hygiene Mode, low and high limits for Survey Mode). Whenever the concentration exceeds any of the preset limits, the alarm buzzer and red flashing LED will be activated immediately to warn user of the alarm condition.

Note: a fully charged battery should show 6.3 volt or higher. Whenever the battery voltage falls bellow 5.5 volt or the UV lamp or sensor module fails, the unit will also activate the buzzer and red LED alarm signal. When the low battery alarm occurs, there will be about 20-30 minutes operating time left from the battery. When the battery voltage falls bellow 5.3 volt, the unit will be turned off automatically.

Note: in Hygiene Mode, the alarm signal of the gas concentration exceeding preset limits is a " two beeps" and "two flashes" per second. The lamp or sensor failure alarm signal is a "single beep" and a "single flash" per second. The battery low alarm signal is a "single flash" per second. A flashing message of "Err xxx.x" in the LCD display indicates the lamp or sensor failure condition. A flashing message of "bAt xxx.x" indicates the low battery condition. In addition, there

will be a "single beep" per minute to remind users that battery voltage is low.

Note: it is extremely important that when the lamp or sensor failure alarm occurs, users should stop the operation of the unit immediately and follow the troubleshooting guide in section 9 to diagnose the problem.

In Survey Mode, the alarm signal is proportional to the magnitude of the gas concentration. Therefore, when gas concentration exceeds preset limits, the alarm signal may vary from a "single beep" and a "single flash" per second to a rapid " 7 beeps" and " 7 flashes" per second when the high threshold level has been exceeded. The higher frequency of alarm signal indicates higher gas concentration.

The lamp or sensor failure alarm signal is a single beep and a single flash per second. The battery low alarm signal is a single flash per second. A flashing message of "Err xxx.x" in the LCD display indicates the lamp or sensor failure condition. A flashing message of "bAt xxx.x" indicates the low battery voltage condition. In addition, there will be a "single beep" per minute to remind users that battery voltage is low.

2.7 Preset Alarm Limits and Calibration

The MiniRAE Plus Professional PID Unit is factory calibrated with standard isobutylene gas, and is programmed with default alarm limits as listed below. Refer to section 4 and 5 for programming procedures if new calibration or new alarm limits are required.

Table 2.2

Factory Calibration and Preset Alarm Limits	
Calibration Standard Gas isobutylene	100 ppm
Hygiene Mode:	
TWA Alarm Limit	10 ppm
STEL Alarm Limit	25 ppm
Peak Alarm Limit	50 ppm
Survey Mode:	
Low Alarm Limit	10 ppm
High Alarm Limit	100 ppm
Battery Low Level	5.5 volt
Power Off Level	5.3 volt

2.8 Datalogging

The MiniRAE Plus Professional PID Unit is capable of recording crucial data during normal operation. The recorded data can be down loaded to Personal Computer later on for record keeping or report generation. The data recorded in two operating modes are different:

Hygiene Mode:
In Hygiene Mode, MiniRAE Plus Professional PID Unit calculates and stores the values of TWA, STEL, Peak concentration and 12 hours of STEL readings taken at 15 minutes interval (a total of 51 readings). In addition, the time stamps which indicate: when the unit was last turned on and off, when the peak occurred and when the TWA alarm occurred (if any) will also be recorded.

In Hygiene Mode, the datalogging operation is activated automatically when the unit is turned on. When power is turned off, the data will be retained in non-volatile memory. At each "turn on" time, the previously stored data will not be cleared and the unit will continue to record data. If users wish to clear the data at power on, they need to follow the special power on sequence as described in section 2.11.

When the data memory is full (12 hours of STEL readings), the unit will stop recording new data and the previously stored data will not be over written.

Survey Mode:
In Survey Mode, the MiniRAE Plus Professional Unit will allow users to record up to 50 readings of average or peak gas concentration over a specified sampling period. In addition, a time stamp and a site number will also be recorded together with each reading. The sampling period can be programmed from 1 second up to 9999 seconds.

Users are allowed to select one of the following two different datalog options:

1) manual sampling option: in this option, users have to press **[enter]** key to start each sampling period. When a sampling period is over, the datalogging operation will stop.

2) continuous sampling option: in this option, users press **[enter]** key once to start the first sampling period. At the end of each sampling period, next sampling period will start automatically. The datalogging operation will not stop until another **[enter]** key is pressed.

Note: in either option, the datalogging operation will stop when **[enter]** key is pressed any time during a sampling period.

User is also allowed to choose to datalog the **average** value or the **peak** value of each sampling period. (see section 5.14 for details)

The site number will automatically advance to next one when a sampling period is over. Users can use "select site number" menu in programming task to change to a different site number. (see section 5.4 for details)

When datalogging is in progress during a sampling period, the unit will not respond to **[menu]** key input to prevent disruption of the datalogging operation. A small letter "d" will also flash next to the site number to indicate that the datalogging is in progress.

When the data memory is full (48 readings), the unit will start to over write old data.

Default sampling period:

The default sampling period for Survey Mode is set to 1 second. With this setup, every time the **[enter]** key is pressed, a single reading will be recorded. This is particularly convenient for leak detection applications.

2.9 Turn Off Buzzer

In Hygiene Mode, the alarm buzzer can be turned off for 60 seconds by pressing **[enter]** key. After the 60 seconds time interval expires, the buzzer will resume if the alarm condition still exists.

Note: this feature is not available in Survey Mode because the **[enter]** key is used to start and stop datalogging operation.

2.10 Back Light

The LCD display is equipped with a red LED back light to assist the readings under poor lighting conditions. This back light can be turned on by pressing the **[up]** key. When the back light is already on, press **[up]** key will turn it off.

Note: the LED back light consumes higher amount of energy from the battery and will shorten the operating time of the unit. Therefore, it is important to turn the back light off when it is not needed.

2.11 Special Power-on Sequence

In MiniRAE Plus Professional PID Unit, all data are automatically retained in non-volatile memory even if the power is turned off. Users can therefore turn off the unit and turn it back on to resume the operation without losing previously stored data during normal operation.

The MiniRAE Plus also provides a special power on sequence in Hygiene Mode **to clear all data** (i.e. the values of TWA, STEL, Peak concentration and 48 STEL readings taken at 15 minutes interval) and start recording new data at power on time. This is accomplished by pressing **[menu]** key first, hold it down and then press **[on]** key to turn on power.

Note: during the special power on sequence, the display will show a " CLr .." message to indicate that all the data is being cleared.

2.12 Diagnostic Power-on Sequence

The MiniRAE Plus Professional PID Unit offers a special diagnostic power on sequence to allow user to read "raw" (or un-calibrated) instrument readings during zero gas calibration procedure. This feature can provides additional information to users regarding the sensor performance. This is accomplished by pressing **[up]** key first, hold it down and then press **[on]** key to turn on power.

Note: using the special diagnostic power on sequence, the unit will perform normally except during zero gas calibration procedure (see section 4.7.1). The display will show a "raw" reading, instead of the "ppm" reading. Typically, the reading should be between "330.0" to "370.0". When exposed to a calibration gas, the reading should go down quickly. The reading can be anywhere between "0.0" to "300.0".

If the reading does not change when exposed to a calibration gas, then it is an indication that the lamp is very weak or the sensor module is defective.

2.13 Disconnect Battery

The MiniRAE Plus Professional PID Unit provides a mechanical switch to allow user to disconnect the battery from the unit. This is to prevent the battery from being deeply discharged when the unit is placed on the shelf or during shipment.

To disconnect the battery, open the rubber cover at the rear side of the unit, find a small switch between the battery charging jack and the multi-interface jack. Use a ball pen to move the switch to OFF position (down). When the switch is in OFF position, the battery will retain 85% of its charge after 6 months.

Note : when the battery is switched off, the real time clock will stop. However, the calibration and datalog information will be preserved for at least 10 years.

Reset Microprocessor

The battery switch also serves as a reset switch for the microprocessor inside the MiniRAE Plus Professional PID unit. If for some reasons, the unit is hang up (no response to key press or display funny characters on LCD display), turn off the switch and then turn it on again should reset the microprocessor.

3.0 OPERATION OF ACCESSORIES

There are a number of accessories for MiniRAE Plus Professional PID Unit:

- 110 V AC charging adapter
- Gas outlet port adapter and sample collection Tedlar bag
- Remote access probe (8 ft.)
- Audio interface adapter cable and earphone
- Analog interface adapter cable
- Water trap disk
- Dilution probe
- UV attenuator ring

The operation details of these accessories are explained in the following sections.

3.1 Charging of the MiniRAE Plus

On the rear side of the MiniRAE Plus Professional PID Unit, there is a battery charging jack which is normally covered by a protective rubber cover. Open the rubber cover and connect the AC adapter (or the automotive DC charging adapter, depending on the power source) to the charging jack.

There is a bi-colored LED inside the LED window which will provide an indication of the charging status:

Red	-battery is being charged
Green	-charging is completed
No Light	- bad connection or defective battery

Plug in the AC (or DC)adapter which will turn on the red charge status LED first. If the battery is fully charged, it will turn to green quickly. A completely discharged battery will be charged to its full capacity within 10 hours.

WARNING:
TO REDUCE THE RISK OF IGNITION OF HAZARDOUS ATMOSPHERES, RECHARGE BATTERY ONLY IN AREA KNOWN TO BE NON HAZARDOUS. REMOVE AND REPLACE BATTERY ONLY IN AREA KNOWN TO BE NON HAZARDOUS.

Note: the factory-supplied battery is designed to last 10 hours of normal operation for a new battery under the best conditions. As the battery becomes older or operated under adverse conditions, the battery capacity will be reduced significantly.

The battery of the MiniRAE Plus unit will be drained slowly even if the unit is turned off. If the unit has not been charged for 4-5 days, the battery voltage will be low. The charging circuit is designed to prevent over charging. Therefore, it is a good practice to always leave the unit in the charger when it is not used so that it is fully charged and ready for immediate use.

There is an optional **single station battery charger** accessory for the MiniRAE Plus Professional PID Unit. This charger will allow users to charge a spare battery outside the unit. Plug the battery to the jack on the back of the charger to charge the spare battery.

There is also an optional **automotive charging adapter cable** which allows user to charge the MiniRAE Plus unit directly from the 12 V cigarette lighter socket inside a car.

3.2 Sample Gas Collection

On the right side of the MiniRAE Plus Professional PID Unit, there is a gas outlet port where the gas sample can be collected after going through the sensor module and pump unit.

A gas outlet port adapter with 2 ft. Tygon tubing is supplied with the basic kit. Insert the threaded end of the adapter into the gas outlet port and turn clock wise to tighten the adapter. The open end of the Tygon tubing can be connected to a sample gas collection bag. A complete gas collection kit which includes a gas outlet adapter, 2 ft. Tygon tubing and a three liter Tedlar sample collection bag is also available as an accessory.

3.3 Remote Access Probe

A remote access probe is available as an optional accessory for the MiniRAE Plus Professional PID Unit. This probe is constructed with an aluminum telescoping pointer and 8 ft. Teflon tubing. The telescoping pointer allows the probe unit to be stored in a compact space when not in use and conveniently extended into a 4 ft. long pointer to reach difficult to reach sampling space, e.g. above a ceiling or inside a large container, etc. The other end of the Teflon tubing can be inserted directly into the gas inlet tube of the PID unit.

Note: when the remote probe is used, there will be an additional delay of about 2-3 seconds of the instrument response because the sample gas has to travel through the 8 ft tubing before it reaches the sensor module inside the unit. The traveling speed of air sample inside the tubing is 3 ft per second.

The sampling pump can pull in sample gas from as far as 200 ft horizontally or 100 ft vertically.

3.4 Audio Interface Adapter and Earphone

On the rear side of the MiniRAE Plus Professional PID Unit, there is an 8 pin round multi-interface jack which is normally covered by a protective rubber cover. An audio interface adapter cable and a small earphone is available as an optional accessory for the MiniRAE Plus Professional PID Unit. . Open the rubber cover and connect the interface cable to the jack.

