DRAFT WORK PLAN BIOSPARGING AND ORC® INJECTION PILOT TESTS WATERVLIET ARSENAL, Watervliet, New York

US Army Corps of Engineers
Baltimore District

US Army Corps
of Engineers
Baltimore District
DRIVEN BY A VISION...to be the BEST

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ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
BOD	Biochemical Oxygen Demand
CMS	Corrective Measures Study
DRO	Diesel Range Organics
DQO	Data Quality Objective
FID	Flame Ionization Detector
FSP	Field Sampling Plan
HASP	Health and Safety Plan
LCS	Laboratory Control Sample
MMA	Main Manufacturing Area
MP	Monitoring Point
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NYSDEC	New York State Department of Environmental Conservation
ORC[7]	Oxygen Release Compound
ORP	Oxidation Reduction Potential
PAH	Polycyclic Aromatic Hydrocarbon
PID	Photoionization Detector
psi	pounds per square inch
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
scfm	standard cubic feet per minute
SOP	Standard of Practice
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
USACE	United States Army Corps of Engineers
USAIOC	United States Army Industrial Operations Command
USEPA	United States

1.0 BACKGROUND AND PURPOSE OF DOCUMENT

1.1 INTRODUCTION

This Work Plan was prepared under Delivery Order No. 164, Modification No. 1 of U.S. Army Corps of Engineers (USACE) Contract DACA31-94-D-0017 for the USACE, Baltimore District and the Watervliet Arsenal (WVA) in support of the Army's Installation Restoration Program. The Work Plan was developed to outline field and laboratory activities involved in the implementation of two pilot-scale tests to treat groundwater contaminated with petroleum hydrocarbons (TPH) at the Siberia Area of the WVA. The pilot tests compare two technologies designed to deliver oxygen to the groundwater with the purpose of stimulating microbial activity to enhance biodegradation of TPH. The two technologies for groundwater oxygenation are biosparging and injection of Oxygen Release Compound (ORC®).

This Work Plan includes a Field Sampling Plan (FSP) detailing the procedures to be followed for the pilot tests, as well as a Quality Assurance Project Plan (QAPP) to ensure that data obtained during the Pilot Study is of acceptable quality for use in future design of corrective measures. In addition, a Site Specific Health and Safety Plan (HASP) is included in Appendix A to the Work Plan.

1.2 SITE DESCRIPTION

The WVA is a 140-acre government-owned installation under the command of the U.S. Army Industrial Operations Command (USAIOC). The WVA is located in the City of Watervliet, New York, west of the Hudson River and five miles north of the City of Albany (see Figure 1-1). The WVA consists of two contiguous areas: the Main Manufacturing Area (MMA) is a 125-acre tract used for manufacturing and administrative operations; the second area, a 15-acre tract known as the Siberia Area, is located to the west of the MMA (see Figure 1-2). Immediately after its purchase in the

early 1940s, the swampy Siberia Area was filled in with debris consisting of slag, cinders, wood, brick and other debris of unknown origin. Currently, the Siberia Area is used as a shipping yard and for the interim storage of raw materials, hazardous materials, finished goods, and supplies brought in from the MMA.

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.

1.3 PREVIOUS SITE INVESTIGATIONS

Malcolm Pirnie, Inc. (Malcolm Pirnie) conducted a Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) at the Siberia Area of the WVA. The RFI was performed during the period of December 1994 to November 1995 under contract to the U.S. Army Corps of Engineers (USACE), Baltimore District. The RFI was performed in accordance with an Administrative Order of Consent between WVA, the New York State Department of Environmental Conservation (NYSDEC), and the United States Environmental Protection Agency (USEPA). The results of the RFI have been presented in the Final RCRA Facility Investigation Report, Siberia Area, Watervliet Arsenal, Watervliet, New York dated December 1997 (Final RFI Report).

Chlorinated organic compounds, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and metals were detected in groundwater and/or in soil at the Siberia Area. A Corrective Measures Study (CMS) has been initiated by Malcolm Pirnie on behalf of the USACE, Baltimore District to evaluate, develop, and recommend Corrective Measures Alternatives for the impacted areas of the Siberia Area. Additional investigations have been completed to define the limits of soil/sediment contamination and the extent of groundwater contamination as part of the CMS. These data are included

in the CMS Field Data Report, Siberia Area, Watervliet Arsenal, Watervliet, New York dated October 1998.

This pilot study addresses petroleum hydrocarbons detected in groundwater monitoring wells screened in the overburden deposit at the Siberia Area. Petroleum hydrocarbons are ubiquitous in the overburden saturated zone under all four Siberia Area quadrants.

1.4 PILOT STUDY GOALS

The goal of the pilot tests is to evaluate the effectiveness of biosparging and ORC® for enhancement of in-situ biotreatment of TPH present in groundwater and saturated soil underlying the Siberia Area. This work will be used to:

- Estimate the rate of TPH degradation in groundwater by in-situ biotreatment.
- Compare the effectiveness of biosparging with the injection of ORC.
- Estimate the areal effect of a biosparging well and an ORC injection.
- Quantify TPH levels after treatment.
- Estimate TPH removal efficiencies.
- Quantify impacts to soil gas concentration in the vadose zone, estimate the potential for surface VOC emissions, and evaluate the need for vapor recovery if biosparging is used.

The results of the pilot tests will be incorporated into the Corrective Measures Study for the Siberia Area.

2.0 PILOT TECHNOLOGY DESCRIPTIONS

2.1 BIOSPARGING DESCRIPTION

Biosparging is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. The biosparging process is similar to air sparging. However, while air sparging removes constituents primarily through volatilization, biosparging promotes biodegradation of constituents rather than volatilization (generally by using lower flow rates than are used in air sparging).

2.2 OXYGEN RELEASE COMPOUND (ORC®) DESCRIPTION

Oxygen Release Compound (ORC®) is a patented formulation of magnesium peroxide (MgO_2) that releases oxygen at a slow rate when hydrated, according to the following equation:

$$MgO_2 + H_2O \prod \frac{1}{2} O_2 + Mg(OH)_2$$

The by-products of the reaction are oxygen and magnesium hydroxide (Milk of Magnesia).

ORC® is shipped as a fine powder. The powder is mixed with water to create a slurry with a consistency that depends on the amount of water used. The ORC® slurry can then be injected in the contaminated saturated zone through hand-augured holes, hydraulic punch equipment, or hollow stem augers. The ORC® slurry installation should span the entire vertical contaminated saturated thickness, including the capillary fringe and 'smear zone'.

Unlike air sparging, which uses atmospheric air, ORC® injection provides pure oxygen. While air-saturated water contains 8 – 10 mg/l of oxygen, the concentration of oxygen from ORC® can build up to approximately 40 mg/l.

2.3 APPLICABILITY OF PILOT TECHNOLOGIES AT THE SIBERIA AREA

2.3.1 Intrinsic Permeability

The effectiveness of biosparging and ORC® injection depends largely on the soil's intrinsic permeability. Intrinsic permeability is a measure of the ability of soil to transmit fluids, and it controls how well oxygen can be delivered to the subsurface microorganisms. Intrinsic permeability of saturated-zone soils is usually determined in the field by aquifer pump tests or slug tests that measure hydraulic conductivity. The following equation is used to convert hydraulic conductivity to intrinsic permeability:

$$k = K(m / rg)$$

where: k = intrinsic permeability (cm^2)

K = hydraulic conductivity (cm/sec)

μ = water viscosity (g/cm·sec)

D = water density (g/cm^3)

g = acceleration due to gravity (cm/sec^2)

At 20°C, $\mu/D\,g = 1.02 \cdot 10^{-5}$ cm·sec

Three unconsolidated deposits are encountered at the Siberia Area. The upper deposit is a fill unit approximately four feet thick. The second deposit is a clayey silt, typically two to six feet thick, which extends to the top of the weathered shale at most locations across the site. Fluvial deposits are the third unit encountered. This third deposit consists primarily of sand and gravel and is found in what appears to be abandoned stream/river channels buried beneath the Siberia Area. Groundwater at the Siberia Area is generally encountered at three to six feet below ground surface (bgs).

During the Siberia Area RCRA Facility Investigation, slug testing was conducted to calculate hydraulic conductivities of wells screened in each of the overburden deposits (Malcolm Pirnie, Inc., December 1997). The wells screened primarily in the fill unit were monitoring wells MW-26, 29, 31, 35, and 37. Hydraulic conductivity values ranged from 2.66×10^{-2} cm/sec (MW-31) to 1.49×10^{-4} cm/sec (MW-29). The wide range of values is attributable to the varying composition of fill material. The calculated

geometric mean for these locations is 3.58 x 10^{-3} cm/sec. Hydraulic conductivities of wells screened primarily in the clayey silt, monitoring wells MW-19, 20, 21, 24, 25, and 27, ranged from 4.8 x 10^{-4} cm/sec (MW-25) to 8.1 x 10^{-5} cm/sec (MW-21). The geometric mean for these six locations was 1.59 x 10^{-4} cm/sec. MW-36, screened in a fluvial sand and gravel deposit beneath the clayey silt, had a calculated hydraulic conductivity of 1.31 x 10^{-3} cm/sec. Based upon these hydraulic conductivities, Table 2-1 below shows the estimated intrinsic permeabilities for each overburden deposit at the Siberia Area.

Table 2-1: Intrinsic Permeabilities for Siberia Area Deposits

Siberia Area Overburden Deposit	Calculated Average Hydraulic Conductivity (cm/sec)	Intrinsic Permeability (cm^2)
Fill Unit	3.58 x 10^{-3}	3.65 x 10^{-8}
Clayey Silt	1.59 x 10^{-4}	1.62 x 10^{-9}
Fluvial Deposit	1.31 x 10^{-3}	1.34 x 10^{-8}

United States Environmental Protection Agency (USEPA) guidance recommends a soil intrinsic permeability of 1 x 10^{-9} cm^2 for biosparging to be generally effective (USEPA, 1994). Thus, the intrinsic permeabilities for the Siberia Area overburden deposits are within the range of effectiveness for biosparging.

2.3.2 Site Bacterial Growth Characteristics

The effectiveness of biosparging and ORC® injection is also dependent on site characteristics that affect bacterial growth. These include groundwater temperature, pH, microbial population density, nutrient concentrations, and dissolved iron concentration. Each of these site characteristics is discussed in detail below.

2.3.2.1 pH and Temperature

Based on previous groundwater monitoring events, the groundwater temperature at the Siberia Ranges from 15ºC in the winter to approximately 23ºC in the summer.

Within the range of 10ºC to 45ºC, the rate of microbial activity typically doubles for every 10ºC rise in temperature. Thus, biosparging and ORC® injection are expected to be somewhat more effective during the summer months.

Optimum pH for bacterial growth is approximately seven; the acceptable range for biosparging is between six and eight (USEPA, 1994). At the Siberia Area, groundwater pH measurements have ranged between 6 and 8. Groundwater pH may rise somewhat during application of ORC®. The pH of magnesium peroxide is 8.5. After it is hydrated and begins to form magnesium hydroxide, the pH rises to 10. However, due to the insoluble nature of ORC®, (the solubility factor is 1.8×10^{-11}) and the end product magnesium hydroxide, pH increase in the subsurface remains localized in the vicinity of the injection point (Regenesis, 2000).

2.3.2.2 Microbial Population

A series of biological treatability studies were conducted from June 1998 to December 1999 to evaluate specified parameters and demonstrate the viability of bioremediation for treatment of contaminated soils at the Siberia Area. These studies included radiotracer phenanthrene tests, microbial isolation experiments, bioslurry evaluations, column evaluations, and pan evaluations. The results of these studies are summarized in the Draft Final Biological Treatability Studies of Siberia Area, Watervliet Arsenal, Watervliet, New York, dated April 2000. The treatability studies confirmed the existence of indigenous microorganisms capable of degrading TPH under aerobic conditions.

2.3.2.3 Nutrients

Bacteria require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Using empirical formulas for cell biomass and other assumptions, the carbon:nitrogen: phosphorus ratios necessary to enhance biodegradation fall in the range of 100:10:1 to 100:1:0.5 (USEPA, 1994). During the course of the pilot tests, groundwater samples will be analyzed for nitrogen (expressed as

ammonia) and phosphate. If necessary, nutrients may be added during full-scale remediation operations.

2.3.2.4 Dissolved Ferrous Iron

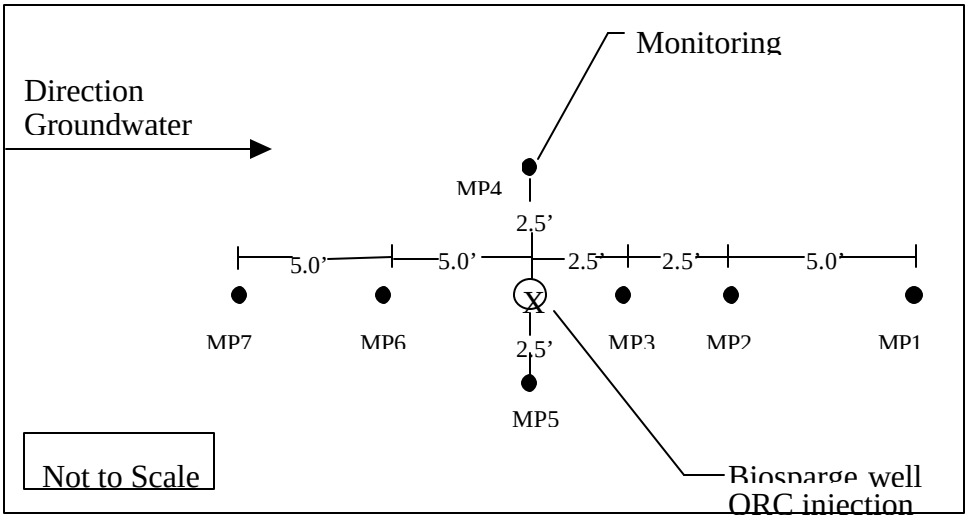
The presence of dissolved ferrous iron (Fe^{2+}) in groundwater can reduce the permeability of the saturated zone soils during the sparging operations. When dissolved ferrous iron is exposed to oxygen, it is oxidized to ferric iron (Fe^{3+}) which, because it is less soluble than ferrous iron, can precipitate within the saturated zone and clog soil pore space. On a large scale, this could reduce the pore space available for air (and groundwater) flow, thereby reducing permeability (USEPA, 1994). Precipitation of iron oxide occurs predominantly in the saturated zone near the sparging well screen or ORC® injection point where oxygen content is highest. USEPA guidance recommends a dissolved iron concentration of less than 10 mg/l to prevent ferric iron precipitation (USEPA, 1994). Groundwater samples collected from the Siberia Area during long-term monitoring had reported ferrous iron concentrations ranging from 0.01 mg/l to 3.3 mg/l. This range of ferrous iron concentrations should not impede effective biosparging and ORC® injection at the Siberia Area.