The audio buzzer signal is brought out through this interface cable. Plug the earphone into the mini-RCA jack on the end of the interface cable. Users can now hear the same alarm signal through the earphone.

WARNING:
TO REDUCE THE RISK OF IGNITION OF HAZARDOUS ATMOSPHERES, DO NOT CONNECT THE EARPHONE OR EXTERNAL ALARM DEVICES TO MINIRAE PLUS IN AREA KNOWN TO BE HAZARDOUS.

Audio alarm signal

The audio alarm signal consists of a series of 2 kHz pulses appearing at pin 7 of the multi-interface jack. The duty cycle of the signal is 50%. Figure 3.1 show the specification and waveform of the alarm signal:

Alarm signal specification:

voltage :	6 V peak to peak
current :	14 mA max
frequency :	2 kHz
duty cycle:	50% square wave
duration:	50 mili-seconds
pin out:	Pin 7 - signal
	Pin 8 - ground

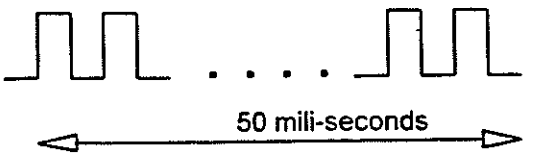


Figure 3.1 Alarm signal waveform

Note: the audio interface can be connected an external alarm box which can amplify the alarm signal or produce a strong flash light signal, if needed. If users need to use their own earphone, make sure that the earphone has at least 200 ohm impedance.

Interferences

High levels of ions which form very insoluble salts of silver may deposit a layer of salt on the membrane, causing electrode malfunction. Strongly reducing solutions may also form a surface layer of silver. In either case, restore performance by polishing the sensing element.

Mercury must be absent from samples.

Measurements can be made in solutions containing oxidizing agents such as Cu^{2+}, Fe^{3+}, and MnO_4^-.

Table 7 gives the maximum allowable concentration of the more common interfering ions, expressed as the ratio of the interfering ion molarity to the sample chloride molarity. If the ratio is exceeded, readings will be in error. If the ratio is less than that listed in the table, neither accuracy of the measurement nor surface of the electrode membrane will be affected. To convert molarity to mg/L, see *Table 1*.

(a) Remove hydroxide interference by acidifying to pH 4 with 1 M HNO_3 (Cat No. 50257).

(b)Measure mixed halides in solution by using CISA to remove interferences or by Gran's Plot titration.

(c) Remove sulfide and cyanide by adding a nickel (2+) solution or by using CISA.

(d) Represents a complexing species. Maximum level can be exceeded without electrode damage. Value shown is for 1% error.

Use of CISA

Interferences to the chloride measurement may be minimized by addition of CISA, an oxidizing agent which will oxidize up to 500 mg/L S^{2-}, 100 mg/L Br^- or I^-, 100 mg/L NH_3, or a 100-fold

Table 7: Maximum Allowable Ratio of Interfering Ion to Chloride

Interference	Maximum Allowable Ratio $\frac{\text{Interference}}{\text{Chloride}}$
[a] OH^-	80
[b] BR^-	3×10^{-3}
[b] I^-	5×10^{-7}
[c] S^{2-}	10^{-6}
[c] CN^-	2×10^{-7}
[d] NH_3	0.12
[d] $S_2O_3^{2-}$	0.01

excess of CN^- over Cl^-. By using CISA, chloride can be measured in the presence of other halides without the need for a Gran's Plot titration.

CISA is available as the Chloride Analysis Reagent Set (Cat. No. 50302-00). It is composed of Nitric Acid and Sodium Bromate, which the customer mixes together before use (see reagent label instructions). Work in a well-ventilated area, preferably under a hood.

Procedure for using CISA

Chloride Analysis Reagent Set (Cat .No. 50302) Composed of Cat. No. 50257, 1 M HNO_3 and 0.1 M $NaBrO_3$ (Cat. No. 50258).

1. Mix CISA in equal volumes with both standards and samples (typically 50 mL of CISA and 50 mL of standard or sample). Allow solutions to stand 10 minutes before measuring.

2. Discard standards mixed with CISA after measuring since chloride will be oxidized upon prolonged standing.

3. Prepare a fresh mixture of standard and CISA for each calibration.

4. Follow procedures for direct measurement after adding CISA.

NOTE: *CISA may be used for about 30 days after mixing*

Complexation and Precipitation

Chloride ion forms complexes with some metal ions. Since the electrode responds only to free chloride ions, the presence of any complexing agents lowers the measured concentration. *Table 8* lists the levels of complexing metals causing a 10% error at 10^{-4} M chloride.

Total concentration in the presence of a large excess (by a factor of at least 50-100) of complexing agent can be measured by the known addition method previously described.

Table 8: Metals Causing 10% Error at 10^{-4} M Chloride

Metal	Level Causing 10% Error
Bi^{3+}	4×10^{-4} M (80 mg/L)
Cd^{2+}	2×10^{-3} M (200 mg/L)
Mn^{2+}	2×10^{-1} M (1100 mg/L)
Pb^{2+}	2×10^{-3} M (400 mg/L)
Sn^{2+}	6×10^{-3} M (700 mg/L)
Ti^{3+}	4×10^{-5} M (8 mg/L)

Theory of Operation

The chloride electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in a solution containing chloride ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free chloride ion in solution, is measured against a constant reference potential with a digital pH/mV meter or specific ion meter. The measured potential corresponding to the level of chloride ion in solution is described by the Nernst equation:

$$E = E^{o} + S \log (A)$$

where:

E = measured electrode potential

E^{o} = reference potential (a constant)

A = chloride ion level in solution

S = electrode slope (about 57 mV per decade)

The level of chloride ion, A, is the activity or "effective concentration" of free chloride ion in solution. The chloride ion activity is related to free chloride ion concentration, C_f, by the activity coefficient, γ:

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$\text{Ionic strength} = 1/2 \sum C_i Z_i^2$$

where:

C_i = concentration of ion i

Z_i = charge of ion i

$\sum$ symbolizes the sum of all the types of ions in solution.

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration. Ionic Strength Adjustor (ISA) is added to all chloride standards and samples so that the background ionic strength is high and constant relative to variable concentrations of chloride ion.

For the chloride electrode, sodium sulfate or sodium nitrate are recommended as ISA. Sodium Sulfate is available as Chloride ISA Powder Pillows (Cat. No. 23180). Use one powder pillow per 25 mL of sample. Sodium Nitrate is available

as Sodium Nitrate ISA Solution (Cat. No. 50300). Use 2 mL per 100 mL of sample. Other solutions can be used if they do not contain ions that would interfere with the electrode's response to chloride ion. If samples have a high ionic strength (above 0.1 M), prepare standards with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, the electrode charge will be charged unequally across the solution boundary, resulting in a potential difference between the two solutions.
During electrode measurements the potential must be the same when the reference is in the standardizing solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable which analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result.

However, there are a few samples where no filling solution adequately fulfills the condition stated above. Particularly troublesome are samples containing high levels of strong acids (pH <2) or strong bases (pH >12) . The high mobility of hydrogen and hydroxide ions in samples makes it impossible to "swamp out" their effect on the junction potential with any concentration of an equitransferent salt. For these solutions, calibrate in the same pH range as the

sample or use a known increment method for ion measurement.

Electrode Life

Each electrode should last about one year in normal laboratory use. In time, electrode slope will decrease and readings will start to drift indicating that the electrode should be replaced. Before replacement, refer to *Table 5 on page 29* to verify that the symptoms are caused by the electrode.



GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make. With that in mind, we have compiled the following information for your convenience.

PARTS AND ACCESSORIES

Replacement Reagents and Apparatus

Clippers, for opening powder pillows 968-00

Chloride Analysis Reagent Set (CISA) 50302-00

Chloride ISA Powder Pillows, 25/pkg..... 23180-68

Chloride Standards

1000 mg/L, 500 mL..... 183-49
12,500 mg/L, 2 mL Ampules, 20/pkg..... 14250-20

Combination Chloride Electrode..... 50255-00

Combination ISE Filling Solution
60 mL, 5/pkg..... 50284-05

Single Junction Reference Filling Solution
60 mL, 5/pkg..... 50281-05

Sodium Nitrate ISA Solution, 473 mL..... 50300-49

Water, demineralized..... 272-56

Optional Apparatus

Beaker, 100 mL, each..... 1080-42

Beaker, 150 mL, each..... 1080-44

Beaker, poly, 50 mL, each..... 1080-41

BNC Shorting Cap, each..... 50071-00

Chloride Analysis Package (includes electrode standard, ISA, beaker..... 23484-00

Demineralizer Body, 177 mL, each..... 14299-00

Electrode Holder and Stir Stand, each..... 45300-01

Electrode Holder, each..... 20893-00

Electrode Support Clamp (used w/20893) ... 20895-00

Model EC10 Portable pH Meter, each..... 50050-00

Model EC20 Portable pH/ISE Meter, each .. 50075-00

Model EC30 Laboratory pH Meter, each 50100-00

Model EC40 Laboratory pH/ISE Meter 50125-00

Printer, Model 50, each..... 50060-00

Scoop, measuring, 3.5 cc, each..... 17044-00

Spatula, stainless steel, each..... 561-62

Stir Bar, each..... 45315-00

Thermometer, armored, -20 to 105 °C 1877-01

HOW TO ORDER

By Phone:
6:00 a.m. to 5:00 p.m. MST
Monday through Friday
800-227-HACH (800-227-4224)

970-669-3050 (Hach Loveland)

By Mail:
Hach Company
P.O. Box 389
Loveland, Colorado 80539 U.S.A.

By Telex:
160840 (Hach Loveland)

By FAX:
970-669-2932 (Hach Loveland)

Information Required

- Hach account number (if available)
- Billing address
- Shipping address
- Your name and phone number
- Purchase order number
- Catalog number
- Brief description or model number
- Quantity

HOW TO ORDER, continued

Call or write for free quotations.

Outside the United States
Hach maintains a network of dealers and distributors throughout the world. In Europe, Mediterranean Africa, and the Middle East, customers can contact their local distributor or obtain help from:

Hach Europe, S.A./N.V.
Chaussée de Namur, 1
B-5150 Floriffoux (Namur), Belgium
Telex: 846-59027
Telephone: (32)(81)44.71.71
FAX: (32)(81)44.13.00

In Canada:

Hach Company Instrument Service Centre
1313 Border Street, Unit 34
Winnipeg, Manitoba R3H 0X4
Telephone: (204) 632-5598
FAX: (204) 694-5134

In other areas, obtain assistance from a nearby Hach Distributor or:

Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, U.S.A. 80539-0389
Telephone: (970) 669-3050
FAX: (970) 669-2932

REPAIR SERVICE

For instrument service, please contact the Hach Service Center serving your location.

In the United States:
Hach Company
100 Dayton Ave.
Ames, Iowa 50010
800-227-4224 (USA only)
Phone: (515) 232-2533
FAX: (515) 232-1276

In Canada:
Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
800-665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa (except Mediterranean Africa) or Pacific Basin:
Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado 80539 U.S.A.
Telephone: (970) 669-3050
Telex: 160840
FAX: (970) 669-2932

In Europe, the Middle East, or in Mediterranean Africa:
Chaussée de Namur, 1
B-5150 Floriffoux (Namur), Belgium
Telex: 846-59027
Telephone: (32)(81)44.71.71
FAX: (32)(81)44.13.00

WARRANTY

Hach warrants its electrodes against defective materials and workmanship for six months from date of shipment. This warranty does not apply to the sensing membrane/glass. Hach's terms and conditions of sale are printed on the back of the invoice.

CLAIMS/RETURN OF ITEMS

We take extreme care to fill and pack orders properly. If errors or damages do occur, report shipping damage to the carrier immediately and contact the Hach Customer Service Department in Loveland, Colorado as soon as possible (always within two weeks of receipt).

Authorization must be obtained from Hach Company before returning items for any reason. For claims, credit, or replacement, call toll-free:

800-227-4224.