3.0 PILOT STUDY DESIGN

3.1 BIOSPARGING PILOT TEST

The biosparging pilot test will consist of injecting air into a single injection point over an eight-week period. The injection point will be constructed of two-inch diameter Schedule 40 PVC pipe with a one foot screen (see Figure 3-1). The screen will be installed at the top of the weathered bedrock, approximately eight to nine feet bgs. A network of seven monitoring points (MPs) will be installed as shown on Figure 3-2. Each MP will be constructed of two-inch diameter Schedule 40 PVC pipe with a three foot screen interval (see Figure 3-3). The screen will be installed just below the water table, approximately three to six feet bgs. During the installation of the injection well and monitoring points, soil samples will be collected from MP1, MP3, MP5, and MP7. Soil samples will be analyzed for the diesel range organics fraction of TPH (TPH-DRO) and total organic carbon (TOC). After completion of the injection well and/or MP installations, groundwater samples will be collected from each MP and analyzed for TPH-DRO, ferrous iron, and biochemical oxygen demand (BOD). A drill rig equipped with a hollow stem auger will be used to install the injection point and the MPs.

Figure 3-2: Biosparging or ORC® Injection Test Area



During the pilot test, a compressor/blower capable of achieving an airflow of seven standard cubic feet per minute (scfm) at 10 psi will be used. An overall system layout of the biosparging pilot test is shown on Figure 3-4. It is assumed that electric power (115 VAC) will be supplied by the Watervliet Arsenal. Initially, air will be injected at rates anticipated to be between two and 10 (scfm). Flow rates will be varied initially to determine the effect on the radius of influence (ROI). The ROI estimates will be made based on pressure measurements, dissolved oxygen measurements and water levels in the MPs. This portion of the pilot study is anticipated to take two days.

After determining the relationship between ROI and air flow, an air flow rate that will maximize radial influence while minimizing the amount of air required to oxygenate the aquifer will be selected and maintained during the remainder of the pilot test. During the steady-state pilot test, the air flow will be maintained at a constant rate and dissolved oxygen readings will be taken at each of the MPs twice per week. Soil gas hydrocarbon measurements will be obtained from the MPs using a flame ionization detector (FID). Soil gas carbon dioxide measurements will be taken at the beginning, middle, and end of the pilot study. At the end of the eight weeks, air injection will be discontinued and post-injection groundwater and soil samples will be collected. Groundwater samples will be collected from each of the MPs and analyzed for TPH-DRO, BOD, and ferrous iron. Soil samples will be collected within two feet of MP1, MP3, MP5, and MP7 using a direct push rig and analyzed for TPH-DRO and TOC.

The biosparging pilot test will be installed on the border of the northeast and southeast quadrants of the Siberia Area, just south of the two metal buildings (see Figure 3-5). The biosparging well will be located so as to allow the air compressor to be plugged into a power source located in the southernmost metal building.

3.2 ORC® PILOT TEST

The ORC® pilot test will consist of a one-time injection, under gravity, of a slurry of ORC® at a single location. The injection will be continuous through the entire overburden, approximately nine feet thick, with an injection rate of one to two pounds of

ORC® per foot of saturated thickness, as recommended by the manufacturer. A network of seven monitoring points will be installed as proposed on Figure 3-1. Each monitoring point will be constructed of two-inch diameter Schedule 40 PVC with a one foot screen interval (see Figure 3-3). Monitoring point screens will be installed at approximately five- to six-foot bgs. During the installation of the monitoring points, soil samples will be collected from MP1, MP3, MP5, and MP7 and analyzed for TPH-DRO and TOC. After completion of the MP installations, groundwater samples will be collected from all of the MPs and analyzed for TPH-DRO, BOD, and ferrous iron. A drill rig equipped with a hollow stem auger will be used to install the MPs, and to collect the initial soil samples.

During the ORC® pilot test, dissolved oxygen and water level measurements will be collected daily during the first week and then weekly for the next 15 weeks (total of 16 weeks duration). Two rounds of groundwater samples will be collected from all of the MPs following the ORC® injection. The first round will be collected at eight weeks after the ORC® injection. The second round will be collected at 16 weeks after the ORC® injection. At the 16-week sampling event, post-injection soil samples will be collected from MP1, MP3, MP5, and MP7 using a direct push rig. The groundwater and soil samples collected will be analyzed for TPH-DRO.

The ORC® injection pilot test will be located in close proximity to the biosparging test, just south of the two metal buildings in the southeast quadrant (see Figure 3-4).

3.3 PILOT TEST SCHEDULE

It is anticipated that the 16-week ORC® injection pilot test will be started in early July 2001. The 8-week biosparging test is scheduled to begin around the beginning of August 2001. Both of the tests will be completed by the end of October 2001.

4.0 FIELD SAMPLING PLAN

4.1 INTRODUCTION AND RATIONALE

Sufficient data will be collected from the pilot tests to enable a comparison of the efficacy of both methods of oxygen delivery and to provide information for full-scale remedial design. This Field Sampling Plan (FSP) has been prepared to describe the specific procedures that will be followed during pilot study field activities.

Specific pilot study parameters to be monitored are presented in Table 4-1. Approximate locations of each pilot test are shown on Figure 3-2.

Table 4-1: Rationale for Data Collection

Data to be Collected	Purpose for Collecting Data
Biosparging Pilot Test	
TPH-DRO concentrations in soils and groundwater	Treatment performance monitoring
Dissolved Oxygen	Effectiveness of pilot technology
Soil Gas – Carbon Dioxide	Treatment performance and sparging efficiency
Biochemical Oxygen Demand	Measure all sources of oxygen demand
Ferrous Iron	Potential for iron fouling/soil permeability loss
Pressure measurements	Determination of sparging bubble radius
Sparging rate and pressure	Optimization of sparging radius
Water level measurements	Hydraulic gradient influence
Nutrients (ammonia, orthophosphate)	Microorganism growth conditions
ORC® Injection Pilot Test	
TPH concentrations in soils and groundwater	Treatment performance monitoring
Dissolved Oxygen	Effectiveness of pilot technology
Water level measurements	Hydraulic gradient influence
Biochemical Oxygen Demand	Measure all sources of oxygen demand
Ferrous Iron	Potential for iron fouling/soil permeability loss
Nutrients (ammonia, orthophosphate)	Microorganism growth conditions

4.2 MONITORING AND SAMPLING FREQUENCIES

4.2.1 Biosparging Test

The biosparging test will be conducted for an eight-week period. Soil samples will be collected during the installation of the injection point and the monitoring points. Groundwater samples will be collected after completion of injection point and monitoring point installation. During the first two days of the study, air flow rates will be varied to determine the relationship between air flow rate and sparging radius of influence. During the initial two-day calibration period, pressure measurements, dissolved oxygen measurements, water level measurements and soil gas FID readings will be collected on approximately an hourly basis during a 10-hour work day. After the initial two days, air will be injected at a constant rate for the remainder of the eight-week period. Dissolved oxygen readings, pressure measurements, water level measurements, and soil gas readings will be taken twice per week during the steady-state sparging stage. At the end of the eight weeks, air injection will be discontinued and post-injection groundwater and soil samples will be collected. The post-injection soil samples will be collected within a two-foot distance from the monitoring point locations. Table 4-2 summarizes the sampling and monitoring program for the biosparging test.

4.2.2 ORC® Injection Test

The ORC® pilot test will consist of one day of ORC® injection followed by 15 weeks of monitoring. Similar to the biosparging test, soil samples will be collected during the installation of the injection point and the monitoring points, and groundwater samples will be collected after completion of injection point and monitoring point installation. During the ORC® pilot test, dissolved oxygen and water level measurements will be collected daily during the first week and then weekly for the next 15 weeks. Two rounds of groundwater samples will be collected following the ORC® injection. The first round will be collected at eight weeks after the ORC injection, and the second round will be collected at 16 weeks after the ORC® injection. At the 16-week sampling event, post-injection soil samples will be collected within a two-foot distance from the monitoring

point locations. Table 4-2 summarizes the sampling and monitoring program for the ORC® injection test.

Table 4-2: Pilot Study Sample Analysis Program

Sample Type	Sampling Frequency	No. of Sampling Events	Samples Per Event	Total No. of Samples	Analyses							
					TPH	Ammonia	Nitrate	Nitrite	Ortho-P	BOD	TOC	pH
Biosparging Test - 8 weeks												
Soil samples	Initial & T=8 weeks	2	4	8	X						X	X
Rinse Blank	Initial & T=8 weeks	2	1	2	X						X	X
Blind Duplicate	Initial & T=8 weeks	2	1	2	X						X	X
Matrix Spike	Initial & T=8 weeks	2	1	2	X						X	X
Matrix Spike Duplicate	Initial & T=8 weeks	2	1	2	X						X	X
Groundwater samples	Initial & T=8 weeks	2	7	14	X	X	X	X	X	X	X	X
Rinse Blank	Initial & T=8 weeks	2	1	2	X	X	X	X	X	X	X	X
Blind Duplicate	Initial & T=8 weeks	2	1	2	X	X	X	X	X	X	X	X
Matrix Spike	Initial & T=8 weeks	2	1	2	X	X	X	X	X	X	X	X
Matrix Spike Duplicate	Initial & T=8 weeks	2	1	2	X	X	X	X	X	X	X	X
ORC Injection - 16 weeks												
Soil samples	Initial & T=16 weeks	2	4	8	X						X	X
Rinse Blank	Initial & T=16 weeks	2	1	2	X						X	X
Blind Duplicate	Initial & T=16 weeks	2	1	2	X						X	X
Matrix Spike	Initial & T=16 weeks	2	1	2	X						X	X
Matrix Spike Duplicate	Initial & T=16 weeks	2	1	2	X						X	X
Groundwater samples	Initial, T=8 weeks; T=16 weeks	3	7	21	X	X	X	X	X	X	X	X
Rinse Blank	Initial, T=8 weeks; T=16 weeks	3	1	3	X	X	X	X	X	X	X	X
Blind Duplicate	Initial, T=8 weeks; T=16 weeks	3	1	3	X	X	X	X	X	X	X	X
Matrix Spike	Initial, T=8 weeks; T=16 weeks	3	1	3	X	X	X	X	X	X	X	X
Matrix Spike Duplicate	Initial, T=8 weeks; T=16 weeks	3	1	3	X	X	X	X	X	X	X	X

4.3 SAMPLING AND MONITORING METHODOLOGIES

4.3.1 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 residues of any previous samples. To accomplish this, 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 isopropanol.
- Rinse thoroughly with analyte-free water.

Air dry.

Wrap in aluminum foil for transport.

4.3.2 Equipment Calibration

Measuring and test equipment shall have an initial calibration and shall be recalibrated at scheduled intervals against certified standards that have known and valid traceability to recognized national standards. Calibration intervals for each item shall be, at a minimum, in accordance with manufacturer's recommendations as defined in the equipment manual. Test equipment used for calibration of sensors shall themselves be recalibrated at least once a year or when maintenance or damage indicates a need for recalibration.

Calibration standards shall be maintained and used in an environment with temperature, humidity, and cleanliness controls that are compatible with the accuracy and operating characteristics of the standards. An inspection will be made during the equipment calibration to evaluate the physical condition of the equipment. The purpose of the inspection is to detect any abnormal wear or damage that may affect the operation of the equipment before the next calibration. Equipment found to be out of calibration or in need of maintenance or repair will be identified and removed from service.

The Project QA/QC Coordinator shall be notified if the test equipment is found to be out of tolerance during inspection and calibration. The corrective actions to be taken include evaluating the validity of previous inspection or test results; evaluating the acceptability of the items inspected or tested since the last calibration check; and repeating the original inspections or tests using calibrated equipment when it is necessary to establish the acceptability of previous inspections or tests.

Each item of measuring and test equipment in the calibration program shall be identified in such a way as to show its calibration status and calibration expiration date. Equipment history records for measurement and test equipment shall be used to indicate calibration status and conditions, corrections to be applied, results of in-service checks, and repair history. This will provide a basis for establishing calibration frequencies and for remedial action if the instrument is found out of calibration.

Measurement equipment to be used during field activities include a pH meter, temperature probe, specific conductivity meter, turbidimeter, reduction potential meter, dissolved oxygen probe, a PID, and a FID. General calibration procedures for each piece of equipment are included in Appendix B. Detailed information regarding maintenance and servicing is available in the operation manual of the specific meter to be used. The results of all calibrations will be recorded in the field log book.

4.3.3 Soil Sampling

Direct push soil sampling will be performed at the frequency indicated in Section 4.2. The soil borings will be advanced to the top of the weathered bedrock, approximately nine feet bgs. Soil samples will be collected from below the water table. The four-foot long soil cores from the direct push sampler will be screened for indications of volatile organic and/or petroleum contaminants using a photoionization detector (PID). The PID will be calibrated each day of use and ambient air readings will be taken. A soil sample will be collected from the soil exhibiting the highest PID reading and be submitted for analytical testing. If no excessive PID readings are detected, the sample will be collected from the interval one foot below the water table.

Soil samples will be homogenized in a stainless steel bowl before being placed into sample containers. Samples will be homogenized by first removing rocks, twigs, leaves, and other debris. The soil will then be placed into a decontaminated stainless steel bowl and thoroughly mixed using a decontaminated stainless steel spoon. The soil in the bowl is scraped from the sides and bottom of the bowl, rolled to the middle of the bowl and initially mixed. The sample is quartered and moved to the four corners of the bowl. Each quarter of the sample is mixed individually and then rolled to the center of the bowl and the entire sample is mixed again. Lastly, the sample is transferred to the appropriate sample containers and placed in a cooler at 4°C and held for laboratory analysis.

The following equipment will be used to collect soil samples:

- 10.2 eV Photoionization Detector (PID).
- Stainless steel spatula or spoon.
- Stainless steel bowl.
- Latex gloves (disposable).

- Neoprene gloves.
- Certified, precleaned sample containers.
- Field logbook and pen.
- Decontamination equipment.

4.3.4 Groundwater Level Measurements

Water levels in the monitoring points will be measured and used in conjunction with horizontal and vertical ground survey data to determine horizontal components of groundwater flow. Water levels will also be used to determine the volume of standing water in the monitoring points for purging activities. The following equipment will be used for the measurement of water levels:

- Electronic water level indicator.
- Oil/water interface probe.
- 10.2 eV Photoionization Detector (PID).
- Field logbook and pen.
- Deionized water.
- Low phosphate detergent (Alconox®).

At each monitoring point, the PVC cap will be removed and the head space and breathing zone's air quality will be monitored with a PID.

The battery of the electric water level indicator will be checked by pressing the battery check button, and waiting for the audible signal to sound or the instrument light to come on. The water level indicator will be decontaminated before collecting a measurement in each well point by using an Alconox® wash and deionized water rinse. The instrument will then be turned on and the probe will be slowly lowered into the monitoring well until the audible signal is heard or the instrument light goes on, indicating that the sensor in the probe has made contact with the water surface. The total depth of each monitoring point will be measured once the depth to water has been determined. The depth to water will be recorded to the nearest one-hundredth of a foot from the top of the measuring mark on the monitoring point. The date, time, monitoring point ID and depth to water will be recorded in the field book.

4.3.5 Groundwater Sampling

Groundwater samples will be collected from the pilot study monitoring points at the frequency specified in Section 4.3.2 for each pilot test. Prior to groundwater sampling, the water level will be measured using an electronic water level probe, as described above. The probe end of the water level meter and the tape will be decontaminated between monitoring points.

Low-flow groundwater sampling will be performed using a peristaltic pump and dedicated polyethylene or nalgene tubing following U.S. Environmental Protection Agency (USEPA) recommended low-flow methodology (see Appendix C). A flowrate of less than 500 ml/min will be used to purge each well. A flow-though cell will be used to continuously monitor the following groundwater parameters:

- Temperature.
- pH.
- Dissolved oxygen concentration.
- Turbidity.
- Specific Conductance.
- Redox potential (Eh).

The groundwater parameters will be recorded every three to five minutes on a purge log. In addition, the water level will be measured periodically throughout purging to ensure minimal drawdown (<0.3 feet). The monitoring points will continue to be purged until parameter stabilization for three successive readings is reached. Three successive readings should be ±0.1 for pH; ±3% for specific conductance; ±10 millivolts (mV) for redox potential; and ±10% for dissolved oxygen and turbidity. If stabilization does not occur, purging will be continued for a maximum of 10 well volumes.

Once purging has been completed, groundwater samples will be collected. Samples will be collected directly into containers, bypassing the flow-through cell, and submitted for analytical testing. The groundwater samples will be placed in a cooler at 4°C and held for laboratory analysis.

The following equipment will be used for groundwater sampling:

- Electric water level indicator.

- # Peristaltic pump capable of achieving low flow withdrawal rate.
- # Flow through cell.
- # Polyethylene or nalgene tubing.
- # External power source (e.g., generator, portable battery).
- # Portable water quality meters (i.e., temperature, pH, dissolved oxygen, specific conductance, redox potential and turbidity).
- # Polyethylene sheeting, volume-incremented bucket, garbage bags, paper towels, disposable nitrile gloves, field notebook.
- # Analyte-free water/decon materials.

4.3.6 Pilot Study Monitoring

4.3.6.1 Dissolved Oxygen/Temperature Measurements

Dissolved oxygen measurements will be recorded at each of the monitoring points. An in-situ dissolved oxygen probe that also measures temperature (e.g., YSI 550 instrument) will be lowered into each monitoring point. The dissolved oxygen probe will be calibrated and maintained in accordance with manufacturer instructions.

4.3.6.2 Pressure Measurements (Biosparging Test)

Pressure measurements will be recorded from each of the monitoring points during the biosparging test. Pressure will be measured using a Magnehelic® pressure gauge. The pressure gauge will be calibrated and maintained in accordance with manufacturer instructions.

4.3.6.3 Carbon Dioxide in Soil Gas (Biosparging Test)

Carbon dioxide in soil gas will be measured at the beginning, middle (i.e., T = 4 weeks) and at the completion of the biosparging test. A gas monitor capable of measuring carbon dioxide (e.g., Landtech® model GA-90) will be utilized. The gas monitor will be calibrated and maintained in accordance with manufacturer's instructions.

4.3.6.4 Ferrous Iron

Groundwater concentrations of ferrous iron will be measured during both the ORC® injection and biosparging pilot tests. Ferrous iron will be measured at each monitoring point using a Hach® field colorimeter. Instructions for ferrous iron measurement are included in Appendix B to this Work Plan.

4.4 SAMPLE DOCUMENTATION AND TRACKING

Sample custody during the field investigations will be performed in three phases. The first phase encompasses sample collection and identification, pre-laboratory treatment procedures (preservation), packaging, and shipping field custody procedures. The second custody phase involves sample shipment, where mode of shipment, airbill numbers, dates and times are documented. The third phase involves the custody procedures employed by the laboratory. All three phases of sample custody will be performed to provide that:

- All samples are uniquely identified;
- The correct samples are tested and are traceable to their source;
- Important sample characteristics are preserved;
- Samples are protected from loss or damage; and
- A record of sample integrity is established and maintained through the entire custody process.

4.4.1 Field Documentation

A bound field logbook will be maintained in which to record daily activities. All entries will be made in indelible ink. The field notebook pages shall be prenumbered. Incorrect entries will be corrected by a single stroke through the error and will be verified with the recorder's initials. Entries to the logbook, in addition to the required sampling entries, will include:

- Date.
- Start and finish times.
- Summary of work performed (including samples collected).

- Names of personnel present.
- Names of visitors.
- Weather.
- Level of personal protection used during various activities.
- Calibration of equipment.
- Observations and remarks.

The following information will be recorded in a field notebook at the time of sampling:

- Sample designation.
- Name of sampler.
- Method of collection.
- Time and date of sampling.
- Type of sample.
- Depth of sample.
- Analyses required and sample container types.
- Field measurements and calibration (if applicable).
- Stratigraphy and/or observed conditions which may impact the chemistry of the sample; and Observations and remarks.

4.4.2 Sample Identification

All samples collected from the site must be identified with a sample label in addition to an entry on a chain-of-custody record. Indelible ink will be used to complete sample labels, then labels will be covered with clear plastic waterproof tape. The field team will be required to complete the following information for each sample label:

- Site Name.
- Sample Number.
- Sample Matrix.
- Parameters to be Analyzed.
- Date of Collection.

Time of Collection.

Preservation Technique Employed.

Sampler's Name.

Sample labels will be attached to the sample bottles.

4.4.3 Chain-of-Custody Record

The chain-of-custody creates an accurate written record that can be used to trace the possession and handling of the sample from the moment of its collection through analysis. Chain-of-custody forms will be completed for each sample at the time of collection and will be maintained while shipping the sample to the laboratory. 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.

4.4.4 Sample Shipment

Custody of samples must be maintained through the shipment of samples to the selected laboratory. Samples will be delivered directly to the laboratory by sampling personnel or shipped via the following procedures:

Use waterproof high-strength plastic ice chests or coolers only.

After filling out the pertinent information on the sample label and tag, put the sample in the bottle or vial and screw on the lid. For all samples except VOA vials, secure the bottle lid with strapping tape.

Tape cooler drain shut.

Place about three inches of inert cushioning material such as vermiculite or styrofoam "popcorn" in the bottom of the cooler. Styrofoam packing shall not be used when sampling for volatile organics.

Enclose the bottles in clear plastic bags through which sample labels are visible, and seal the bag. Place bottles upright in the cooler in such a way that they do not touch and will not touch during shipment.

- Put in additional inert packing material to partially cover sample bottles (more than half-way). Place bags of ice or ice-gel packs around, among, and on top of the sample bottles.
- Fill the remaining space in the cooler with cushioning material.
- If sending the samples by common carrier, sign the chain-of-custody under "Relinquished by," enter the carrier name and airbill number, retain a copy for field records and put the chain-of-custody record in a waterproof plastic "ziplock" bag and tape it with masking tape to the inside lid of the cooler. If sending the samples by courier or field team shipper, follow the above procedures, but also have the receiving carrier sign under "Received by."
- Apply custody seals to the front and back of the cooler, across the lid.
- Secure lid by taping. Wrap the cooler completely with strapping tape at a minimum of two locations. Do not cover any labels.
- Attach completed shipping label to top of the cooler. The shipping label shall have a return address.
- Ship the cooler by overnight express or courier to the respective laboratory.

4.4.5 Laboratory Custody Procedures

When the sample arrives at the laboratory, the sample custodian receives the sample. The label 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 notify the Project QA/QC Coordinator, Site Field Manager, or the Project Manager immediately if any inconsistencies exist in the paper work associated with the samples.

4.5 INVESTIGATION-DERIVED WASTE

Purge water and aqueous decontamination wastes generated from low-flow groundwater sampling will be placed in sealable 55-gallon drums as the sampling is performed between MP locations. At the end of a day of sampling, the aqueous waste will be discharged to the recharge pit associated with the active pilot landfarming plot in the northeast quadrant of the Siberia Area (see Figure 3-2).

Soil cuttings from installation of the monitoring points for the each pilot test will be placed in DOT-approved 55-gallon drums. Following installation of the injection/sparging points and MPs associated with each pilot test, the drummed soil cuttings will be taken to the active landfarming pilot plot and spread on top of the existing pile for biotreatment.

Waste disposable personal protective equipment (PPE) will also be generated. Attempts will be made to wash surface contamination off so that PPE (i.e., gloves and other disposal items) may be disposed of as ordinary solid waste.

5.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

5.1 LABORATORY QA/QC PROCEDURES

5.1.1 Data Quality Objectives (DQOs)

Data quality objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions, and are developed to achieve the level of data quality required for the anticipated data use. DQOs are implemented so that for each task the data is legally and scientifically defensible. The development of DQOs for a specific site and measurement takes into account project needs, data uses and types, and data collection. These factors determine whether the quality and quantity of data are adequate for its end use. Sampling protocols have been developed and sample documentation and handling procedures have been identified to realize the required data quality.

Data produced from this study should be of sufficient quality and quantity to enable a comparison of the effectiveness of biosparging versus ORC® injection for oxygen delivery to groundwater underlying the Siberia Area. The data should allow for calculation of the radius of influence of oxygen addition under both of the technologies. Information collected from the pilot studies will be used to decide which technology is most suitable for full-scale application at the Siberia Area. The pilot studies will provide information for full-scale remediation system design. In addition, the collected data should allow for an estimation of the rate of TPH degradation by in-situ biotreatment for groundwater and saturated soils underlying the Siberia Area.

5.1.2 Quality Control Elements

Data quality is measured by how well the data meet the quality assurance/quality control (QA/QC) goals for the project. Quality control elements include precision, accuracy, representativeness, completeness, comparability, and sensitivity:

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.

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

where: V_1 = value 1; V_2 = 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 field sampling program. The sampling program 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:

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

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 objective for this Site is 95 percent.

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 FSP.

Sensitivity is a measure of a method's detection limit and ability to distinguish between two values. Sensitivity is determined through the laboratory's IDL and MDL studies.

5.1.3 Laboratory Quality Control Samples

All analyses shall include the following minimal QC procedures, when applicable. However, the laboratory must follow their own SOP for each method (see Appendix D for laboratory SOPs).

Procedure	Frequency
Calibration	As required
Standards	Daily
Method Blanks	Daily
Duplicates	5%
Matrix Spikes/Matrix Spike Duplicates	10%
Surrogates	Where applicable
QC Check Samples	Daily

A standard laboratory quality control data package will be requested for each sampling event. Quality control samples routinely analyzed by the laboratory include: laboratory control samples (LCS), method blanks, internal and surrogate standards, matrix spike (MS) and matrix spike duplicate (MSD) samples. Established acceptance criteria for these samples will be used to determine the acceptability of the data. Quality control samples which fall outside of these criteria serve as flags to indicate potential biases associated with the data. The definition of each of the quality control samples and the frequency at which the laboratory analyzes them are discussed in this section.

5.1.3.1 Laboratory Control Samples

A control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analytical

methods employed for each analytical method. In addition, an LCS serves to monitor the extraction efficiency during sample preparation procedures as well as verification of the current instrument calibration.

5.1.3.2 Method Blanks

A method blank consists of laboratory-grade pure water containing all of the reagents utilized in the analytical procedure. The method blank is prepared in the same manner as a sample and is processed through all of the analytical steps, including any sample preparation. If samples require a preparatory procedure such as a digestion prior to analysis, then a method blank must be analyzed in addition to the instrument calibration blanks.

Method blanks are performed to determine whether there is a reagent, instrument or laboratory contamination. Method blanks are analyzed as part of the initial or daily calibration process (calibration blanks). Additionally, method blanks are analyzed at the designated frequency sited within each method.

5.1.3.3 Surrogate Standards

As required by the GC/MS and most GC methods, surrogate standards are run to evaluate the efficiency of the sample introduction process. Surrogate standards are included with each sample and run in accordance with the method procedures.

5.1.3.4 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) Samples

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples are two separate aliquots taken from a single field sample and spiked with target analytes prior to sample preparation and analysis. MS and MSD samples will be obtained from the same container as the field sample (i.e., additional sample jars will not be submitted). MS and MSD samples are spiked with the appropriate analyte at concentrations between 10 and 50 times the method detection limits. For inorganic analyses, the spiked concentration must be greater than five times the initial sample concentration.