HACH COMPANY
WORLD HEADQUARTERS
P.O. Box 389
Loveland, Colorado 80539-0389
Telephone: (970) 669-3050
FAX: (970) 669-2932

HACH EUROPE
Chaussée de Namur, 1
B-5150 Floriffoux (Namur), Belgium
Telephone: (32)(81) 44.71.71
FAX: (32)(81) 44.13.00

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. - **Call toll-free 800-227-4224**
Outside the U.S.A. - **Contact the HACH office or distributor serving you.**
On the Worldwide Web - **http://www.hach.com**; E-mail - **techhelp@hach.com**

APPENDIX F

Sample Nonconformance and Corrective Action Report

NONCONFORMANCE AND CORRECTIVE ACTION REPORT

Date_____

NCR No._____

Description of Nonconformance and Cause_____

_____

_____

_____

_____

_____

Proposed Disposition_____

_____

_____

_____

_____

Submitted by:_____ Date:_____

Approved by:_____

DISPOSITION (by Project Manager or Designee)

Implementation of Disposition Assigned to:_____

Actual Disposition _____

_____

_____

_____

_____

Disposition completed on:_____

Date

_____

Signature

VERIFICATION

Disposition reviewed and work inspected by: _____on_____

Disposition verified by:_____on_____

(Use additional sheet or memo if necessary.)

APPENDIX G

Site Specific Safety and Health Plan

SITE SPECIFIC HEALTH AND SAFETY PLAN

MALCOLM PIRNIE

SECTION 1: GENERAL INFORMATION AND DISCLAIMER		PROJECT NUMBER:	0285890
PROJECT NAME:	SIBERIA AREA CHEMICAL OXIDATION PILOT STUDY	CLIENT NAME:	ARMY CORP OF ENGINEERS BALTIMORE DISTRIC
PROJECT MANAGER:	KEN GOLDSTEIN	PROJECT LEADER:	ANDY VITOLINS
PREPARED BY:	DARIA NAVON	DATE:	02/26/02

NOTE: This site specific Health and Safety Plan - Short Form (HASP-SF) has been prepared for use by **Malcolm Pirnie, Inc.** employees for work at this site / facility. **The plan is written for the specific site / facility conditions, purposes, tasks, dates and personnel specified, and must be amended and reviewed by those personnel named in Section 4 if these conditions change.** Malcolm Pirnie, Inc. is not responsible for its use by others.

Subcontractors shall be solely responsible for the health and safety of their employees and shall comply with all applicable laws and regulations. In accordance with 1910.120(b)(1)(iv) and (v), Malcolm Pirnie, Inc. will inform subcontractors of the site / facility emergency response procedures, and any potential fire, explosion, health, safety or other hazards by making this Site Specific Safety and Health Plan and site information obtained by others available during regular business hours. All contractors and subcontractors are responsible for: (1) developing their own Health and Safety Plan, including a written Hazard Communication Program and any other written hazard specific programs required by federal, state and local laws and regulations, that details subcontractor tasks, potential or actual hazards identified as a result of a risk analysis of those tasks, and the engineering controls, work practices and personal protective equipment to be utilized to minimize or eliminate the hazard exposure; (2) providing their own personal protective equipment; (3) providing documentation that their employees have been health and safety trained in accordance with applicable federal, state and local laws and regulations; (4) providing evidence of medical surveillance and medical approvals for their employees; and (5) designating their own site safety officer responsible for ensuring that their employees comply with their own Health and Safety plan and taking any other additional measures required by their site activities.

The making available of this Malcolm Pirnie plan to subcontractors, does not establish, nor is it intended to establish a "joint employer" relationship between the Contractor and Malcolm Pirnie. This allowance does not establish, nor is it intended to establish, a direct or indirect employer/employee relationship with subcontractor's employees.

THIS SITE SPECIFIC HASP MUST BE REVIEWED AND APPROVED BY CORPORATE HEALTH AND SAFETY FOR ONE OR MORE OF THE FOLLOWING CONDITIONS: IF AN UPGRADE TO "LEVEL C" OR ABOVE IS ANTICIPATED; A PERMIT REQUIRED CONFINED SPACE ENTRY OR ENTRY INTO AN EXCAVATION IS ANTICIPATED; SAMPLING OF UNKNOWN DRUMS AND/OR IN UNKNOWN CONDITIONS IS ANTICIPATED, OR RADIATION LEVELS GREATER THAN 0.5 mR (500μR)/HOUR.

SECTION 2: EMERGENCY INFORMATION

(A) LOCAL RESOURCES	SERVICE NAME	TELEPHONE NUMBER
EMERGENCY MEDICAL SERVICES	WVA Duty Officer	dial "0"
HOSPITAL (Directions attached)	Albany Medical Center	(518) 262-3131
FIRE DEPARTMENT	WVA Fire/Spill	(518) 266-5333
POLICE / SECURITY	WVA Duty Officer	dial "0"
HAZMAT/ SPILL / OTHER RESPONSE	WVA Fire/Spill	(518) 266-5333

(B) CORPORATE RESOURCES

MALCOLM PIRNIE 24 / 7 EMERGENCY / INCIDENT TELEPHONE NUMBERS		**(800) 478-6870**
CORPORATE HEALTH AND SAFETY **	MARK MCGOWAN, CIH, CSP	(914) 641-2484 WHI
	JOSEPH GOLDEN, EMT-P, CET, CHMM	(914) 641-2978 WHI
CORPORATE HEALTH PHYSICIST	NIDEL AZZAM	(201) 398-4302 NNJ
CORPORATE HUMAN RESOURCES **	HOLLY LYONS (WORKERS COMP / OSHA LOG)	(914) 641-2674 WHI
LEGAL DEPARTMENT **	JERRY CAVALUZZI	(914) 694-2100 WHI
	BRUCE NELSON	(518) 786-7349 (W)
	** TO BE NOTIFIED IN CASE OF ACCIDENT	(518) 861-6345 (H)

SECTION 3: PROJECT INFORMATION

(A) SITE / FACILITY INFORMATION:

SITE NAME: Main Manufacturing/Siberia Areas
Watervliet Arsenal

ADDRESS: Watervliet, New York

☒ FEDERAL ☐ STATE

SITE CLIENT CONTACT: JoAnn Kellogg

PHONE NUMBER: (518) 266-5286

SITE SAFETY CONTACT: Andy Vitolins

☐ MUNICIPAL / REGIONAL ☐ PRIVATE

(B) **SITE CLASSIFICATION:** (check all that apply)

☒ HAZARDOUS (RCRA)	☐ UST / LUST	☐ REFINERY
☐ HAZARDOUS (CERCLA / STATE)	☐ BROWNFIELD	☐ WTP / WWTP
☐ CONSTRUCTION	☐ CHEMICAL PLANT	☐ OTHER:
☐ LANDFILL (NON-HAZARDOUS)	☒ MANUFACTURING	
☒ ACTIVE	☐ INACTIVE	

(C) **TYPE OF FIELD ACTIVITY**

☐ HAZARDOUS WASTE	☐ SOLID WASTE	☐ CONSTRUCTION
☒ HYDROGEOLOGY	☒ ENVIRONMENTAL	☐ AIR / ODOR
☐ WASTE WATER	☒ WATER	☐ OTHER:

(D) **FIELD OBJECTIVES** (Check all that apply)

☐ PRE-JOB VISIT	☐ AUDIT	**SAMPLING:**	
☒ CONTRACTOR OVERSIGHT	☐ OTHER:	☐ AIR	☐ SEDIMENT
☐ CONSTRUCTION MGMT		☐ SURFACE WATER	☐ SURFACE SOIL
☐ INSPECTION		☒ GROUND WATER	☐ LANDFILL
☐ INVESTIGATION SURVEY		☐ WASTE WATER	☐ OTHER
		☐ WASTE STREAM	

DATE(S) OF FIELD ACTIVITIES: Conduct Pilot Studies at the MMA during 2001-2002.

(E) **FIELD TASKS**

MALCOLM PIRNIE TASKS

M1. Oversee drill rig and chemical oxidation injections

M2. Collect groundwater samples from the monitoring wells identified in the Siberia Area Pilot Study Workplan.

TASKS PERFORMED BY OTHERS

01. A subcontractor (EBSI) will provide chemical oxidation services.

02. University of Waterloo staff will collect and analyze rock core samples.

03. American Auger, a drilling subcontractor, will install bedrock groundwater monitoring wells.

04.

SECTION 4: PROJECT ORGANIZATION, HEALTH AND SAFETY TRAINING, AND MEDICAL MONITORING

(A) PROJECT ORGANIZATION AND COORDINATION - The following Malcolm Pirnie personnel are designated to carry out the stated project job functions on site. THE SITE SAFETY OFFICER, OR A DESIGNATED ALTERNATE WILL BE ON-SITE DURING **ALL** SITE ACTIVITIES. (NOTE: One person may carry out more than one job function.)

PROJECT MANAGER:	Kenneth Goldstein
SITE SAFETY OFFICER:	Andy Vitolins
ALTERNATE SAFETY OFFICER(S):	John Hilton
PUBLIC INFORMATION OFFICER:	Andy Vitolins
SITE RECORDKEEPER:	Diane Zehrfuhs
FIELD TEAM LEADER:	Aaron Bobar
OTHER FIELD TEAM LEADERS:	Diane Zehrfuhs
	Monique DeJesus
	Andy Vitolins
	Daria Navon
	Kelley Roe

The following subcontractors and governmental agencies have been informed by Malcolm Pirnie of emergency response procedures, and any potential fire, explosion, health, safety or other hazards of the site / facility by making this Site Specific Health and Safety Plan and site information obtained by others available during regular business hours. Subcontractors and governmental agencies shall be solely responsible for the health and safety of their employees and shall comply with all applicable laws and regulations as described in **Section 1** of this plan.

SUBCONTRACTOR(S):	
FEDERAL AND STATE AGENCY REPS:	
OTHER AGENCY REPS:	

(B) HEALTH AND SAFETY TRAINING, MEDICAL MONITORING, AND FIT TESTING PROGRAM

The following project staff is included in the Malcolm Pirnie Health and Safety and Medical Monitoring programs. (NOTE: At least one CPR/First Aid Trained person must be on-site during HAZWOPER and confined space entry activities.)

	HAZWOPER TRAINING				OTHER TRAINING								
NAME	INITIAL (DATE)	8HR (DATE)	MGR (DATE)	DOT (DATE)	CSE (DATE)	CPR / FA / BBP / (DATE)			MEDICAL (DATE)	FIT TEST (MAKE/TYPE/SIZE/DATE)			
Aaron Bobar	08/99	10/01				09/01			05/02	MSA	M	FF	8/01
Monique DeJesus	07/99	11/02							09/02				
Andy Vitolins	11/95	12/01				04/03	04/03	04/02	06/02	MSA	S	FF	3/99
Diane Zehrfuhs									10/02				
Daria Navon	02/97	11/02							10/02	MSA	S	FF	

SECTION 5: HAZARD ANALYSIS

(A) **ACTUAL OR POTENTIAL PHYSICAL HAZARDS** - CHECK ALL THAT APPLY

- ☐ ANIMALS / PLANTS
- ☐ ASBESTOS / LEAD
- ☒ CHEMICAL EXPOSURE (See Section 4B/4C)
- ☐ CONFINED SPACE (See Section 12)
- ☐ DEMOLITION
- ☒ DRILLING
- ☐ DRUM HANDLING (See Section 7)
- ☐ DUST, HARMFUL
- ☐ DUST, NUISANCE
- ☐ ELECTRICAL
- ☐ EXCAVATIONS (See Section 13)
- ☐ EXTREME COLD (See Section 7)
- ☐ FALL, >6' VERTICAL
- ☐ FALLING OBJECTS
- ☐ HEAT STRESS
- ☒ HEAVY EQUIPMT
- ☐ HEAVY LIFTING
- ☐ HOT WORK
- ☐ HUNTING SEASON
- ☐ IMMERSION
- ☐ IONIZING RADIATION
- ☐ LIGHT RADIATION (i.e., Welding, High Intensity)
- ☐ LIMITED CONTACT
- ☐ MOVING PARTS (LO / TO)
- ☐ NOISE (> 85 dB)
- ☐ NON-IONIZING RADIATION
- ☐ OVERHEAD OBJECTS
- ☐ POWERED PLATFORMS
- ☐ POOR VISIBILITY
- ☐ ROLLING OBJECTS
- ☐ SCAFFOLDING
- ☐ SHARP OBJECTS
- ☐ STEEP / UNEVEN TERRAIN
- ☐ TRAFFIC (STRUCK BY)
- ☐ OTHER: _____

(B) **PRESENCE OF HAZARDOUS MATERIALS STORED OR USED ON SITE** (CHECK ALL THAT APPLY)

☐ YES By Client / Owner ☒ YES By Malcolm Pirnie (See Section 11) ☐ NO

TYPE

- ☐ EXPLOSIVES
- ☐ COMPRESSED GASES
- ☒ FLAMMABLE / COMBUSTIBLE LIQUIDS
- ☐ FLAMMABLE / REACTIVE SOLIDS
- ☐ OXIDIZERS
- ☐ TOXIC / INFECTIOUS
- ☐ RADIOACTIVE
- ☐ CORROSIVE
- ☐ MISCELLANEOUS
- ☐ HAZARDOUS WASTE (Stored)

(C) **CHEMICAL HAZARDS OF CONTAMINANTS INFORMATION**

(1) IDENTIFIED CONTAMINANTS

Known or suspected hazardous/toxic materials (attach historical information, physical description, map of contamination and tabulated data, if available)

SUBSTANCES INVOLVED	CHARACTERISTICS	MEDIA	ESTIMATED CONCENTRATIONS	TLV, or PEL or REL
See Attached	Sampling summary	GW	Table	☐ PPM ☐ mg/m^3

Media types: GW (ground water), SW (surface water), WW (wastewater), AIR (air), SL (soil), SD (sediment), WL (waste, liquid), WS (waste, solid), WD (waste, sludge), WG (waste, gas), OT (other).

Characteristics: CA (corrosive, acid), CC (corrosive, caustic), IG (ignitable), RA (radioactive), VO (volatile), TO (toxic), RE (reactive), BIO (infectious), UN (unknown), OT (other, describe

(2) DESCRIBE POTENTIAL FOR CONTACT WITH EACH MEDIA TYPE FOR EACH OF THE MPI TASKS LISTED IN SEC 3 (E):

MPI TASK	ROUTE OF EXPOSURE (INHAL/INGEST/CONTACT/ABSORB)	POTENTIAL FOR CONTACT (HIGH / MEDIUM / LOW)	METHOD OF CONTROL
M1	Inhal/Contact	Low	PPE
M2	Inhal/Contact	Low	PPE

The Site Safety Officer will brief the MPI field team on symptoms and signs of overexposure to chemical hazards

SECTION 6: SITE CONTROL MEASURES

(A) WORK ZONES - EXCAVATIONS, DRILLING OPERATIONS, AND HEAVY EQUIPMENT

Andy Vitolins has been designated to coordinate access control and security for Malcolm Pirnie operations on site. It is a Malcolm Pirnie policy that Malcolm Pirnie personnel will not enter trench or excavated areas without approval of Corporate Health and Safety. A safe perimeter has been established at the boundary of any excavation and/or a safe distance from excavators, drill rigs and other heavy equipment.

These boundaries are identified by: An area of approximately ten feet from the well being drilled, injected into or sampled.

Safety tape and/or cones will be erected around active areas of investigation.

No unauthorized person should be within this area.

(B) WORK ZONES - CONTAMINATION

The prevailing wind conditions are from the west A wind direction indicator is used to determine daily wind direction. The Command Post is located upwind from the Exclusion Zone or at a sufficient distance to prevent exposure should a release occur.

Control boundaries have been established and Exclusion Zone(s) (the contaminated area) have been identified. (Attach site map)

These boundaries are identified by: N/A

No unauthorized person should be within this area.

SECTION 7: SAFETY PROCEDURES / EQUIPMENT REQUIRED

Identify all procedures and equipment needed to eliminate or minimize exposure to hazards identified in this Section.

- ☐ AIR MONITORING EQUIPMENT (See Section 9)
- ☒ BARRIER TAPE
- ☐ COMMUNICATIONS - ONSITE
- ☐ COMMUNICATIONS - OFFSITE (i.e., cell/digital phones if no other means)
- ☐ CONFINED SPACE PROGRAM & EQUIPMENT (See Section 12)
- ☒ EYE WASH
- ☐ EMERGENCY SHOWERS
- ☒ EMERGENCY AIR HORN
- ☐ FALL PROTECTION PROGRAM & EQUIPMENT
- ☒ FIRE EXTINGUISHER(S) - ABC
- ☒ FIRST AID KIT / BBP KIT
- ☐ FLOTATION DEVICE (USCG)
- ☐ GFCI EXTENSION CORDS
- ☐ HARNESS(S) / LIFELINE(S)
- ☐ INSECT / TICK REPELLANT
- ☐ HUNTING SEASON
- ☐ LADDER(S)
- ☐ LIGHTING - HAND HELD
- ☐ LIGHTING - FIXED / EMERGENCY
- ☐ LOCKOUT/TAGOUT PROGRAM & EQUIPMENT
- ☒ MSDSs - ATTACHED (See Section 11)
- ☐ MSDSs - FACILITY / OTHERS
- ☐ PPE - PHYSICAL HAZARDS (See Section 15)
- ☐ PPE - CHEMICAL HAZARDS (See Section 15)
- ☐ RESPIRATORY PROTECTION PROGRAM & EQUIPMENT (APR) (See Section 15)
- ☐ RESPIRATORY PROTECTION PROGRAM & EQUIPMENT (SAR) (See Section 15)
- ☒ TRAFFIC CONES
- ☐ VENTILATION EQUIPMENT
- ☐ OTHER:

SECTION 8: COMMUNICATIONS AND SAFE WORK PRACTICES

(A) COMMUNICATIONS - ONSITE

Whenever possible, communications between site personnel should be face-to-face. When verbal communications is not possible, radio communications shall be established.

In case of radio communications failure, or when respiratory protection is in use, the following hand signals will be used:

OK; I AM ALL RIGHT; I UNDERSTAND	THUMBS UP
NO; NEGATIVE	THUMBS DOWN
NEED ASSISTANCE	BOTH HANDS ON TOP OF HEAD
DANGER - NEED TO LEAVE AREA, NO QUESTIONS	GRIP PARTNERS WRIST WITH BOTH HANDS
HAVING DIFFICULTY BREATHING	HANDS TO THROAT

(B) COMMUNICATIONS - OFF SITE

If applicable, telephone communication to the Command Post should be established as soon as practical.

Telephone numbers that can be used to reach the command post are: _____ and _____

(C) SAFE WORK PRACTICES

1. A "BUDDY SYSTEM" IN WHICH ANOTHER WORKER IS CLOSE ENOUGH TO RENDER IMMEDIATE AID WILL BE IN EFFECT. CLIENTS AND/OR CONTRACTORS MAY SERVE AS A "DESIGNATED BUDDY."
2. WHERE THE EYES OR BODY MAY BE EXPOSED TO CORROSIVE MATERIALS, SUITABLE FACILITIES FOR QUICK DRENCHING OR FLUSHING SHALL BE AVAILABLE FOR IMMEDIATE USE (SEE SECTION 7).
3. DO NOT KNEEL ON THE GROUND WHEN CHEMICAL PROTECTIVE CLOTHING IS BEING USE.
4. IF DRILLING EQUIPMENT IS INVOLVED, HAVE A CURRENT UTILITY SURVEY, AND KNOW WHERE THE 'KILL SWITCH' IS.
5. CONTACT WITH SAMPLES, EXCAVATED MATERIALS, OR OTHER CONTAMINATED MATERIALS MUST BE MINIMIZED.
6. ALL ELECTRICAL EQUIPMENT USED IN OUTSIDE LOCATIONS, WET AREAS OR NEAR WATER MUST BE PLUGGED INTO GROUND FAULT CIRCUIT INTERRUPTER (GFCI) PROTECTED OUTLETS (SEE SECTION 7).
7. IN THE EVENT OF TREACHEROUS WEATHER-RELATED WORKING CONDITIONS (I.E., THUNDERSTORM, LIMITED VISIBILITY, EXTREME COLD OR HEAT) FIELD TASKS WILL BE SUSPENDED UNTIL CONDITIONS IMPROVE OR APPROPRIATE PROTECTION FROM THE ELEMENTS IS PROVIDED.
8. SMOKING, EATING, CHEWING GUM OR TOBACCO, OR DRINKING ARE FORBIDDEN EXCEPT IN CLEAN OR DESIGNATED AREAS.
9. USE OF CONTACT LENSES NEAR CHEMICALS OR DURING USE OF RESPIRATORY PROTECTION IS PROHIBITED AT ALL TIMES.
10. GOOD HOUSEKEEPING PRACTICES ARE TO BE MAINTAINED.
11. SITE / FACILITY SPECIFIC SAFE WORK PRACTICES:

_____

_____

_____

SECTION 9: ENVIRONMENTAL MONITORING ☐ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

(A) The following environmental monitoring instruments shall be used on site at the specified intervals and recorded in the site logbook. (NOTE: If monitoring period is "OTHER", monitoring schedule will be attached to this plan.)

EQUIPMENT	MONITORING PERIOD				ACTION LEVEL
☐ Combustible Gas Indicator	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ O_2 Meter	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Toxics: ☐ CO ☐ H_2S	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Other: _____	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☒ PID (Lamp 10.2 eV)	☒ Continuous	☐ Hourly	☐ x Day	☐ Other	1 ppm
☐ FID					
☐ Colorimetric tubes:					
_____	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
_____	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Radiation: ☐ α ☐ β ☐ gamma	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Respirable Dust Meter	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Noise Meter	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
☐ Other:	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
_____	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	
_____	☐ Continuous	☐ Hourly	☐ x Day	☐ Other	

(B) Monitoring equipment is to calibrated according to manufacturers' instructions. Record calibration data and air concentrations in the Health and safety on-site log book.

(C) Recommended Action Levels for Upgrade or Downgrade of Respiratory Protection, or Site Shutdown and Evacuation. These are average values. Consideration should be given to the potential for release of highly toxic compounds from the waste or from reaction by-products. Levels are for persistent (> 10 min) breathing zone measurements in non-confined spaces. **Any unexpected conditions require all work to stop and Corporate Health and Safety contacted.**

Oxygen Levels	
Less than 19.5%	Level B necessary for work to start / continue. Consider toxicity potential.
19.5% to 23.5%	Work may start / continue. Investigate changes from 20.8%.
Greater than 23.5%	PROHIBITED WORK CONDITION
Flammability / Explosive Hazards	
Less than 10% of LEL	Work may start / continue. Consider toxicity potential.
10% to 25% of LEL	Work may start / continue. Increase monitoring frequency
Greater than 25% of LEL	PROHIBITED WORK CONDITION.
Uncharacterized Airborne Organic Vapors or Gases	
Background*	Work may start / continue. Continue to monitor conditions.
Up to 5 meter units (m.u. or "ppm") above background	Level C necessary for work to start / continue. Continue to monitor conditions.
Up to 500 m.u. above background	Level B necessary for work to start / continue. Continue to monitor conditions.
Greater than 500 m.u.	PROHIBITED WORK CONDITION.
*** Off-site «clean air measurement**	
Characterized Airborne Organic Vapors or Gases**	
Up to 50% of TLV, or PEL or REL	Work may start / continue. Continue to monitor conditions.
Up to 25 times the TLV, or PEL or REL	Level C necessary for work to start / continue. Continue to monitor conditions.
Up to 500 times the TLV, or PEL or REL	Level B necessary for work to start / continue. Continue to monitor conditions.
Greater than 500 times the TLV, or PEL or REL	PROHIBITED WORK CONDITION.
**** Use mixture calculations (% allowed = $\sum C_N EL_N$) if more than one contaminant is present.**	
Radiation	
Less than 0.5 mR/Hour (500 μR)	Work may start / continue. Continue to monitor conditions.
Up to 1 mR/Hour above background	Work may start / continue with Radiation Safety Officer present on site.
Greater than 1 mR/Hour above background	PROHIBITED WORK CONDITION.