Results from the analysis of MS and MSD samples are used to evaluate the effect of sample matrix on precision and accuracy. The percent recoveries are calculated for

each of the target analytes and are used to assess analytical accuracy. The relative percent difference (RPD) between the MS and MSD samples is calculated and used to assess analytical precision. MS and MSD samples are generally analyzed at the rate of one in every 20 samples. However, since matrix interferences are anticipated for samples collected for this project, MS/MSD samples will be analyzed at the rate of one in every 10 samples.

5.2 QUALITY ASSURANCE OBJECTIVES FOR CHEMICAL DATA

Several measures will be taken to ensure the precision and accuracy of chemical data generated for TPH and for nutrient analyses. At a minimum, the laboratory analysis of chemical parameters will meet the standards for precision and accuracy set forth in the corresponding methods of analysis listed in Table 5-1. Laboratory method detection limits and practical quantitation limits are also included on Table 5-1. The laboratory will provide full data deliverables including raw data in accordance with the NYSDEC June 2000 Analytical Services Protocol (ASP).

Table 5-1: Method Detection and Quantitation Limits

COMPOUND	METHOD	MDL's		POL's	
		WATER	SOIL	WATER	SOIL
		ug/L	mg/Kg	ug/L	mg/Kg
TPH - Diesel Range	Modified Oklahoma Method	37	1.2	100	10.0
Ammonia	EPA350.2	1.0	22.0	3	100
Nitrate	EPA300.0	0.041	0.3	0.123	0.9
Nitrite	EPA300.0	0.023	0.3	0.069	0.9
Ortho Phosphorus	EPA300.0	0.055	0.2	0.165	0.6

As discussed above, blind duplicates will be submitted to the analytical laboratory to measure and ensure the precision of chemical data. Matrix spike and matrix spike duplicates will be submitted to the analytical laboratory to ensure and measure the accuracy of laboratory analytical methods. Rinsate blanks from field equipment will be submitted to the analytical laboratory to ensure sampling accuracy. These quality assurance samples will be collected according to the schedule summarized in Table 4-2.

5.3 ANALYTICAL METHODS AND SAMPLE HOLDING TIMES

The extraction and analytical procedure method numbers, holding time requirements, and preservation methods are indicated on Table 5-2 below.

Table 5-2: Analytical Procedure Holding Times and Preservatives

Matrix/ Parameter	Analytical Procedure	Holding Time Sample/Extract	Preservative
Groundwater			
TPH	Modified Oklahoma	14 days/40 days	Ice to 4°C
Biochemical Oxygen Demand (20-day)	EPA 405.1	48 Hours	Ice to 4°C
N-Ammonia	EPA 350.2	14 days	Ice to 4°C
Nitrate	EPA 300.0	14 days	Ice to 4°C
Nitrite	EPA 300.0	14 days	Ice to 4°C
Ortho Phosphate	EPA 300.0	14 days	Ice to 4°C
pH	SW-846 9045C	48 hours	Ice to 4°C
Soils			
TPH	Modified Oklahoma	14 days/40 days	Ice to 4°C
Total Organic Carbon	EPA 415.1	28 days	Ice to 4°C

Southwest Laboratory of Oklahoma will perform the laboratory analyses of soils and groundwater. The laboratory address is as follows:

Southwest Laboratory of Oklahoma, Inc.
1700 W. Albany
Broken Arrow, OK 74012-1421
918-251-2858 (phone)
918-251-2599 (fax)

Sample management and custody procedures are discussed in Section 4.0 of this work plan.

5.4 FIELD QUALITY CONTROL CHECKS

5.4.1 Field Measurements

Simple field checks should be made to ensure that no obvious problems are developing due to the purging process. At a minimum, ORP and DO values should be in relative agreement. For example, DO values should be <1 mg/l when ORP is negative. Also, DO and ORP normally decrease, or may remain the same during purging. An increase in both parameters during purging is an indication of artificial aeration of the water or mixing of water inside the well from different intervals.

The QC checks employed for field instruments include the following:

QC Method	Purpose	Frequency
Calibration Check	Insures proper working order of field instrument. Measures accuracy and sensitivity.	Daily
Field Duplicate Sample	Measures instrument precision	10%

5.4.2 Field QC Samples

Field quality control (QC) are defined as samples collected in the field to assess certain aspects of the overall quality of the project. QC samples are analyzed by the designated subcontract laboratory. The field QC samples will consist of field duplicate samples; trip blanks will not be collected since no VOC analyses are being performed for the pilot tests.

Field duplicate samples are two samples collected from the same source at the same time and which are submitted separately to one laboratory, one as the primary sample and one as a blind duplicate. The collection frequency of duplicate samples is approximately 10 percent (see Table 4-2). The purpose of duplicate samples is to assess the consistency of the overall sampling effort; the purpose of submitting them "blind" is to assess the laboratory analytical system's consistency or precision.

6.0 REPORTING

6.1 PILOT TEST REPORT

Upon completion of both of the pilot tests, a Pilot Test Report will be prepared. The report shall address the following:

- Site conditions;
- Pilot Test results and conclusions; and
- Recommendations for full-scale implementation.

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

6.2 DATA ANALYSIS

Chemical data and field measurements will be analyzed to compare each pilot technology for the following criteria:

- Radius of influence of each technology.
- Sustainable concentrations of dissolved oxygen.
- Reduction of concentration of TPH in groundwater and in saturated soils.
- Costs of full-scale implementation.
- Ease of implementation at the Siberia Area.

Recommendations for full-scale groundwater remediation will be made based upon the above criteria.

7.0 REFERENCES

Malcolm Pirnie, Inc.(MPI), 1997. *Final RCRA Facility Investigation Report, Siberia Area, Watervliet Arsenal, Watervliet, New York.* Latham, New York, December 1997.

Malcolm Pirnie, Inc. (MPI), 2000. *Draft Final Biological Treatability Studies of Siberia Area, Watervliet Arsenal, Watervliet, New York.* Latham, New York, April 2000.

Regenesis Bioremediation Products, Inc., 2000. *Frequently Asked Questions About Oxygen Release Compound, ORC®*. http://www.regenesis.com/ORC/question.htm

U.S. Environmental Protection Agency (USEPA), 1994. *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers.* Chapter VIII, Biosparging. EPA 510-B-94-003

APPENDIX A

Health and Safety Short Form

SITE SPECIFIC HEALTH AND SAFETY PLAN

MALCOLM PIRNIE

SECTION 1: GENERAL INFORMATION AND DISCLAIMER		PROJECT NUMBER:	0285774
PROJECT NAME:	Watervliet Arsenal - Siberia Area Groundwater Pilot Studies	CLIENT NAME:	U.S. Army Corps of Engineers
PROJECT MANAGER:	Ken Goldstein	PROJECT LEADER:	Christopher Gaule
PREPARED BY:	Daria Navon	DATE:	7/2/2004

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; (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

Subcontractors may use this Malcolm Pirnie Health and Safety Plan as the basis of their own Health and Safety Plan under the following conditions: (1) The subcontractor develops a written addendum to the Malcolm Pirnie plan 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) Subcontractor personnel signs the Malcolm Pirnie plan and the subcontractor task-specific plan addendum; and (3) Subcontractors must implement and monitor the Malcolm Pirnie plan and task-specific addendum as their own site specific health and safety plan while they and their employees are performing work pursuant to the contract with Malcolm Pirnie.

The allowance that subcontractors may use the Malcolm Pirnie plan with addendum as their own plan, 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	Albany County	911
HOSPITAL (Directions attached)	Albany County	911
FIRE DEPARTMENT	Albany County	911
POLICE / SECURITY	Albany County	911
HAZMAT/ SPILL / OTHER RESPONSE	Albany County	911

(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) 529-0858, X316 NNJ
CORPORATE HUMAN RESOURCES **	LORI HEILMAN (WORKERS= COMP / OSHA LOG)	(914) 641-2447 WHI
LEGAL DEPARTMENT **	JERRY CAVALUZZI	(914) 694-2100 WHI

**** TO BE NOTIFIED IN CASE OF ACCIDENT**

SECTION 3: PROJECT INFORMATION

(A) SITE / FACILITY INFORMATION:

SITE NAME: Watervliet Arsenal - Siberia Area

ADDRESS: Broadway, Watervliet, New York

☒ FEDERAL ☐ STATE ☐ MUNICIPAL / REGIONAL ☐ PRIVATE

SITE CLIENT CONTACT: Steve Wood

PHONE NUMBER: (410) 962-3506

SITE SAFETY CONTACT: Jim Kardas, 518-266-5716

(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: Pilot Tests for groundwater treatment	☒ AIR	☐ SEDIMENT
☐ CONSTRUCTION MGMT		☐ SURFACE WATER	☐ SURFACE SOIL
☐ INSPECTION		☒ GROUND WATER	☐ LANDFILL
☐ INVESTIGATION SURVEY		☐ WASTE WATER	☒ OTHER Sub-surface soils
		☐ WASTE STREAM	

DATE(S) OF FIELD ACTIVITIES: Approx. mid-March 2001 to mid-September 2001

(E) **FIELD TASKS**

MALCOLM PIRNIE TASKS

M1. Groundwater sampling

M2. Soil sampling

M3. Pressure, dissolved oxygen, and water level measurements

M4.

TASKS PERFORMED BY OTHERS

01. Installation of monitoring points

02.

03.

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: Ken Goldstein

SITE SAFETY OFFICER: Matthew Bokus

ALTERNATE SAFETY OFFICER(S): Patrick Rabideau

PUBLIC INFORMATION OFFICER: Christopher Gaule

SITE RECORDKEEPER: Matthew Bokus

FIELD TEAM LEADER: Matthew Bokus

OTHER FIELD TEAM LEADERS: Andy Vitolins

Patrick Rabideau

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): Drilling contractor

FEDERAL AND STATE AGENCY REPS: USEPA

USACE

OTHER AGENCY REPS: NYSDEC

NYSDOH

(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)			
Andrew Vitolins	11/95	03/01				07/00	07/00	07/99	06/01				
Matthew Bokus	08/98	03/01							04/01				
Patrick Rabideau	01/98	03/01	05/99			11/00	11/00	11/99	09/01	MSA	RG	FF	01/9
Christopher Gaule	05/88	03/01	06/91			03/99	03/99	03/99	06/01	MSA	RG	FF	10/9

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
PAHs, VOCs	IG, TO	GW	5 ppm	1 ppm
PAHs, VOCs	IG, TO	SL	400 ppm	1 ppm

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	Skin/Inhalation	low	PPE
M2	Skin/Inhalation	low	PPE
M3	Inhalation	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

Matthew Bokus 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 ex cavation and/or a safe distance from excavators, drill rigs and other heavy equipment.

These boundaries are identified by: no excavations/drilling operations are required for this work.

No unauthorized person should be within this area.

(B) WORK ZONES - CONTAMINATION

The prevailing wind conditions are 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: 20 foot radius around each site activity

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 = $3C_N/EL_N$) 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 _____ ºF. If it is determined that heat stress or cold stress monitoring is required (mandatory for heavy exertion in PPE at temperatures over 70ºF, or at temperatures under 40ºF 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:

Alconox	Isopropanol
Oxygen Release Compound (magnesium peroxide)	

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 Modified Level D decontamination protocol shall be used with the following decontamination stations:

(1) Level 'D' protection will be provided for all professionals working on this project.

(2) Upon exiting the work zone, obviously contaminated gloves and overalls will be removed and discarded

(3) Boots, if contaminated will be washed with detergent-water solution and rinsed with water

(4) Equipment will be decontaminated as specified in the work plan

(5)

(6)

(7)

(8)

(Other)

The following decontamination equipment is required:

☒ Decon Pad (Plastic Sheet) ☐ Dry Brushes ☒ Buckets Other
☒ Trash Cans/Bags ☐ Wet Brushes ☐ Hose / Spray

Detergent (Alconox)/Water solution 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	FF/OV	UP	C	LN	S	HH
M2	FF/OV	UP	C	LN	S	HH
M3	FF/OV	UP	C	LN	S	HH

* Same as Section 3E

**UP = Upgrade
CONT = Continuous

CODES:

RESPIRATORS[1]	CARTRIDGES[1]	CLOTHING	GLOVES[2]	BOOTS	OTHER
HF = Half Face APR	P = Particulate	N/S = No Special	Co = Cotton	SL = Leather Safety	HH = Hard Hat
FF = Full Face APR	OV = Organic Vapors	C = Coveralls	Le = Leather	H = Hip (Fireman)	G = Safety Glasses
ESCBA = Escape Bottle	AG = Acid Gas	T = Tyvek	L = Latex		GP = Glare Protection
SAR = Airline	Mult = Multi-Gas/Vapor	Sx = Saranex	N = Nitrile		GI = Goggles - Impact
SCBA = SCBA	Other	PT = PE Tyvek	B = Butyl		GS = Goggles - Splash
			Neo = Neoprene		FS = Face Shield
			V = Viton		HP = Hearing Protection
			PVC = Polyvinyl Chloride		
			PVA = Polyvinyl Alcohol		
			Other:		

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: As defined in Section 9

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):

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 10 minutes from the site and the ambulance response time is 10 minutes. _____ of Samaritan Hospital Was 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: Exit the site at Main Entrance. Turn left onto Broadway. Proceed to intersection with State Route 2. Turn right onto Route 2, go over bridge. Proceed on Route 2 through City of Troy - continue up hill. Turn left onto 15th Street. Continue on 15th Street. Turn right onto Peoples Ave. Samaritan Hospital is on the left.

(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

APPENDIX B

Field Equipment Manuals

DR/2000 SPECTROPHOTOMETER

Combines Stored Programs and Advanced Optics

Pg 1

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.

permanent records of your data and generate written reports of your results.

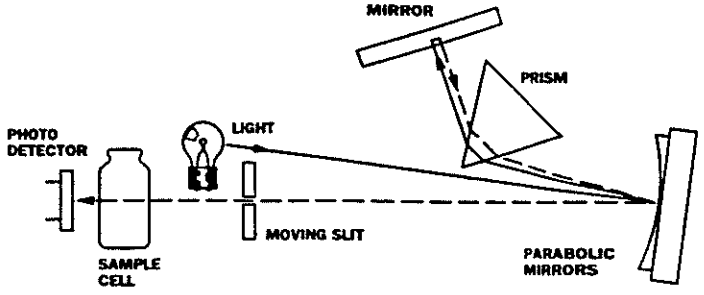
Multi-language Prompting

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.