SECTION 10: PERSONAL MONITORING ☒ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

(A) PERSONAL EXPOSURE SAMPLING

The following personal monitoring will be in effect on site: _____

A copy of personal monitoring results is to be sent to Corporate Health and Safety for inclusion in the Employee's Confidential Exposure Record File.

(B) HEAT / COLD STRESS MONITORING

The expected air temperature will be 45 °F. If it is determined that heat stress or cold stress monitoring is required (mandatory for heavy exertion in PPE at temperatures over 70°F, or at temperatures under 40°F or wind chill equivalent), the following procedures shall be followed (describe procedures in effect, for heat stress i.e., monitoring body temperature, body weight, pulse rate; for cold stress i.e., appropriate clothing, shelter breaks):

SECTION 11: HAZARD COMMUNICATION PROGRAM ☐ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

If chemicals are introduced to the site by Malcolm Pirnie (e.g., decontamination liquids, preservatives, etc.), a copy of the Malcolm Pirnie Hazard Communication Program and Material Safety Data Sheets (MSDSs) of chemicals introduced by Malcolm Pirnie to the site is attached to this plan. The Site Safety Officer will review this information with all field personnel prior to the start of the project, and will inform other employers (e.g., Owner, Contractor and Subcontractors) the availability and location of this information. The Comprehensive List of Chemicals introduced by Malcolm Pirnie to this site is:

Isopropanol, Nitric Acid — Potassium Permanganate

Alconox Soap

All chemicals being introduced to the site, hazardous/potentially hazardous samples prepared at the site, and/or any hazardous materials previously sent to the site, **that will be stored at the site or will be transported from the site by common carrier**, will be packaged, labeled and identified as hazardous materials in accordance with U.S. Department of Transportation (DOT) and/or International Air Transport Association (IATA) regulations by a trained HazMat employee.

(NOTE: At multi-employer sites, the Site Safety Officer will obtain information, if applicable, on hazardous chemicals other employers may produce or introduce to the job site to which Malcolm Pirnie employees may be exposed, including the location of their written hazard communication program(s), labeling program(s), and Material Safety Data Sheet(s).

SECTION 12: CONFINED SPACE ENTRY ☒ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

If a permit-required confined space entry will be made on site, a copy of the Malcolm Pirnie Confined Space Entry Program, and a completed Malcolm Pirnie Confined Space Pre-Entry Inspection Check List will be attached to this plan. A Confined Space Entry Permit must be completed and posted outside the confined space prior to entry, and the entry will follow the Malcolm Pirnie Confined Space Entry written program. Permits are to be saved and logged with project documentation.

SECTION 13: EXCAVATION SAFETY ☒ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

Excavations being created in order to accomplish Malcolm Pirnie tasks or in progress during Malcolm Pirnie inspection of other activities or tasks, shall be shored or slopped or otherwise protected to prevent accidental collapse prior to entry, in accordance with Subpart F of 29 CFR 1926. It is Malcolm Pirnie policy that Malcolm Pirnie personnel will not enter trench or excavated areas without approval of Corporate Health and Safety. If an entry into an excavation by Malcolm Pirnie personnel is necessary, a Excavation Plan identifying the Competent Person and the protective measure to be used (i.e., sloping, shoring, trench box) will be attached to this plan.

SECTION 14: DECONTAMINATION PROCEDURES ☐ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

Personnel and equipment leaving the Exclusion Zone shall be thoroughly decontaminated. The Site Safety Officer is responsible for monitoring adherence with this decontamination plan.

A standard level D decontamination protocol shall be used with the following decontamination stations:

(1) Level "D" protection will be provided for all of the professionals working on this project. It will consist of work clothes, gloves, eye protection devices, and steel-toe shoes for the professionals working at or visiting the site.

(2) Upon exiting the work zone, obviously contaminated boots and gloves will be removed and cleaned or discarded as necessary.

(3) Thoroughly wash outer boot covers with detergent-water solution and rinse with copious amounts of water.

The following decontamination equipment is required:

☒ Decon Pad (Plastic Sheet) ☒ Dry Brushes ☒ Buckets Other
☒ Trash Cans/Bags ☐ Wet Brushes ☐ Hose / Spray

Alcohol, isopropanol, nitric acid. Will be used as the decontamination solution

SECTION 15: PERSONAL PROTECTIVE EQUIPMENT

TASK	RESPIRATORS & CARTRIDGE[1]	USE** (See Section 16)	CLOTHING	GLOVES	BOOTS	OTHER
M1	Mult	UP	C	L, N	SL	HH, G, HP
M2	Mult	UP	C	L, N	SL	HH, G

* Same as Section 3E

**UP = Upgrade
CONT = Continuous

CODES:

RESPIRATORS[1]
HF = Half Face APR
FF = Full Face APR
ESCBA = Escape Bottle
SAR = Airline
SCBA = SCBA

CARTRIDGES[1]
P = Particulate
OV = Organic Vapors
AG = Acid Gas
Mult = Multi-Gas/Vapor
Other

CLOTHING
N/S = No Special
C = Coveralls
T = Tyvek
Sx = Saranex
PT = PE Tyvek

GLOVES[2]
Co = Cotton
Le = Leather
L = Latex
N = Nitrile
B = Butyl
Neo = Neoprene
V = Viton
PVC = Polyvinyl Chloride
PVA = Polyvinyl Alcohol
Other:

BOOTS
SL = Leather Safety
H = Hip (Fireman)

OTHER
HH = Hard Hat
G = Safety Glasses
GP = Glare Protection
GI = Goggles - Impact
GS = Goggles - Splash
FS = Face Shield
HP = Hearing Protection

1 - List all that apply, i.e., FF w/ OV/AG/P

2 - Use same codes for clothing and boots of same material

Respiratory protection will be upgraded under the following conditions:

The following cartridge change out schedule is to be followed onsite (attach any calculations to plan):

SECTION 16: EMERGENCY ACTION PLAN

The following standard emergency response procedures will be used by onsite personnel. The Site Safety Officer shall be notified of any onsite emergencies and be responsible for ensuring that the appropriate procedure are followed.

(A) EVACUATION

All work activities are suspended and the site is to be EVACUATED IMMEDIATELY, when there is a threat to life or health as determined by individual good judgement, i.e. fire, hazardous chemical spill, dangerous gas leak, severe weather (i.e., tornado); or when notified by other site / facility staff and local fire or police officials.

If an evacuation is called for, the emergency alarm system for weather-related, medical, fire and other evacuation emergencies is:

Evacuation from the Exclusion Zone should whenever possible occur through the decontamination line. In those situations where egress in this manner cannot occur, the following emergency escape routes have been designated (document on map if possible):

If during sampling activities escape is required form the site, sampling personnel egress the sampling areas and exit the site at the nearest gate, as show on the attached figure.

Once evacuated off site, all staff should gather a safe distance of a minimum of 250 feet away from the incident.

(B) FIRE OR EXPLOSION

Upon discovery of a fire or an explosion, the above designated emergency signal shall be sounded and all personnel shall assemble at the decontamination line. The fire department is to be notified and all personnel moved to a safe distance (minimum 250') from the involved area.

If a person's clothing should catch fire, burning clothing may be extinguished by having the individual drop to the floor and roll. If necessary, physically restrain the person and roll them around on the floor to smother the flames. Use a fire blanket or extinguisher if one is readily available and you have been trained in its use. Call emergency medical services if not already done so.

If a person's clothing should become saturated with a chemical, douse the individual with water from the nearest safety shower if available. Consult the chemical Material Safety Data Sheets (MSDSs) for further information. Call emergency medical services if indicated by the MSDSs.

If a person's clothing should become saturated with a chemical, douse the individual with water from the nearest safety shower if available. Consult the chemical Material Safety Data Sheets (MSDSs) for further information. Call emergency medical services if indicated by the MSDSs.

NEVER RE-ENTER THE SITE / FACILITY until the emergency has been declared over and permission to re-enter has been given by site / facility health and safety staff or local fire or police officials. If any staff appear to be missing, notify a individual in charge.

(C) MEDICAL EMERGENCY

If you discover a medical emergency and are by yourself, CALL OUT FOR HELP. When someone arrives, tell them to call for help. If no one comes or you know you are alone, provide whatever care you can for 1 minute, then make the call yourself. (See Section 2)

NEVER RE-ENTER THE SITE / FACILITY until the emergency has been declared over and permission to re-enter has been given by site / facility health and safety staff or local fire or police officials. If any staff appear to be missing, notify a individual in charge.

Upon notification of an injury in the Exclusion Zone, the designated emergency signal shall be sounded. All site personnel shall assemble at the decontamination line. The Site Safety Officer or alternate should evaluate the nature of the injury, and the affected person should be decontaminated to the extent possible prior to movement to the Support Zone The onsite CPR/FA personnel shall initiate the appropriate first aid, and contact should be made for an ambulance (and other emergency services as needed) and with the designated medical facility (if required). No persons shall reenter the Exclusion Zone until the cause of the injury or symptoms is determined

The hospital is 15 minutes from the site and the ambulance response time is _____ minutes.

of _____ as contacted on _____ and briefed on the situation, the potential hazards, and the substances involved. When IDLH conditions exist, arrangements should be made for onsite standby of emergency services.

A map for directions to the nearest hospital is attached to this plan If not, the directions are: See attached map.

(D) SAFETY EQUIPMENT FAILURE

If any other equipment (i.e., air monitoring) on site fails to operate properly, the Field Team Leader and/or Field Safety Officer shall be notified to determine the effect of this failure on continuing operations on site. If the failure affects the safety of personnel or prevents completion of the Work Plan tasks, all personnel shall leave the work area until the situation is evaluated and appropriate actions taken

(E) FOLLOW-UP

In all situations, when an on site / facility emergency results in evacuation of the work area, staff shall not resume work until:

- The conditions resulting in the emergency have been corrected,
- The hazards reassessed by the SSO and Health and Safety Corporate;
- The HASP has been reviewed by the SSO and Corporate Health and Safety; and
- Site personnel have been briefed on any changes in the HASP by the SSO.

SECTION 17: SPILL CONTAINMENT / CONTROL ☐ THIS SECTION NOT APPLICABLE TO SITE ACTIVITIES

For most chemicals introduced to the worksite, or under control of Malcolm Pirnie employees, spills of chemicals would be considered incidental and would be controlled in the immediate area of the spill. Such spills shall be handled utilizing precautions appropriate for the chemical characteristics specified in the MSDS for the chemical including spill control methods and selection and use of minimum personal protective equipment.

For chemicals introduced to the worksite, or under control of Malcolm Pirnie employees, that would cause a "large spill" (greater than 55 gallons), a copy of the appropriate Emergency Response Guidebook (ERG) guide shall be attached to this plan, and a spill response contractor shall be identified in Section 2.

SECTION 18: EMPLOYEE ACKNOWLEDGEMENTS

PLAN REVIEWED BY: DATE

Project Manager: _____ _____

Project Leader: _____ _____

Local H&S Coordinator: _____ _____

Corporate H & S _____ _____

I acknowledge that I have read the information on this HASP, attached Material Safety Data Sheets (MSDSs), DOT Emergency Response Guides, and Health and Safety Programs.
I understand the site / facility hazards as described and agree to comply with the contents of the plan.

EMPLOYEE (Print Name)

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

VISITOR (Print Name)

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

ATTACHED DOCUMENTS

☒ MSDS(s) ☐ Hazard Communication Program ☐ Confined Space Entry Program ☐ DOT ERG Guides

☒ Hospital Directions ☐ Emergency Action Plan ☒ Evacuation Routes ☐ Cartridge Change Out Calculations

☒ Other – Chemical Hazards Information

Storage Color Code: Orange (General Storage)

Potential Health Effects

Inhalation:
May cause irritation to the respiratory tract. Symptoms may include coughing and shortness of breath.
Ingestion:
May cause irritation to the gastrointestinal tract. Symptoms may include nausea, vomiting and diarrhea.
Skin Contact:
No adverse effects expected.
Eye Contact:
May cause irritation, redness and pain.
Chronic Exposure:
No information found.
Aggravation of Pre-existing Conditions:
No information found.

4. First Aid Measures

Inhalation:
Remove to fresh air. Get medical attention for any breathing difficulty.
Ingestion:
If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention.
Skin Contact:
Wash exposed area with soap and water. Get medical advice if irritation develops.
Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire:
Not expected to be a fire hazard.
Explosion:
No information found.
Fire Extinguishing Media:
Dry chemical, foam, water or carbon dioxide.
Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

6. Accidental Release Measures

Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Spills: Pick up and place in a suitable container for reclamation or disposal, using a method that does not generate dust. When mixed with water, material foams profusely. Small amounts of residue may be flushed to sewer with plenty of water.

7. Handling and Storage

Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Moisture may cause material to cake. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

---

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
- OSHA Permissible Exposure Limit (PEL):
15 mg/m3 total dust, 5 mg/m3 respirable fraction for nuisance dusts.
- ACGIH Threshold Limit Value (TLV):
10 mg/m3 total dust containing no asbestos and < 1% crystalline silica for Particulates Not Otherwise Classified (PNOC).

Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded, a half-face dust/mist respirator may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face piece dust/mist respirator may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency, or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-facepiece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection:
Wear protective gloves and clean body-covering clothing.

Eye Protection:
Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area.

---

9. Physical and Chemical Properties

Appearance:
White powder interspersed with cream colored flakes.

Odor:
No information found.

Solubility:
Moderate (1-10%)

Specific Gravity:
No information found.

pH:
No information found.

% Volatiles by volume @ 21C (70F):
0

Boiling Point:
No information found.

Melting Point:
No information found.

Vapor Density (Air=1):

No information found.
Vapor Pressure (mm Hg):
No information found.
Evaporation Rate (BuAc=1):
No information found.

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage.
Hazardous Decomposition Products:
Carbon dioxide and carbon monoxide may form when heated to decomposition.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
No information found.
Conditions to Avoid:
No information found.

11. Toxicological Information

No LD50/LC50 information found relating to normal routes of occupational exposure.

--------\Cancer Lists\----------

Ingredient	---NTP Carcinogen--- Known	Anticipated	IARC Category
Alconox(R) proprietary detergent mixture	No	No	None

12. Ecological Information

Environmental Fate:
This product is biodegradable.
Environmental Toxicity:
No information found.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste disposal facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Not regulated.

15. Regulatory Information

--------\Chemical Inventory Status - Part 1\----------

Ingredient	TSCA	EC	Japan	Australia
Alconox(R) proprietary detergent mixture	Yes	No	No	No

--------\Chemical Inventory Status - Part 2\----------

Ingredient	Korea	--Canada-- DSL	NDSL	Phil.
Alconox(R) proprietary detergent mixture	No	No	Yes	No

--------\Federal, State & International Regulations - Part 1\----------

Ingredient	-SARA 302- RQ	TPQ	------SARA 313------ List	Chemical Catg.
Alconox(R) proprietary detergent mixture	No	No	No	No

--------\Federal, State & International Regulations - Part 2\----------

Ingredient	CERCLA	-RCRA- 261.33	-TSCA- 8(d)
Alconox(R) proprietary detergent mixture	No	No	No

Chemical Weapons Convention: No TSCA 12(b): No CDTA: No
SARA 311/312: Acute: Yes Chronic: No Fire: No Pressure: No
Reactivity: No (Pure / Solid)

Australian Hazchem Code: No information found.
Poison Schedule: No information found.
WHMIS:
This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

16. Other Information

NFPA Ratings: Health: **0** Flammability: **0** Reactivity: **0**
Label Hazard Warning:
CAUTION! MAY BE HARMFUL IF SWALLOWED OR INHALED. MAY CAUSE IRRITATION TO EYES AND RESPIRATORY TRACT.
Label Precautions:
Avoid contact with eyes.
Keep container closed.
Use with adequate ventilation.
Avoid breathing dust.
Wash thoroughly after handling.
Label First Aid:
If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. If not breathing, give artificial

respiration. If breathing is difficult, give oxygen. In case of eye contact, immediately flush eyes with plenty of water for at least 15 minutes. In all cases, get medical attention.

Product Use:

Laboratory Reagent.

Revision Information:

MSDS Section(s) changed since last revision of document include: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 16.

Disclaimer:

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Prepared by: Strategic Services Division
Phone Number: (314) 539-1600 (U.S.A.)

MSDS Material Safety Data Sheet

From: Mallinckrodt Baker, Inc.
222 Red School Lane
Phillipsburg, NJ 08865

Mallinckrodt CHEMICALS | J.T.Baker

24 Hour Emergency Telephone: 908-859-2151
CHEMTREC: 1-800-424-9300

National Response in Canada
CANUTEC: 613-996-6666

Outside U.S. and Canada
Chemtrec: 703-527-3887

NOTE: CHEMTREC, CANUTEC and National Response Center emergency numbers to be used only in the event of chemical emergencies involving a spill, leak, fire, exposure or accident involving chemicals.

All non-emergency questions should be directed to Customer Service (1-800-582-2537) for assistance.

NITRIC ACID, 50-70%

MSDS Number: N3660 --- *Effective Date: 07/13/00*

1. Product Identification

Synonyms: Aqua Fortis; Azotic Acid; Nitric Acid 50%; Nitric Acid 65%; nitric acid 69-70%
CAS No.: 7697-37-2
Molecular Weight: 63.01
Chemical Formula: HNO3
Product Codes:
J.T. Baker: 411D, 412D, 5371, 5555, 5801, 5826, 5876, 9597, 9598, 9600, 9601, 9602, 9603, 9604, 9606, 9607, 9616, 9617
Mallinckrodt: 1409, 2703, 2704, 412D, 6623, H988, H993, H998, V069, V077, V336, V561, V633, V650

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Nitric Acid	7697-37-2	50 - 70%	Yes
Water	7732-18-5	30 - 50%	No

3. Hazards Identification

Emergency Overview

POISON! DANGER! STRONG OXIDIZER. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE. CORROSIVE. LIQUID AND MIST CAUSE SEVERE BURNS TO ALL BODY TISSUE. MAY BE FATAL IF SWALLOWED OR INHALED. INHALATION MAY CAUSE LUNG AND TOOTH DAMAGE.

J.T. Baker SAF-T-DATA(tm) Ratings (Provided here for your convenience)

Health Rating: 3 - Severe (Poison)
Flammability Rating: 0 - None
Reactivity Rating: 3 - Severe (Oxidizer)
Contact Rating: 4 - Extreme (Corrosive)
Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES
Storage Color Code: Yellow (Reactive)

Potential Health Effects

Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison.

Inhalation:
Corrosive! Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract.
Ingestion:
Corrosive! Swallowing nitric acid can cause immediate pain and burns of the mouth, throat, esophagus and gastrointestinal tract.
Skin Contact:
Corrosive! Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color.
Eye Contact:
Corrosive! Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Chronic Exposure:
Long-term exposure to concentrated vapors may cause erosion of teeth and lung damage. Long-term exposures seldom occur due to the corrosive properties of the acid.
Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders, eye disease, or cardiopulmonary diseases may be more susceptible to the effects of this substance.

4. First Aid Measures

Immediate first aid treatment reduces the health effects of this substance.
Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
Ingestion:
DO NOT INDUCE VOMITING! Give large quantities of water or milk if available. Never give anything by mouth to an unconscious person. Get medical attention immediately.
Skin Contact:
In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.
Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

5. Fire Fighting Measures

Fire:
Not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or

combustibles may cause ignition. Can react with metals to release flammable hydrogen gas.
Explosion:
Reacts explosively with combustible organic or readily oxidizable materials such as: alcohols, turpentine, charcoal, organic refuse, metal powder, hydrogen sulfide, etc. Reacts with most metals to release hydrogen gas which can form explosive mixtures with air.
Fire Extinguishing Media:
Water spray may be used to keep fire exposed containers cool. Do not get water inside container.
Special Information:
Increases the flammability of combustible, organic and readily oxidizable materials. In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

6. Accidental Release Measures

Ventilate area of leak or spill. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Neutralize with alkaline material (soda ash, lime), then absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer! US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

J. T. Baker NEUTRASORB(R) or TEAM(R) 'Low Na+' acid neutralizers are recommended for spills of this product.

Handling and Storage

Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Protect from physical damage. Keep out of direct sunlight and away from heat, water, and incompatible materials. Do not wash out container and use it for other purposes. When diluting, the acid should always be added slowly to water and in small amounts. Never use hot water and never add water to the acid. Water added to acid can cause uncontrolled boiling and splashing. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
-OSHA Permissible Exposure Limit (PEL):
2 ppm (TWA), 4 ppm (STEL)
-ACGIH Threshold Limit Value (TLV):
2 ppm (TWA); 4 ppm (STEL)

Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.
Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded, wear a supplied air, full-facepiece respirator, airlined hood, or full-facepiece self-contained breathing apparatus. Nitric acid is an oxidizer and should not come in contact

with cartridges and canisters that contain oxidizable materials, such as activated charcoal. Canister-type respirators using sorbents are ineffective.
Skin Protection:
Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.
Eye Protection:
Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

9. Physical and Chemical Properties

Appearance:
Colorless to yellowish liquid.
Odor:
Suffocating, acrid.
Solubility:
Infinitely soluble.
Specific Gravity:
1.41
pH:
1.0 (0.1M solution)
% Volatiles by volume @ 21C (70F):
100 (as water and acid)
Boiling Point:
122C (252F)
Melting Point:
-42C (-44F)
Vapor Density (Air=1):
2-3
Vapor Pressure (mm Hg):
48 @ 20C (68F)
Evaporation Rate (BuAc=1):
No information found.

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage. Containers may burst when heated.
Hazardous Decomposition Products:
When heated to decomposition, emits toxic nitrogen oxides fumes and hydrogen nitrate. Will react with water or steam to produce heat and toxic and corrosive fumes.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
A dangerously powerful oxidizing agent, concentrated nitric acid is incompatible with most substances, especially strong bases, metallic powders, carbides, hydrogen sulfide, turpentine, and combustible organics.
Conditions to Avoid:
Light and heat.

11. Toxicological Information

Nitric acid: Inhalation rat LC50: 244 ppm (NO2)/30M; Investigated as a mutagen, reproductive effector. Oral (human) LDLo: 430 mg/kg.

--------\Cancer Lists\----------

Ingredient	---NTP Carcinogen--- Known	Anticipated	IARC Category
Nitric Acid (7697-37-2)	No	No	None
Water (7732-18-5)	No	No	None

12. Ecological Information

Environmental Fate:
No information found.
Environmental Toxicity:
No information found.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be managed in an appropriate and approved waste facility. Although not a listed RCRA hazardous waste, this material may exhibit one or more characteristics of a hazardous waste and require appropriate analysis to determine specific disposal requirements. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Domestic (Land, D.O.T.)

Proper Shipping Name: NITRIC ACID (WITH NOT MORE THAN 70% NITRIC ACID)
Hazard Class: 8
UN/NA: UN2031
Packing Group: II
Information reported for product/size: 150LB

International (Water, I.M.O.)

Proper Shipping Name: NITRIC ACID (WITH NOT MORE THAN 70% NITRIC ACID)
Hazard Class: 8
UN/NA: UN2031
Packing Group: II
Information reported for product/size: 150LB

International (Air, I.C.A.O.)