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

New 3.1 Software Improves Operation

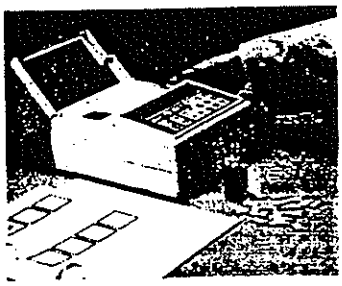
All new DR/2000 Spectrophotometers are now preprogrammed with version 3.1 software, an important update that has made the instrument easier to use without changing its operating methodology.

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 #173 for more information.

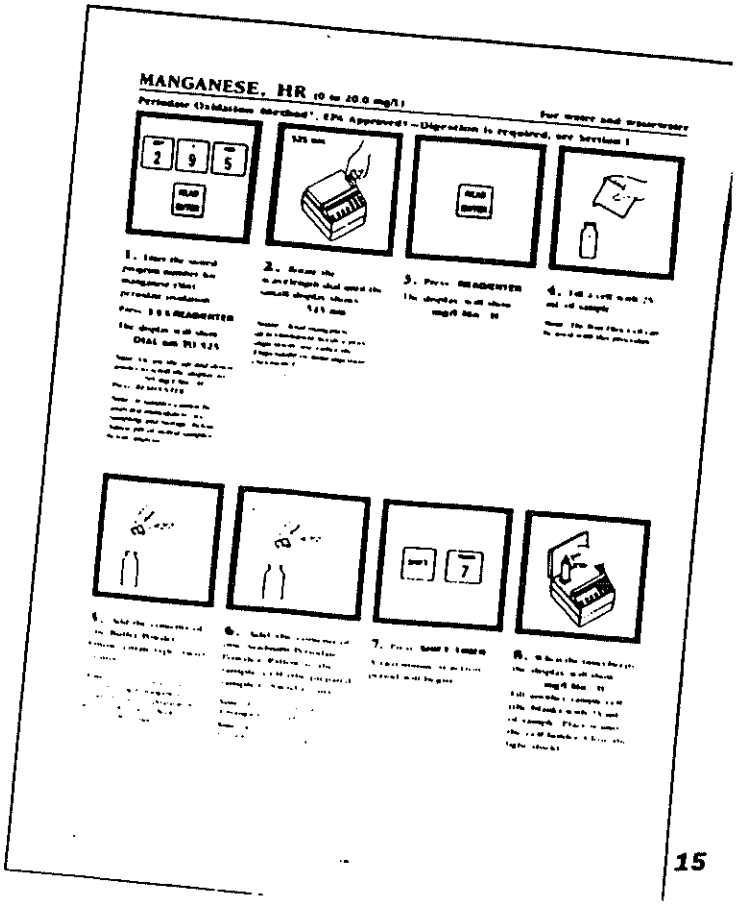
Complete Procedures Manual*

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.

* Available in English, French, Spanish and German

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

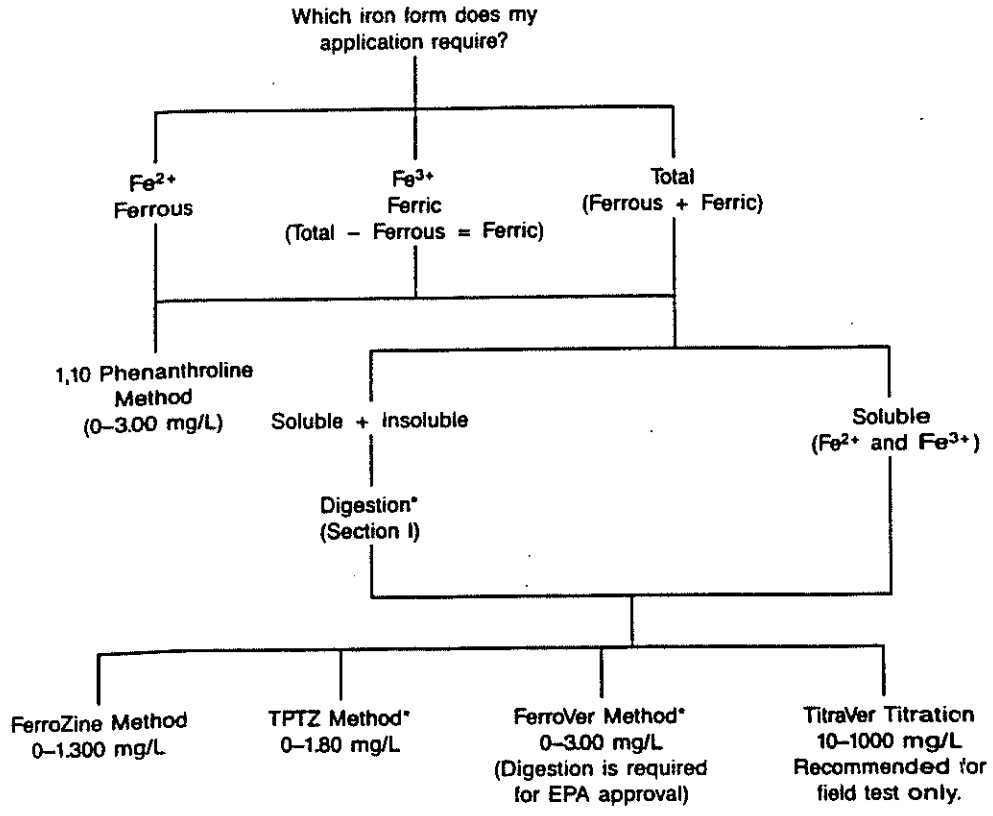


How to Select the Right Iron Procedure

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

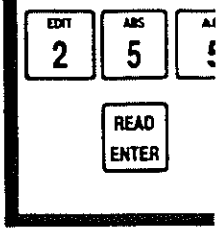


*Note: TPTZ and FerroVer will recover most insoluble iron oxides without digestion.

IRON, FER

1,10 Phenanthrol

USING POWDE



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

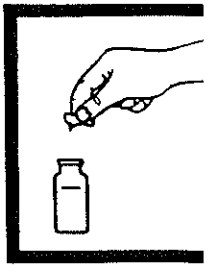
Press: **2 5 5 READ/EN**

The display will sho
DIAL nm TO 5

***Note:** DR/2000s with so versions 3.0 and greater display "P" and the prog number.*

***Note:** Instruments with s versions 3.0 and greater not display "DIAL nm T message if the wavelengt already set correctly. The display will show the me in Step 3. Proceed with*

***Note:** Analyze samples a as possible to prevent ai oxidation of ferrous iron ferric, which is not dete*



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

***Note:** An orange color form if ferrous iron is p.*

***Note:** Undissolved pow not affect accuracy*

*Adapted from Standard Me

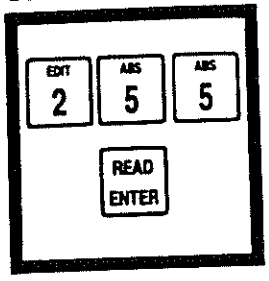
IRON, FERROUS (0 to 3.00 mg/L)

For water, wastewater and seawater

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

ATTACHMENT 2
Pg 2

USING POWDER PILLOWS



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

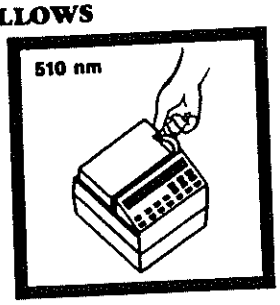
Press: **2 5 5 READ/ENTER**

The display will show:
DIAL nm TO 510

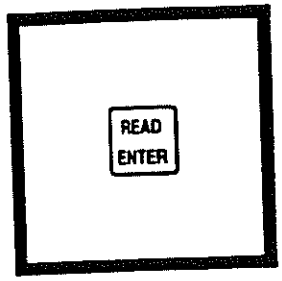
***Note:** DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

***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*

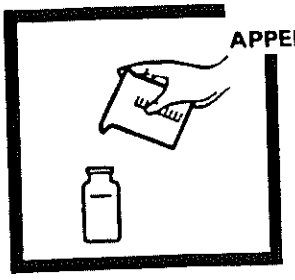


2. Rotate the wavelength dial until the small display shows:
510 nm



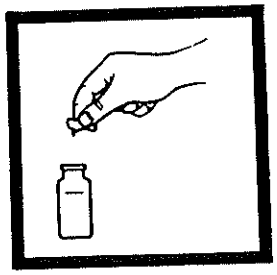
3. Press: **READ/ENTER**

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



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

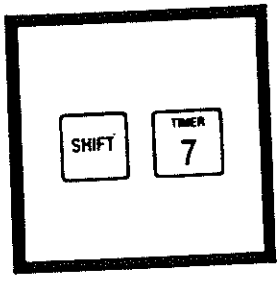
***Note:** For proof of accuracy, use a 1.0 mg/L ferrous iron standard solution (preparation given in the Accuracy Check) in place of the sample.*



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

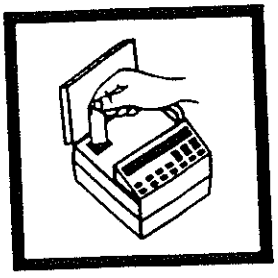
***Note:** An orange color will form if ferrous iron is present*

***Note:** Undissolved powder does not affect accuracy*



6. Press. **SHIFT TIMER**

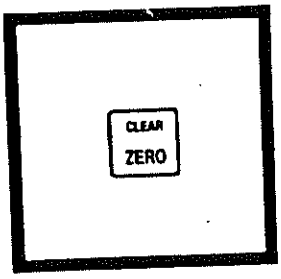
A three-minute reaction period will begin



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 Pour Thru Cell can be used with this procedure*



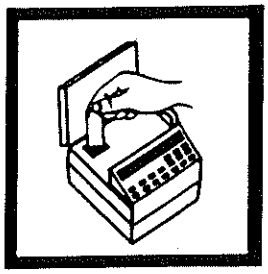
8. Press: **ZERO**

The display will show:
WAIT

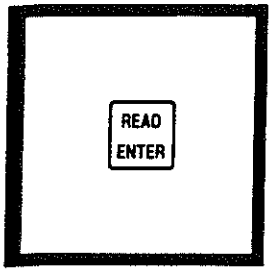
then:
0.00 mg/l Fe^{2+}

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

Attachment 2
Pg 3



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

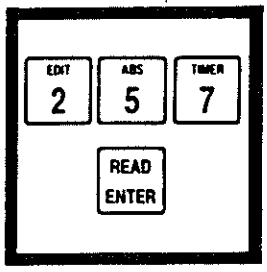


10. Press: **READ/ENTER**

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.

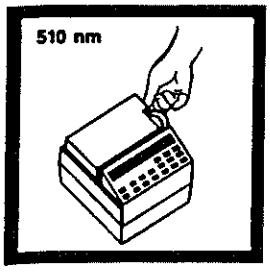
Press: **2 5 7 READ/ENTER**

The display will show:
DIAL nm TO 510

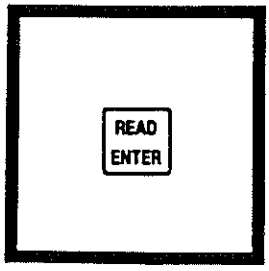
***Note:** DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

***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 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*

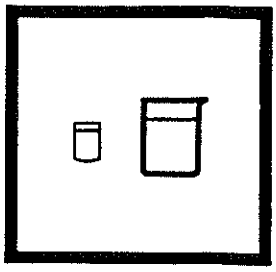


2. Rotate the wavelength dial until the small display shows:
510 nm



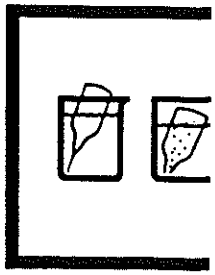
3. Press: **READ/ENTER**

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



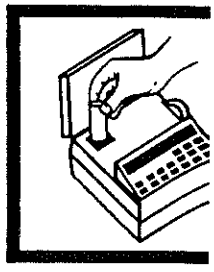
4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

***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.*



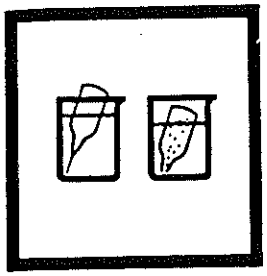
5. Fill a Ferrous Ir AccuVac Ampul with sample.

***Note:** Keep the tip immc while the ampul fills completely.*



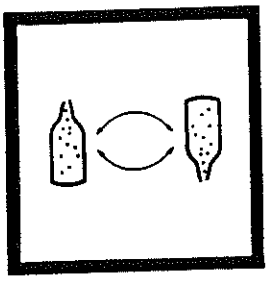
9. When the timer the display will sho
mg/l Fe^{2+} AV
Place the blank into cell holder. Close th light shield.

IRON, FERROUS, continued



5. Fill a Ferrous Iron AccuVac Ampul with sample.

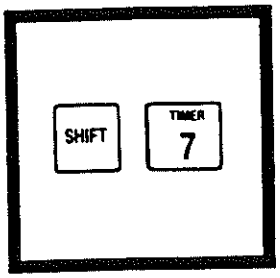
Note: Keep the tip immersed while the ampul fills completely.



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

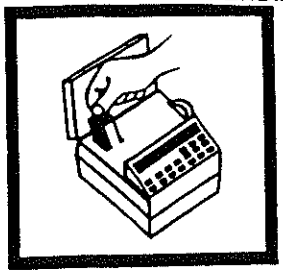
Note: An orange color will form if ferrous iron is present.

Note: Undissolved powder does not affect accuracy.



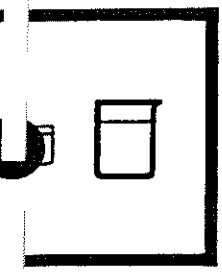
7. Press: **SHIFT TIMER**

A three-minute reaction period will begin.