Proper Shipping Name: NITRIC ACID (WITH NOT MORE THAN 70% NITRIC ACID)
Hazard Class: 8
UN/NA: UN2031
Packing Group: II
Information reported for product/size: 150LB

5. Regulatory Information

--------\Chemical Inventory Status - Part 1\----------

Ingredient	TSCA	EC	Japan	Australia
Nitric Acid (7697-37-2)	Yes	Yes	Yes	Yes
Water (7732-18-5)	Yes	Yes	Yes	Yes

--------\Chemical Inventory Status - Part 2\----------

Ingredient	Korea	--Canada-- DSL	NDSL	Phil.
Nitric Acid (7697-37-2)	Yes	Yes	No	Yes
Water (7732-18-5)	Yes	Yes	No	Yes

--------\Federal, State & International Regulations - Part 1\----------

Ingredient	-SARA 302- RQ	TPQ	------SARA 313------ List	Chemical Catg.
Nitric Acid (7697-37-2)	1000	1000	Yes	No
Water (7732-18-5)	No	No	No	No

--------\Federal, State & International Regulations - Part 2\----------

Ingredient	CERCLA	-RCRA- 261.33	-TSCA- 8(d)
Nitric Acid (7697-37-2)	1000	No	No
Water (7732-18-5)	No	No	No

Chemical Weapons Convention: No TSCA 12(b): No CDTA: No
SARA 311/312: Acute: Yes Chronic: Yes Fire: Yes Pressure: No
Reactivity: No (Mixture / Liquid)

Australian Hazchem Code: 2PE
Poison Schedule: S6
WHMIS:
This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

16. Other Information

NFPA Ratings: Health: **3** Flammability: **0** Reactivity: **0** Other: **Oxidizer**
Label Hazard Warning:
POISON! DANGER! STRONG OXIDIZER. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE. CORROSIVE. LIQUID AND MIST CAUSE SEVERE BURNS TO ALL BODY TISSUE. MAY BE FATAL IF SWALLOWED OR INHALED. INHALATION MAY CAUSE LUNG AND TOOTH DAMAGE.
Label Precautions:
Do not get in eyes, on skin, or on clothing.
Do not breathe vapor or mist.
Use only with adequate ventilation.
Wash thoroughly after handling.
Keep from contact with clothing and other combustible materials.
Do not store near combustible materials.

Store in a tightly closed container.
Remove and wash contaminated clothing promptly.

Label First Aid:

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In all cases get medical attention immediately.

Product Use:

Laboratory Reagent.

Revision Information:

MSDS Section(s) changed since last revision of document include: 1.

Disclaimer:

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Prepared by: Environmental Health & Safety
Phone Number: (314) 654-1600 (U.S.A.)

MATERIAL SAFETY DATA SHEET

CAIROX® Potassium Permanganate

Section 1 Chemical Product and Company Identification

PRODUCT NAME: CAIROX® potassium permanganate, $KMnO_4$
SYNONYMS: Permanganic acid potassium salt
Chameleon mineral
Condy's crystals
Permanganate of potash

MANUFACTURER'S NAME: CARUS CHEMICAL COMPANY

MANUFACTURER'S ADDRESS:
Carus Chemical Company
1500 Eighth Street
P. O. Box 1500
LaSalle, IL 61301

TRADE NAME: CAIROX® potassium permanganate

TELEPHONE NUMBER FOR INFORMATION: 815/223-1500

EMERGENCY TELEPHONE NO: 800/435-6856

AFTER HOURS NO. 815/223-1565
5:00 PM-8:00 AM Central Standard Time
Monday-Friday, Weekends and Holidays

CHEMTREC TELEPHONE NO.: 800/424-9300

Section 2 Composition/Information on Ingredients

Material or component	CAS No.	%	Hazard Data	
Potassium permanganate	7722-64-7	97% min. $KMnO_4$	PEL-C	5 mg Mn per cubic meter of air
			TLV-TWA	0.2 mg Mn per cubic meter of air

Section 3 Hazards Identification

1. Eye Contact
   Potassium permanganate is damaging to eye tissue on contact. It may cause severe burns that result in damage to the eye.

2. Skin Contact
   Contact of solutions at room temperature may be irritating to the skin, leaving brown stains. Concentrated solutions at elevated temperature and crystals are damaging to the skin.

3. Inhalation
   Acute inhalation toxicity data are not available. However, airborne concentrations of potassium permanganate in the form of dust or mist may cause damage to the respiratory tract.

4. Ingestion
   Potassium permanganate, if swallowed, may cause severe burns to mucous membranes of the mouth, throat, esophagus, and stomach.

Section 4 First Aid Measures

1. Eyes
   Immediately flush eyes with large amounts of water for at least 15 minutes holding lids apart to ensure flushing of the entire surface. Do not attempt to neutralize chemically. Seek medical attention immediately. Note to physician: Soluble decomposition products are alkaline. Insoluble decomposition product is brown manganese dioxide.

2. Skin
   Immediately wash contaminated areas with large amounts of water. Remove contaminated clothing and footwear. Wash clothing and decontaminate footwear before reuse. Seek medical attention immediately if irritation is severe or persistent.

3. Inhalation
   Remove person from contaminated area to fresh air. If breathing has stopped, resuscitate and administer oxygen if readily available. Seek medical attention immediately.

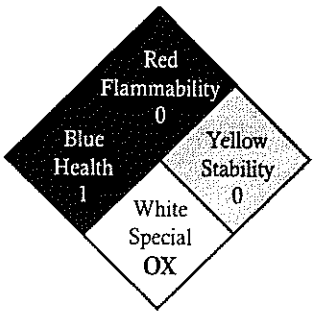
4. Ingestion
   Never give anything by mouth to an unconscious or convulsing person. If person is conscious, give large quantities of water. Seek medical attention immediately.

Section 5 Fire Fighting Measures

NFPA* HAZARD SIGNAL

Health Hazard	1	=	Materials which under fire conditions would give off irritating combustion products.
(less than 1 hour exposure)			Materials which on the skin could cause irritation.
Flammability Hazard	0	=	Materials that will not burn.
Reactivity Hazard	0	=	Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.
Special Hazard	OX	=	Oxidizer

***National Fire Protection Association 704**



FIRST RESPONDERS:

Wear protective gloves, boots, goggles, and respirator. In case of fire, wear positive pressure breathing apparatus. Approach site of incident with caution. Use Emergency Response Guide NAERG 96 (RSPA P5800.7). Guide No. 140.

FLASHPOINT	None
FLAMMABLE OR EXPLOSIVE LIMITS	Lower: Nonflammable Upper: Nonflammable
EXTINGUISHING MEDIA	Use large quantities of water. Water will turn pink to purple if in contact with potassium permanganate. Dike to contain. Do not use dry chemicals, CO_2, Halon® or foams.
SPECIAL FIREFIGHTING PROCEDURES	If material is involved in fire, flood with water. Cool all affected containers with large quantities of water. Apply water from as far a distance as possible. Wear self-contained breathing apparatus and full protective clothing.

Section 6 Accidental Release Measures

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Clean up spills immediately by sweeping or shoveling up the material. Do not return spilled material to the original container. Transfer to a clean metal drum. EPA banned the land disposal of D001 ignitable waste oxidizers. These wastes must be deactivated by reduction. To clean floors, flush with abundant quantities of water into sewer, if permitted by Federal, State, and Local regulations. If not permitted, collect water and treat chemically (Section 13).

PERSONAL PRECAUTIONS

Personnel should wear protective clothing suitable for the task. Remove all ignition sources and incompatible materials before attempting clean-up.

Section 7 Handling and Storage

WORK/HYGENIC PRACTICES

Wash hands thoroughly with soap and water after handling potassium permanganate, and before eating or smoking. Wear proper protective equipment. Remove contaminated clothing.

VENTILATION REQUIREMENTS

Provide sufficient area or local exhaust to maintain exposure below the TLV-TWA.

CONDITIONS FOR SAFE STORAGE

Store in accordance with NFPA 430 requirements for Class II oxidizers. Protect containers from physical damage. Store in a cool, dry area in closed containers. Segregate from acids, peroxides, formaldehyde, and all combustible, organic or easily oxidizable materials including anti-freeze and hydraulic fluid.

Section 8 Exposure Controls/Personal Protection

RESPIRATORY PROTECTION

In the case where overexposure may exist, the use of an approved NIOSH-MSHA dust respirator or an air supplied respirator is advised. Engineering or administrative controls should be implemented to control dust.

EYE

Faceshield, goggles, or safety glasses with side shields should be worn. Provide eye wash in working area.

GLOVES

Rubber or plastic gloves should be worn.

OTHER PROTECTIVE EQUIPMENT

Normal work clothing covering arms and legs, and rubber or plastic apron should be worn.

Section 9 Physical and Chemical Properties

APPEARANCE AND ODOR	Dark purple solid with a metallic luster, odorless
BOILING POINT, 760 mm Hg	Not applicable
VAPOR PRESSURE (mm Hg)	Not applicable
SOLUBILITY IN WATER % BY SOLUTION	6% at 20°C (68°F), and 20% at 65°C (149°F)
PERCENT VOLATILE BY VOLUME	Not volatile
EVAPORATION RATE (BUTYL ACETATE=1)	Not applicable
MELTING POINT	Starts to decompose with evolution of oxygen (O_2) at temperatures above 150°C (302°F). Once initiated, the decomposition is exothermic and self-sustaining.
OXIDIZING PROPERTIES	Strong oxidizer
SPECIFIC GRAVITY	2.7 @ 20°C (68°F)
VAPOR DENSITY (AIR=1)	Not applicable

Section 10 Stability and Reactivity

STABILITY Under normal conditions, the material is stable.

CONDITIONS TO AVOID Contact with incompatible materials or heat (>150°C/302°F).

INCOMPATIBLE MATERIALS Acids, peroxides, formaldehyde, anti-freeze, hydraulic fluids, and all combustible organic or readily oxidizable inorganic materials including metal powders. With hydrochloric acid, toxic chlorine gas is liberated.

HAZARDOUS DECOMPOSITION PRODUCTS When involved in a fire, potassium permanganate may liberate corrosive fumes.

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION Material is not known to polymerize.

Section 11 Toxicological Information

Potassium permanganate: Acute oral LD_{50}(rat) = 780 mg/kg Male (14 days); 525 mg/kg Female (14 days)
The fatal adult human dose by ingestion is estimated to be 10 grams. (Ref. Handbook of Poisoning: Prevention, Diagnosis & Treatment, Twelfth Edition)

EFFECTS OF OVEREXPOSURE

1. Acute Overexposure
   Irritating to body tissue with which it comes into contact

2. Chronic Overexposure
   No known cases of chronic poisoning due to potassium permanganate have been reported. Prolonged exposure, usually over many years, to heavy concentrations of manganese oxides in the form of dust and fumes, may lead to chronic manganese poisoning, chiefly involving the central nervous system.

3. Carcinogenicity
   Potassium permanganate has not been classified as a carcinogen by OSHA, NTP, IARC.

4. Medical Conditions Generally Aggravated by Exposure
   Potassium permanganate will cause further irritation of tissue, open wounds, burns or mucous membranes.

   Registry of Toxic Effects of Chemical Substances
   RTECS #SD6476000

Section 12 Ecological Information

Entry to the Environment

Potassium Permanganate has a low estimated lifetime in the environment, being readily converted by oxidizable materials to insoluble manganese dioxide (MnO_2).

Bioconcentration Potential

In non-reducing and non-acidic environments manganese dioxide (MnO_2) is insoluble and has a very low bioaccumulative potential.

Aquatic Toxicity

Rainbow trout, 96 hour LC_{50}: 1.8 mg/L
Bluegill sunfish, 96 hour LC_{50}: 2.3 mg/L

Section 13 Disposal Consideration

DEACTIVATION OF D001 IGNITABLE WASTE OXIDIZERS BY CHEMICAL REDUCTION

Reduce potassium permanganate in aqueous solutions with sodium thiosulfate (Hypo), or sodium bisulfite or ferrous salt solution. The thiosulfite or ferrous salt may require some dilute sulfuric acid to promote rapid reduction. If acid was used, neutralize with sodium bicarbonate to neutral pH. Decant or filter, and mix the sludge with sodium carbonate and deposit in an approved landfill. Where permitted, the sludge can be drained into sewer with large quantities of water. Use caution when reacting chemicals. Contact Carus Chemical Company for additional recommendations.