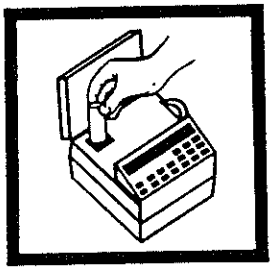
8. Place the AccuVac Vial Adapter into the cell holder.

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



Fill a zeroing vial
ank) with at least
of sample. Collect
ast 40 mL of sample
50-mL beaker.

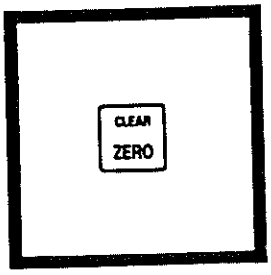
or proof of accuracy, a
. ferrous iron standard
on (preparation given in
ccuracy Check) can be
place of the sample.



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.



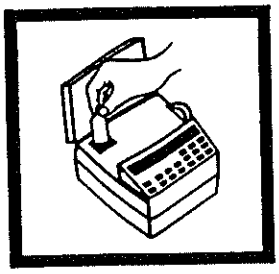
10. Press: **ZERO**

The display will show:

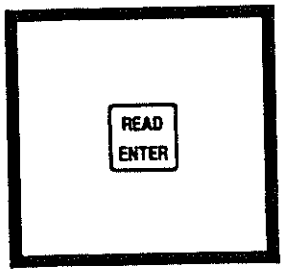
WAIT

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

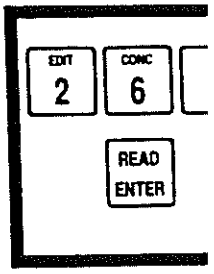
AccuVac Snapper Kit		each	24052-00
Clippers, shears, 7-1/4"		each	23694-00
Flask, volumetric, 100 mL, Class B		each	547-42
Flask, volumetric, 1000 mL, Class B		each	547-53
Pipet, volumetric, 1 mL		each	515-35
Pipet Filler, safety bulb		each	14651-00
Pour-Thru Cell Assembly Kit		each	45215-00

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



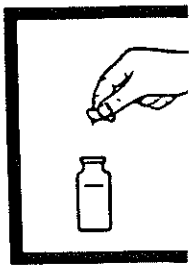
1. Enter the store program number f iron (Fe), FerroZin method.

Press: 2 6 0 READ/

The display will sh
DIAL nm TO

Note: DR/2000s with 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 wavele 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

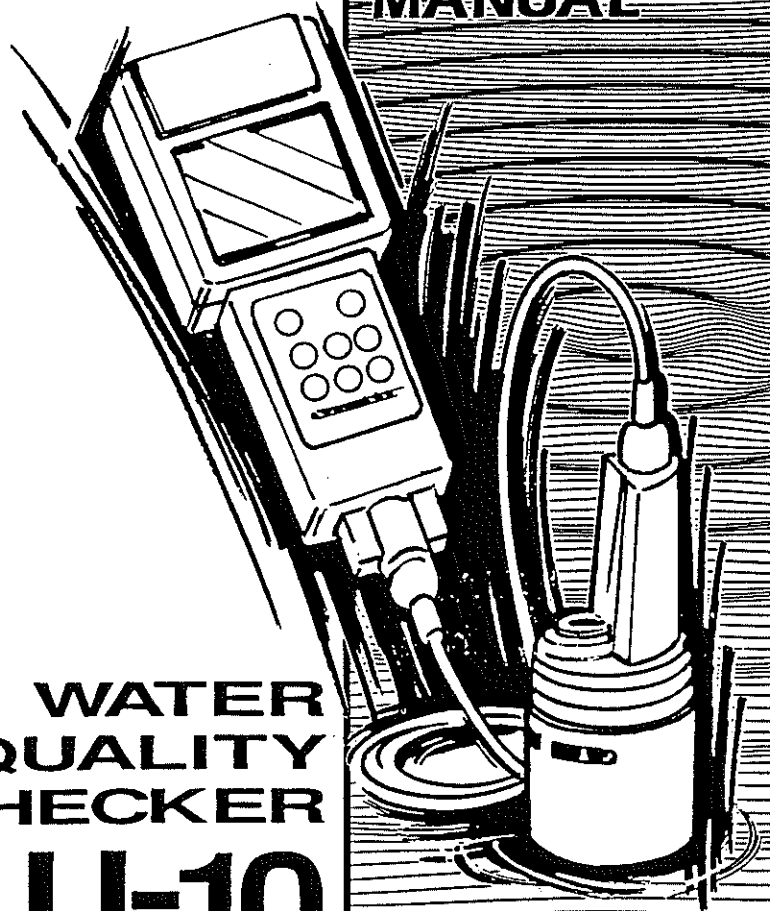
Note: 0.5 mL of Fer Reagent Solution can place of the solution preferred.

Note: If the sample rust, see Interference

*Adapted from Stookey,

HORIBA

INSTRUCTION MANUAL



WATER QUALITY CHECKER U-10

CODE: 04080-1000HK-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.

The 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 your U-10 Water Quality Checker, please read this *Instruction Manual* carefully 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*.

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

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Contents of Tables

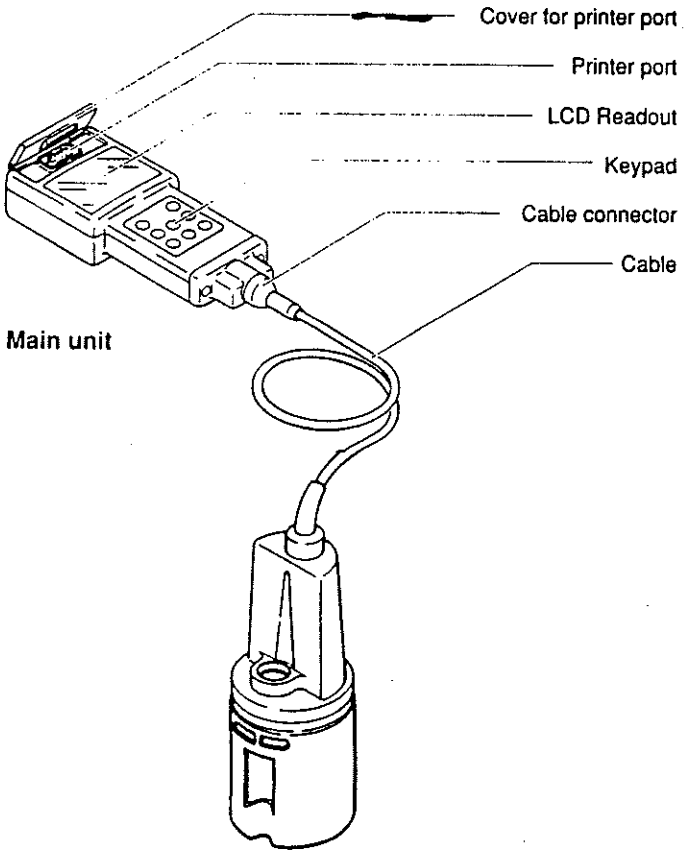
Section 1

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

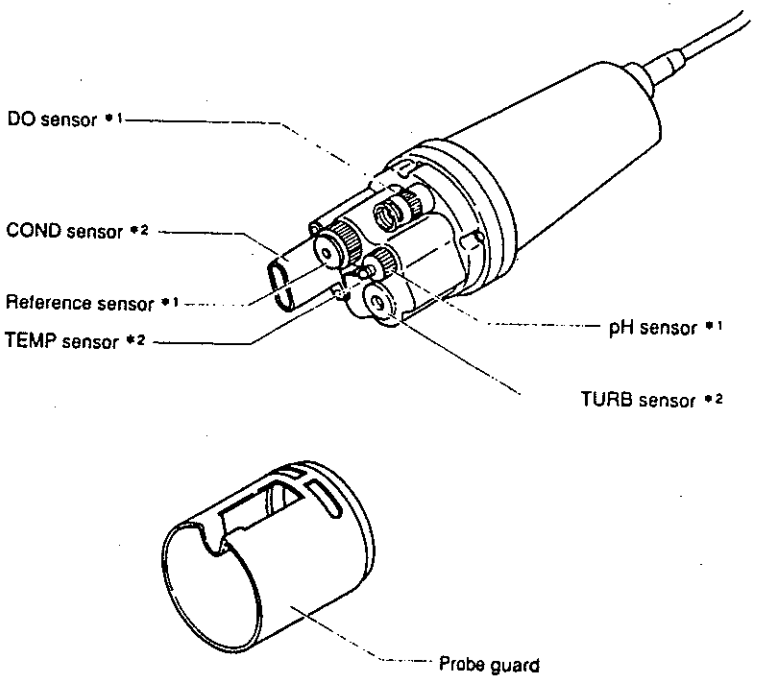
Main unit



Main unit

Probe

Probe

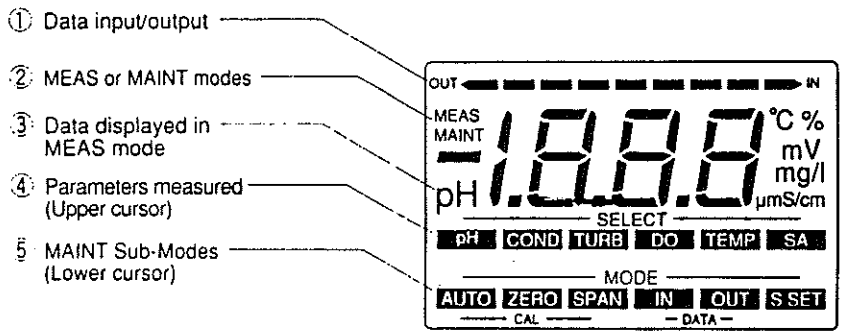


*1. Removable
DO (Dissolved oxygen)
Reference
pH

*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

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

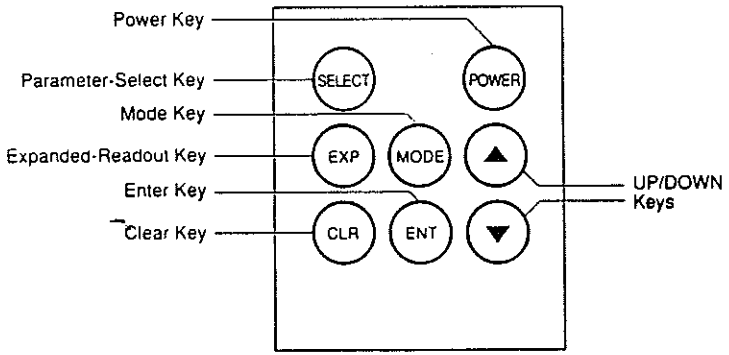
SPAN Manual span calibration

IN Data input

OUT Data output

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.

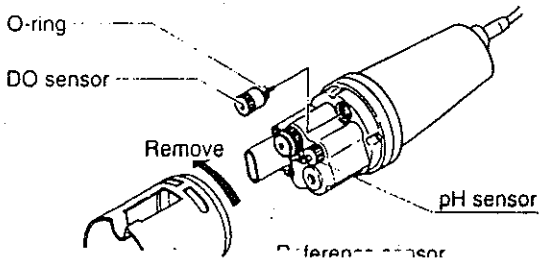
Inserting the DO sensor

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.



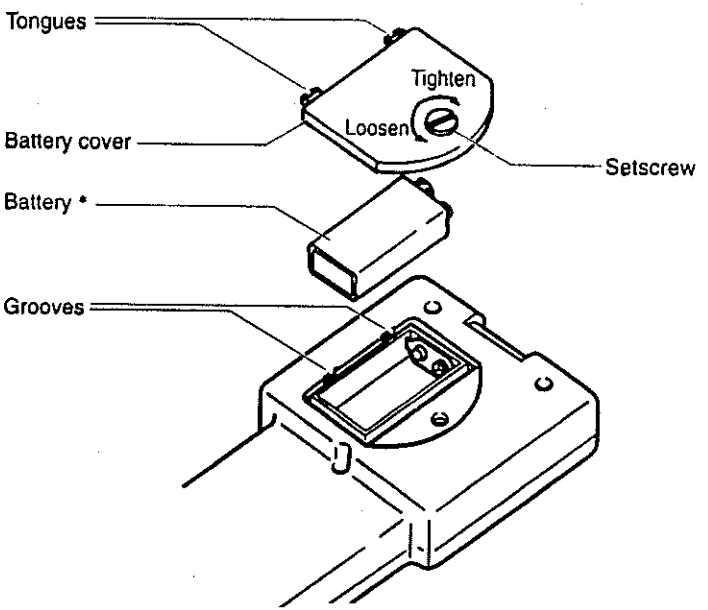
Inserting the battery

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.

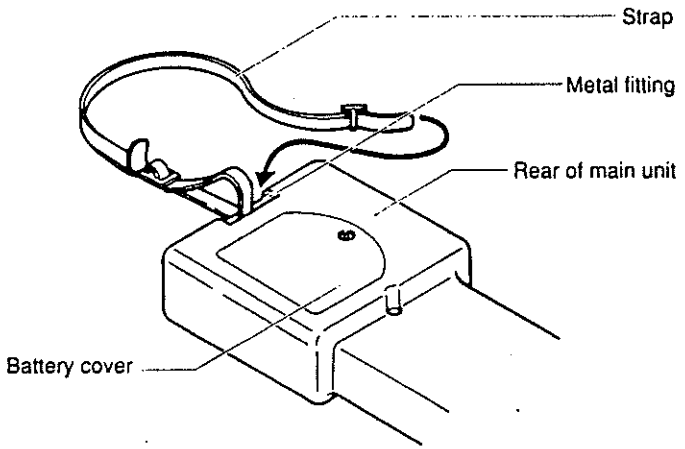
If the readout shows the message Er 1, it means that the battery is defective or exhausted and should be replaced.

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.



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

POWER **1** Turn the power on.

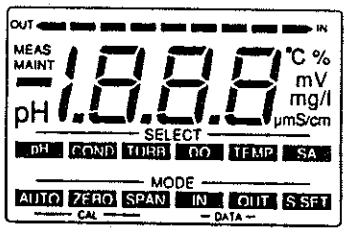
2 Gently place the probe into the water sample.

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.

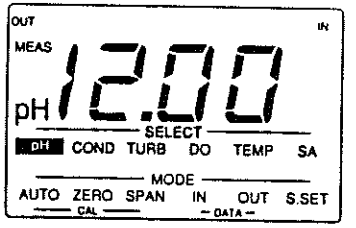
Be careful!
Never drop or throw the probe into the water. It is a precision instrument containing five delicate sensors and five pre-amps; you can damage it beyond repair by unnecessary rough handling.

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.

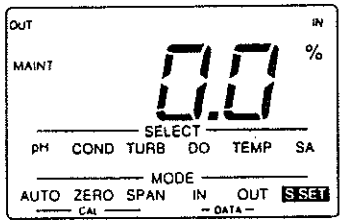
Measuring fresh water

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

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. 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.)

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.

After measurement: Cleaning and storing the U-10

POWER

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.

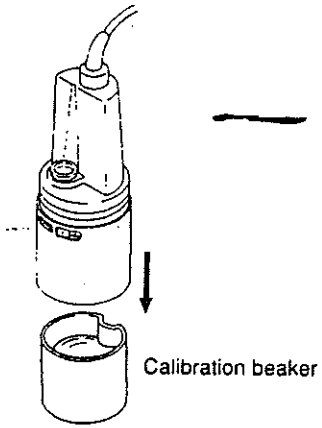
Manual calibration for each of the four parameters is more accurate but, of course, also more time-consuming. This method should be used for more precise measurement. The manual calibration procedure is explained below in detail, following the description of the auto-calibration procedure.

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

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.

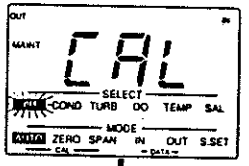


Calibration beaker

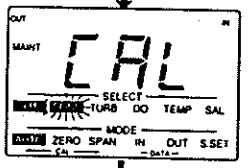
MODE With the power on, press the MODE Key to put the unit into the MAINT mode. The lower cursor should be on the AUTO Sub-Mode; if it is not, use the MODE Key to move the lower cursor to AUTO.

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.

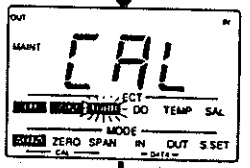
The upper cursor will blink while the auto-calibration is being made. When the auto-calibration has



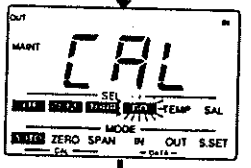
First, pH is being auto-calibrated



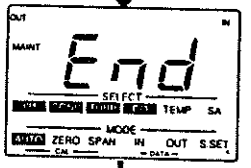
Then, COND is being auto-calibrated



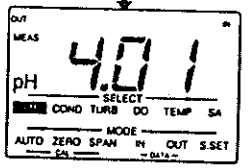
Next, TURB is being auto-calibrated



Finally, DO is being auto-calibrated



Auto-calibration now ends

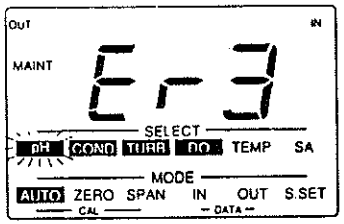


And the readout switches to the MEAS mode

Note: If you wish to abort the auto-calibration for

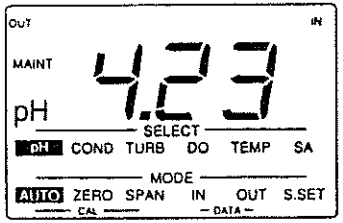
Auto-calibration error

After the DO auto-calibration, if the unit does not switch to the MEAS mode as it should, and the readout shows either Er3 or Er4, 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.

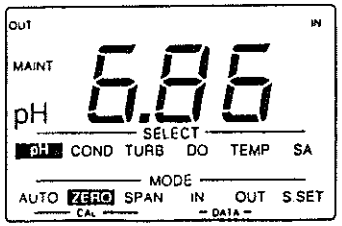
Operation

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.



2. Span calibration

Use either a pH4 or a pH9(10) standard solution for the span calibration.

Operation

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.

3. Press the ENT Key to complete the span calibration for pH.

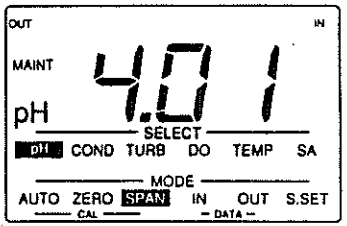


Table 2 pH values of standard solutions at various temperatures*

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

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

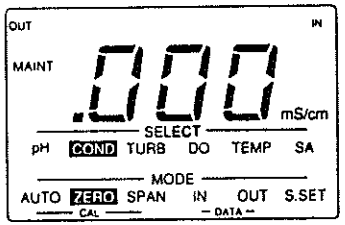
Wash the probe 2-3 times, using de-ionized or distilled water. Shake the probe to remove any water droplets from the COND sensor. Then allow it to dry by exposing it to fresh air.

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/ of de-ionized or distilled water.
3. Then weigh out 50 g of hexamethylenetetramine, and dissolve it in 400 m/ of de-ionized or distilled water.
4. Mix these two solutions, add enough de-ionized or distilled water to make 1,000 m/, 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/ of the 4,000-NTU solution into a 250-m/ 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/ 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.

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%.

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.

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.

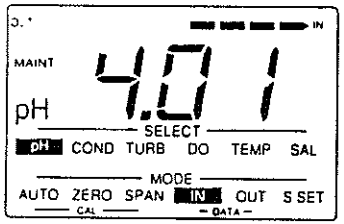
Storing data

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

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.

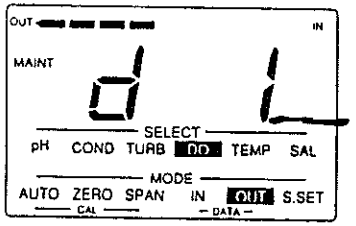
Recalling data

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.



▲ ▼

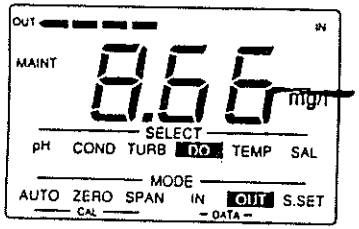
3. Use the UP/DOWN Keys to display the Data-Set No. of the values you wish to recall.

SELECT

4. Use the SELECT Key to move the upper cursor to the parameter you wish to view.

ENT

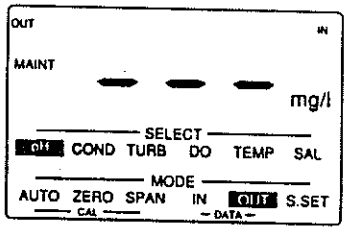
5. Press the ENT Key to display the data on the readout.



If a printer is connected, all six parameters in this

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

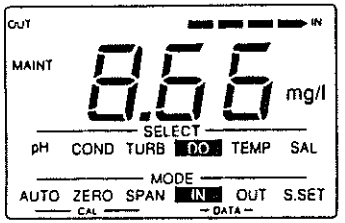
Set the U-10 as if you were going to input data:

MODE

1. Press the MODE Key to put the U-10 in the MAINT mode.

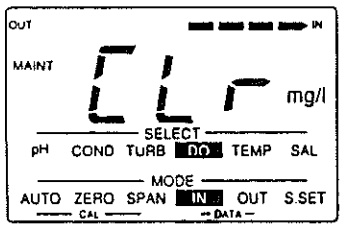
MODE

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.

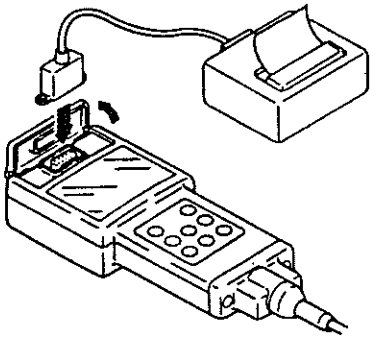


Be careful!
You cannot delete individual Data-Sets. The CLR Key always erases all data from memory.

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     3.8    ‰
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.

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

Error Code	Cause	Action
Span-calibration error		
E r 4	*DO Auto-calibration*	
	• Broken DO sensor membrane.	• Check DO sensor membrane. If defective, replace.
	• Excessive difference between DO sensor temperature and atmospheric temperature.	• Leave DO sensor in atmosphere for 30-60 min.
	DO aqueous solution calibration	
	• Broken DO sensor membrane.	• Check DO sensor membrane. If defective, replace.
	• Contaminated electrode.	• Clean the electrode using a soft brush, taking care not to scratch membrane.
	• Insufficient agitation of solution.	• Agitate solution thoroughly.
Memory full		
E r 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 r 6	• Jammed printer paper.	• Eliminate jamming of printer paper.
	• Poor cable connection .	• Replace the cable.
	• Wrong printer.	• Use proper parallel Centronics printer.
	• Defective printer.	• Replace the printer as necessary.

Normal probe maintenance

Washing the turbidity sensor

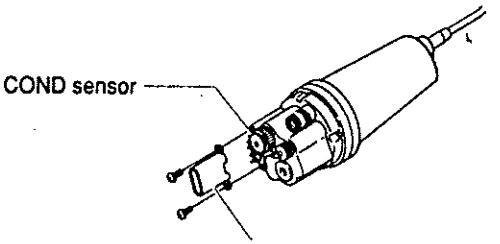
The sensor is a glass tube. Wash out the tube and remove stains carefully, using tap water and a test tube brush.

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.

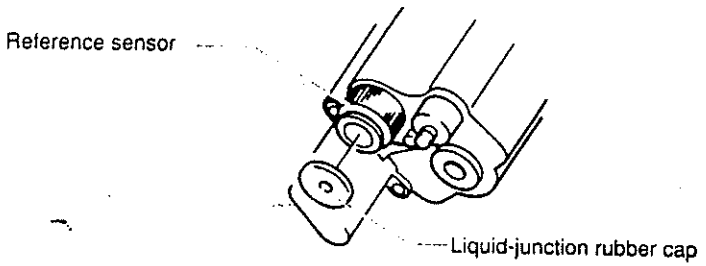
Be sure to replace the COND sensor guard before taking measurements.



Recharging the reference sensor with reference solution

Recharge the reference sensor with reference solution about once every two months, as follows.

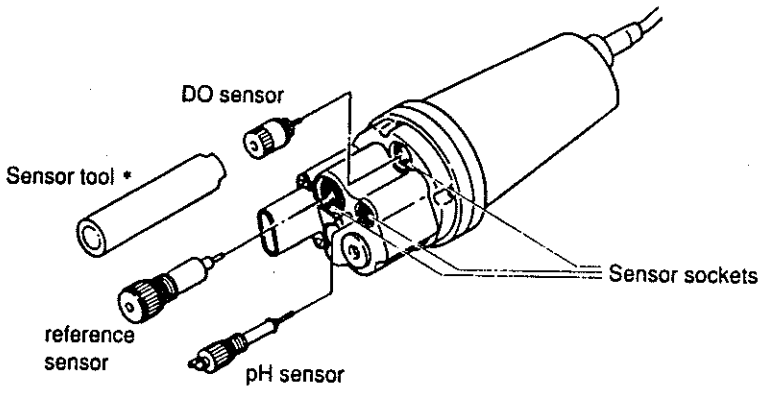
1. Remove the liquid-junction rubber cap from the reference sensor, and pour out the old solution.
2. Fill the reference sensor completely with new reference solution. Make sure there are no air bubbles.
3. Replace the liquid-junction rubber cap.
4. Carefully wash off all excess reference solution from 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.

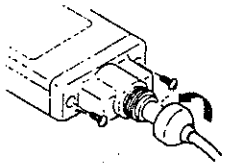


* When replacing the DO sensor, use the sensor tool provided as an accessory.

Replacing a faulty probe

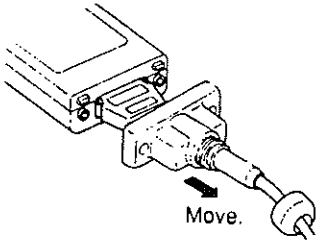
Disconnect the cable from the main unit

1. Loosen the cable gasket cap, and remove cap from gasket.



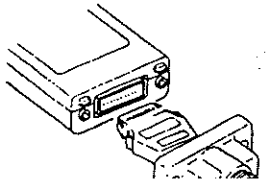
2. Slide back the gasket.

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.

Section 6

Reference Materials

The following descriptive information is provided for a better understanding of the U-10 Water Checker and its functions.

Conductivity (COND)

Principle of measurement

Conductivity is an index of the flow of electrical current in a substance.

Salts dissolved in water are separated into cations and anions. Such a solution is called an electrolytic solution. An electrolytic solution has the property of allowing the flow of current according to Ohm's law. This property is referred to *ionic conductivity*, since current flow is due to ion movement in an electrolytic solution. Metals, on the other hand, allow the flow of current by means of electrons. This property is called *electronic conductivity*, which is distinguished from ionic conductivity.

A cube 1 cm on each side, as each shown in **Fig. 1**, is used to demonstrate an electrolytic solution. Two electrode plates are placed on opposite sides, and the cube is filled with a solution. If the resistance between these two electrode plates represented by $r\,(\Omega)$, the conductivity of the solution L ($S.cm^{-1}$) is $L=1/r$. S stands for *Siemens*, a unit of measurement of conductance.

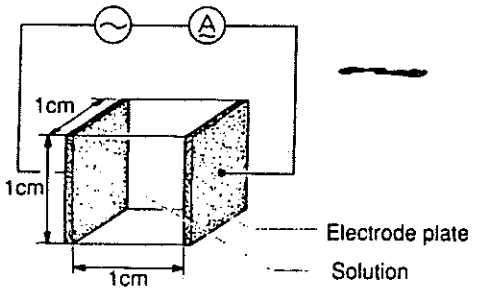


Fig. 1 Definition of conductivity

The most general method for measuring conductivity is based on the above principle, and is called the 2-electrode method. In this method, to take a measurement, it is necessary to allow flow of

If direct current is sent between them, it will cause electroplating or decomposition, i.e., polarization; this results in inaccurate measurement of conductivity.