Section 14 Transport Information

U. S. DEPARTMENT OF TRANSPORTATION INFORMATION:

Proper Shipping Name:	49 CFR 172.101	Potassium Permanganate
ID Number:	49 CFR 172.101	UN 1490
Hazard Class:	49 CFR 172.101	Oxidizer
Division:	49 CFR 172.101	5.1
Packing Group:	49 CFR 172.101	II

Section 15 Regulatory Information

TSCA Listed in the TSCA Chemical Substance Inventory

CERCLA **Hazardous Substance**

Reportable Quantity: RQ - 100 lb 40 CFR 116.4; 40 CFR 302.4

RCRA Oxidizers such as potassium permanganate meet the criteria of ignitable waste. 40 CFR 261.21

SARA TITLE III Information

Section 302	Extremely hazardous substance: Not listed
Section 311/312	Hazard categories: Fire, acute and chronic toxicity
Section 313	CAIROX® potassium permanganate contains 97% Manganese Compound as part of the chemical structure (manganese compounds CAS Reg. No. N/A) and is subject to the reporting requirements of Section 313 of Title III, Superfund Amendments and Reauthorization Act of 1986 and 40 CFR 372.

Section 15 Regulatory Information (cont.)

STATE LISTS	Michigan Critical Materials Register:	Not listed
	California Proposition 65:	Not listed
	Massachusetts Substance List:	5 F8
	Pennsylvania Hazard Substance List:	E
FOREIGN LISTS	Canadian Domestic Substances List (DSL)	Listed
	Canadian Ingredient Disclosure List	Listed
	European Inventory of Existing Chemical Substances (EINECS)	2317603

Section 16 Other Information

NIOSH	National Institute for Occupational Safety and Health
MSHA	Mine Safety and Health Administration
OSHA	Occupational Safety and Health Administration
NTP	National Toxicology Program
IARC	International Agency for Research on Cancer
TSCA	Toxic Substances Control Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act of 1980
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act of 1986
PEL-C	OSHA Permissible Exposure Limit-OSHA Ceiling Exposure Limit
TLV-TWA	Threshold Limit Value - Time Weighted Average (American Conference of Governmental Industrial Hygienists)

Kenneth Krogulski
May 2000

CARUS

Responsible Care®
A Public Commitment

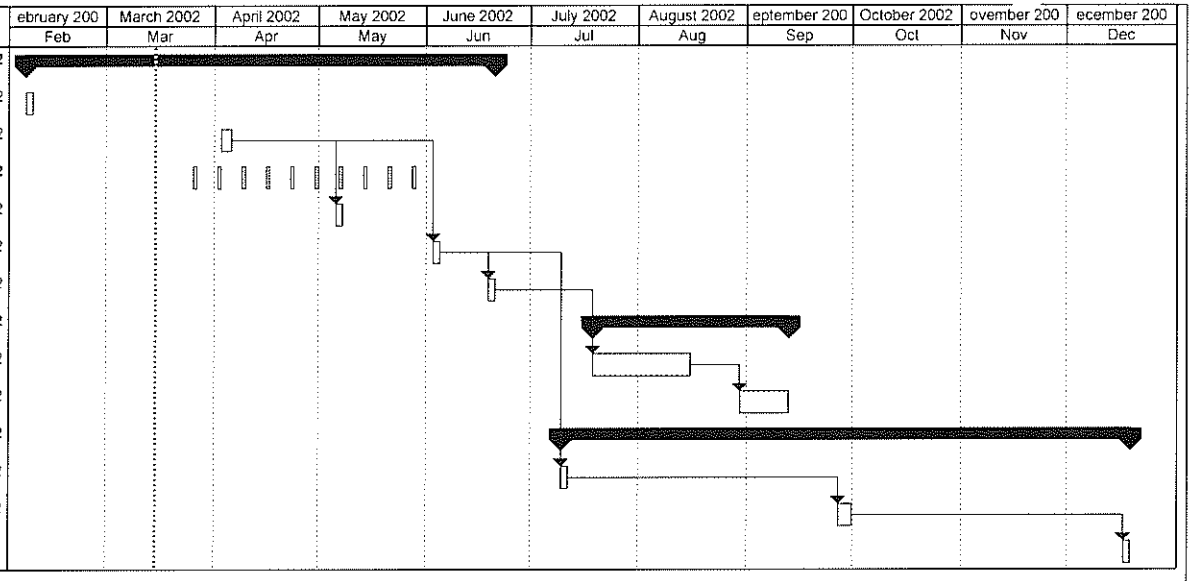
The information contained is accurate to the best of our knowledge. However, data, safety standards and government regulations are subject to change; and the conditions of handling, use or misuse of the product are beyond our control. Carus Chemical Company makes no warranty, either express or implied including any warranties of merchantability and fitness for a particular purpose. Carus also disclaims all liability for reliance on the completeness or confirming accuracy of any information included herein. Users should satisfy themselves that they are aware of all current data relevant to their particular uses.

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Responsible Care® is a service mark of the Chemical Manufacturers Association.

APPENDIX H

Project Schedule

ID	Task Name	Duration	Start	Finish
1	**Siberia Area Chemox Pilot Study**	**97 days**	**Wed 02/06/02**	**Thu 06/20/02**
2	Baseline Monitoring	2 days	Wed 02/06/02	Thu 02/07/02
3	Potassium Permanganate Injection	3 days	Wed 04/03/02	Fri 04/05/02
4	**Field Monitoring (Permanganate Only)**	**46 days**	**Tue 03/26/02**	**Tue 05/28/02**
15	Full Monitoring Event 1	2 days	Mon 05/06/02	Tue 05/07/02
16	Full Monitoring Event 2	2 days	Mon 06/03/02	Tue 06/04/02
17	Core Drilling	2 days	Wed 06/19/02	Thu 06/20/02
18	**Pilot Study Reporting**	**40 days**	**Fri 07/19/02**	**Thu 09/12/02**
19	Draft Pilot Study Report	20 days	Fri 07/19/02	Thu 08/15/02
20	Final Pilot Study Report	10 days	Fri 08/30/02	Thu 09/12/02
21	**Rebound Monitoring**	**116 days**	**Wed 07/10/02**	**Wed 12/18/02**
22	Rebound Monitoring Event 1	2 days	Wed 07/10/02	Thu 07/11/02
23	Rebound Monitoring Event 2	2 days	Fri 09/27/02	Mon 09/30/02
24	Rebound Monitoring Event 3	2 days	Tue 12/17/02	Wed 12/18/02



Project: draft_SA_schedule
Date: Fri 03/15/02

Task | Milestone | Rolled Up Split | External Tasks
Split | Summary | Rolled Up Milestone | Project Summary
Progress | Rolled Up Task | Rolled Up Progress

Note: This schedule assumes 1 injection during the Siberia Study. It may be necessary to do additional injections. Quarterly rebound sampling is assumed. This assumption is subject to change based on field and laboratory results.

APPENDIX I

Monitoring Well Construction Details and Baseline Sampling Results

Summary of Injection and Monitoring Well Construction
Bedrock Chemical Oxidation Pilot
Siberia Area
Watervliet Arsenal, Watervliet, New York

Monitoring Well	Diameter	Surface Casing Depth (feet, bgs)	Total Depth (feet, bgs)
MW-78*	6-inch	17.5	54
MW-79	4-inch	33	54
MW-80	4-inch	13	34
MW-81	4-inch	34	54
MW-82	4-inch	13	34
MW-83	4-inch	34	54
MW-84	4-inch	13	34

Notes:
* Injection well
bgs: below ground surface

SIBERIA AREA, WATERVLIET ARSENAL, WATERVLIET, NEW YORK
BASELINE SAMPLING RESULTS
CHEMICAL OXIDATION PILOT STUDY

VOC (Groundwater)

ANALYTE	NYS Water Quality Standards (GA) (ug/l)	MW-KS-1 (Duplicate) 02/07/2002 (ug/l)	MW-78 02/07/2002 (ug/l)	MW-79 02/07/2002 (ug/l)	MW-80 02/06/2002 (ug/l)	MW-81 02/07/2002 (ug/l)	MW-82 02/06/2002 (ug/l)	MW-83 02/07/2002 (ug/l)	MW-84 02/06/2002 (ug/l)
Vinyl Chloride	2	5.5	1700	5.8	32	870	12	940	1300
Carbon Disulfide	60	1 U	44 U	1 U	0.6 J	18 U	0.26 J	29 U	37 U
Chloroform	7	1 U	44 U	1 U	1 U	18 U	1 U	29 U	9.2 J
Trichloroethene	5	1 U	1000	1 U	7.6	5.8 J	1 U	29 U	37 U
Tetrachloroethene	5	0.61 J	730	0.62	1 U	18 U	1 U	29 U	37 U
TICS		8.1	1450	11.32	88.56	510	16.63	550	736

SVOC (Groundwater)

ANALYTE	NYS Water Quality Standards (GA) (ug/l)	MW-KS-1 (Duplicate) 02/07/2002 (ug/l)	MW-78 02/07/2002 (ug/l)	MW-79 02/07/2002 (ug/l)	MW-80 02/06/2002 (ug/l)	MW-81 02/07/2002 (ug/l)	MW-82 02/06/2002 (ug/l)	MW-83 02/07/2002 (ug/l)	MW-84 02/06/2002 (ug/l)
Diethylphthalate	50	10 U	11 U	10 U	0.64 J	10 U	10 U	11 U	10 U
bis(2-Ethylhexyl)phthalate	5	10 U	2.1 JB	10 U	10 U	10 U	10 U	11 U	10 U
TICS		13.9	252.8	55.3	770.5	5.3	137.3	2.9	180.3

TOC (Groundwater)

ANALYTE (GROUNDWATER)	NYS Water Quality Standards (GA) (mg/l)	MW-78 02/07/2002 (mg/l)	MW-79 02/07/2002 (mg/l)	MW-80 02/06/2002 (mg/l)	MW-81 02/07/2002 (mg/l)	MW-81 (MS) 02/07/2002 (mg/l)	MW-81(REP) 02/07/2002 (mg/l)	MW-82 02/06/2002 (mg/l)	MW-83 02/07/2002 (mg/l)	MW-84 02/06/2002 (mg/l)
Total Organic Carbon		9.2	5.4	13.3	4.1	13.9	5	4	4.3	18.2

Diesel/Oil (Groundwater)

ANALYTE	NYS Water Quality Standards (GA) (ug/l)	MW-KS-1 (Duplicate) 02/07/2002 (ug/l)	MW-78 02/07/2002 (ug/l)	MW-79 02/07/2002 (ug/l)	MW-80 02/06/2002 (ug/l)	MW-81 02/07/2002 (ug/l)	MW-82 02/06/2002 (ug/l)	MW-83 02/07/2002 (ug/l)	MW-84 02/06/2002 (ug/l)
Diesel Fuel		0.10 U	0.14	0.10 U	0.10 U	0.10 U	0.10 U	0.11 U	0.13
Motor Oil		0.18 Z	0.66	0.14 Z	0.67 Z	0.10 U	0.20 Z	0.11 U	0.33 Z
Total		0.18	0.8	0.14	0.67	0	0.2	0	0.46

IRON (Groundwater)

ANALYTE	NYS Water Quality Standards (GA) (ug/l)	MW-KS-1 (Duplicate) 02/07/2002 (ug/l)	MW-78 02/07/2002 (ug/l)	MW-79 02/07/2002 (ug/l)	MW-80 02/06/2002 (ug/l)	MW-81 02/07/2002 (ug/l)	MW-82 02/06/2002 (ug/l)	MW-83 02/07/2002 (ug/l)	MW-84 02/06/2002 (ug/l)
Iron	600	1020	7730	2000	1950	254	5390	681	10900