Even a flow of alternating current will also cause a certain amount of polarization. Measures must be taken to minimize the effect of this polarization, such as the application of platinum black plating to the electrode surfaces. In spite of such measures, however, the effect of polarization cannot be neglected in conductivity measurements of a high-conductivity solution. This makes accurate measurement difficult. Furthermore, depositions or stains on the electrode surfaces can cause a large apparent resistance, also making accurate conductivity measurement difficult.

The U-10 Water Checker has adopted the 4-electrode method to overcome these disadvantages of the the 2-electrode method. As shown in **Fig. 2**, the U-10 Water Checker uses two voltage-detecting electrodes and two voltage-applying electrodes, for a total of total four electrodes.

The voltage-detecting electrodes are for detecting AC voltage, and the voltage-applying electrodes are for applying AC voltage.

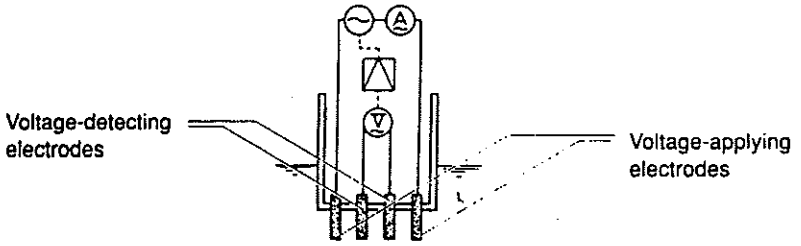


Fig. 2 Principle of the 4-electrode method

Let us assume that the current, *I(A)*, flows in a sample of conductivity *L*—under automatic control of the voltage-applying electrodes—so that the voltage at the voltage detecting-electrodes, *E(V)*, remains constant at all times. Then, the resistance of the sample, *R* (Ω), across the voltage-detecting electrodes is *R=E/I*. The resistance, *R*, of the sample is inversely proportional to its conductivity, *L*. That is, the conductivity, *L*, is proportional to the current, *I*. Accordingly, calibration of a standard solution of known conductivity, *Ls*, enables calculation of conductivity of a sample according to the formula *L=Ls(I/Is)* from the relation of *L:Ls=I:Is*.

Even in the 4-electrode method, polarization occurs, since *AC* current flows in the voltage-applying electrodes. The voltage-detecting electrodes are, however, free from the effects of polarization, since they are separated from the voltage-applying electrodes, and furthermore, current flow is negligible. Therefore, the 4-electrode method is an excellent method to enable measurement of conductivity covering a very high range.

Temperature compensation

In general, the conductivity of a solution varies largely with its temperature. The conductivity of a solution depends on ionic conductivity, described earlier. As the temperature rises, conductivity becomes higher, since ions begin to move more actively.

The temperature coefficient shows the change in % of conductivity per °C, with a certain temperature taken as the reference temperature. This is expressed in units of %/°C. The temperature coefficient assumes the premise that the conductivity of a sample changes linearly according to temperature. Strictly speaking, with actual samples, however, conductivity changes along a curve.

Furthermore, these curves form different shapes depending on the type of sample. In the ranges of smaller temperature changes, however, samples are said to have the temperature coefficient of 2%/°C; this holds for most samples, except in certain special cases. The U-10 Water Checker uses an automatic temperature conversion function to calculate conductivity at 25°C at a temperature coefficient of 2%/°C, based on the measured value of the temperature. Results are displayed on the readout. The U-10's temperature conversion function is based on the following formula.

$$L_{25}=L_t / [1+0.02(t-25)]$$

Where,

- L_{25}: Conductivity of solution converted to 25°C (value displayed on U-10)
- t: Temperature of solution at time of measurement (°C)
- L_t: Conductivity of solution at t (°C)

Turbidity (TURB)

Principle of measurement

From among several types of turbidity-measuring methods available, the U-10 uses the light-absorption-scattering method, shown in Fig. 3.
Irradiation of a beam of light onto a sample brings about separation of the beam into (1) the light transmitted by the solution and (2) the light scattered by turbidity components in the sample. In the light-absorption-scattering method, the intensity of both transmitted light and the scattered light are measured using separate receptors, and the turbidity is obtained based on the ratio of the two.

With the U-10, the light source is a pulse-lighting infrared-emission diode. The scattered light is measured at a point 30° offset from the light source. This light-absorption-scattering method has several advantages, including the fact that (1) the actual color of the sample fluid has little effect on the measurement of turbidity, (2) fluctuations in light quantity from the light source are easily compensated for, and (3) it allows the U-10 to be operated with relatively low-power consumption.

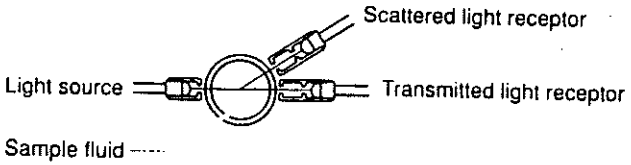


Fig. 3 Principle of the light-absorption-scattering method

NTUs (Nephelometric Turbidity Units)

For the calibration of turbidity, the U-10 uses a standard formazine solution.

Kaolin has been the conventional standard solution for many years. However, the composition of kaolin solutions often vary depending on the country of origin, and turbidity varies with the degree of purify. Furthermore, there is often individual error in preparing the solution. Kaolin is thus known for bringing about very large disparity in measurement results. As a turbidity standard solution, formazine standard solution is now increasingly being used internationally. In view of these facts, the U-10 uses the formazine standard solution for its calibration of turbidity.
In addition, the U-10 uses *NTUs* as the unit of turbidity. Other units conventionally used are formazine degrees and *FTUs*.
When the measurement of turbidity is based on the phenomenon of scattering, the use of *NTUs* is preferable, and in fact, these are being used increasingly. It should be noted that *NTUs* used as turbidity units of the formazine standard solution are equivalent to formazine degrees and to *FTUs*.

Salinity (SAL)

The U-10 is designed to measure salinity as well as the other parameters.

Note that the "salinity" referred to here is the salinity of sea water. There is a constant relation between conductivity and salinity at certain temperatures.

Therefore, if data on the conductivity and temperature are available, the corresponding salinity is known. In other words, the salinity measurement of the U-10 is based on the principle of calculating the salt content, making use of the measured values of conductivity and temperature.

Note carefully, therefore, that measured results of all substances whose conductivity is detected are displayed as salinity. For example, the measured result is displayed as NaCl concentration, even if in fact the sample component is, for example, hydrochloric acid (HCl).

Temperature

Temperature changes in water have extreme biological effects on the life cycles of fish and seaweed, as well as on that of the minute organisms that cleanse the water of organic pollutants. In general, as the temperature of water increases, the amount of oxygen dissolved in the water decreases and there is a tendency for the amount of pollutants to increase.

The U-10 uses a thermistor to measure temperature. A thermistor also measures the change in electrical resistance accompany changes in temperature; these changes in resistance are measured by the thermistor and are used to calculate the temperature.

This temperature data is used by the U-10 in four different ways: (1) in pH temperature compensation, (2) in conductivity temperature conversion, (3) in the calculation of salinity, and (4) in dissolved-oxygen temperature compensation.

Dissolved-Oxygen (DO)

Principle of measurement

The "DO" referred to here means the concentration of oxygen dissolved in water.

Fig. 4 shows the principle of measurement using a DO sensor.

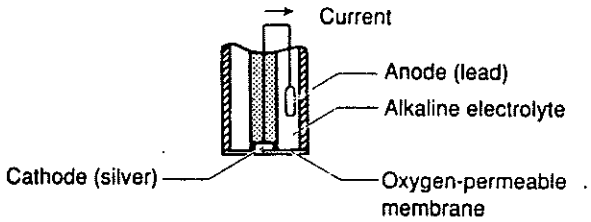


Fig. 4 Principle of DO sensor

A noble metal (silver) is fitted closely to an oxygen-permeable diaphragm to make the cathode; a base metal (lead) is used as the anode. Both are immersed in an alkaline electrolyte with the anode-to-cathode external circuit complete. Oxygen diffusing through the oxygen-permeable membrane causes a reduction reaction at the cathode; this allows flow of current in the external circuit:

$$O_2 + 2H_2O + 4e^- = 4OH^-$$

At the anode, oxidation reaction occurs as follows:

$$2Pb = 2Pb^{2+} + 4e^-$$

The current is proportional to the quantity of oxygen diffusing through the oxygen-permeable diaphragm. Accordingly, measurement of the current makes the DO in a sample known.

The DO measuring method based on this principle is called the *membrane-electrode method*. This method allows convenient measurement of DO, especially when compared with chemical-analysis methods, which need complicated pre-treatment to eliminate the effects of oxidizing or reducing substances.

DO correction for salinity

When a solution and air are in contact and in complete equilibrium (saturated), DO:C[mg/*l*] in the solution, and the oxygen partial-pressure:Ps[MPa] in air are in the following relation:

$$C = Ps/H$$

H [*MPa*/(mg/*l*)] is referred to as Henry's constant, which depends on the composition of the solution. In general, *C* becomes smaller as the salinity in the solution increases, since *H* becomes larger.

A DO sensor is intended to detect *Ps* in the above expression. Therefore, the DO measurement of an aqueous solution containing salt would be in error if the DO electrode were standardized either on air-saturated pure water or on air. To settle this problem, it is necessary to correct the DO reading based on the salinity of the sample.

Conventional DO meters make this salinity correction by inputting a known salinity value. This poses no problems if the salinity of the sample is known. In practice, however, the salinity of the sample is usually not known, unless measured by a device such as the U-10. Therefore, until now, DO meters have not been practical, even if they were provided with a salinity-correcting function.

The U-10 is capable of measuring the salinity of a sample and automatically correcting the DO reading for the amount salinity measured in the sample.

pH

Principle of measurement

The following is the basic equation for obtaining pH:

$$pH = -\log aH^+$$

Where,

aH^+ : the activity of hydrogen ions

If a thin glass membrane is used to separate two liquids of differing pH values, an electric current will be generated in proportion to the difference between these two pH values. The value of this electrical current, *E(V)* , is shown by the folowing Nernst equation:

$$E = 0.0001983T\,(pH_I - pH_0) + e$$

Where,

- **T :** the temperature of the liquids
- **pH_I :** the pH of the internal liquid (i.e., inside the glass membrane)
- **pH_0 :** the pH of the sample liquid (i.e., the iliquid outside the glass membrane)
- **e :** the assymetric potential

A conventional glass electrode for measuring pH contains a fluid inside the electrode with a pH of 7. If this is used to measure a sample that also has a pH value of 7, the assymetric potential will be close to 0V. Consequently, when a glass pH electrode is immersed in an acid solution, a positive electric current is generated; when it is immersed in an alkaline solution, a negative electric current is generated.

For actual use in a pH meter, a pair of reference electrodes with extremely stable characteristics is used. These are configured as shown in **Fig. 5**. As shown in **Fig. 5**, it can be seen that the electrical potentials generated in the internal electrodes, *E'* and *E"*, are canceled out by each other, so that the only electrical potential difference obtained is the

In pH meters a readout of this voltage between the two terminals is obtained by increasing it with an amplifier. In actual practice, the pH meter is first calibrated using a standard reference solution of known pH, then the pH of the sample liquid is measured.

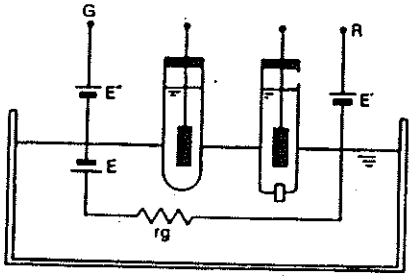


Fig. 5 Principle for Measuring pH

Specifications

pH

Principle	Glass electrode
Range	pH0-14
Resolution	Standard : 0.1pH
	Expanded : 0.01pH
Repeatability	±0.05pH
Temperature compensation	0°-50°C
Readout	LCD
Calibration	1-point auto (Zero)
	Manual 2-point

Temperature

Principle	Thermistor
Range	0°-50°C
Resolution	Standard : 1°C
	Expanded : 0.1°C
Repeatability	±0.3°C
Temperature compensation	—
Readout	LCD
Calibration	—

DO

Principle	Membrane galvanic cell
Range	0-19.9mg/*l*
Resolution	Standard : 0.1mg/*l*
	Expanded : 0.01mg/*l*
Repeatability	±0.1mg/*l*
Temperature compensation	0°-40°C
Readout	LCD
Calibration	1-point auto (Span)
	Manual 2-point

Conductivity

Principle	4-electrode
Range	0-100ms/cm
Resolution	Standard: 0-1mS/cm : 0.01mS/cm 0-10mS/cm : 0.1mS/cm 10-100mS/cm : 1mS/cm Expanded: 0-1mS/cm : 0.01mS/cm 0-10mS/cm : 0.1mS/cm 10-100mS/cm : 1mS/cm
Repeatability	±1%/F.S. within each measurement range
Temperature compensation	0°-50°C
Readout	LCD
Calibration	1-point auto (Span) Manual 2-point

Turbidity

Principle	Scattered/Transmitted light
Range	0-800 NTU
Resolution	Standard : 10 NTU Expanded : 1 NTU
Repeatability	±3%/F.S.
Temperature compensation	—
Readout	LCD
Calibration	1-point auto (Zero) Manual 2-point

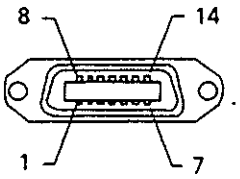
Salinity

Principle	Conversion based on conductivity
Range	0-4%
Resolution	Standard : 0.1% Expanded : 0.01%
Repeatability	±0.1%
Temperature compensation	0°-30°C
Readout	LCD

Common specification

Data storage	Max. 20 samples
Printer output	Centronics specs.
Power	Battery 9V, with auto power-off function
Operating temperature	0° - 45°C
Weight	Main unit: Approx. 400g Probe, with 2-m cable: Approx. 800g

- Output connector pin layout



Pin No.	Name	Pin No.	Name
1	STB	8	DB_6
2	DB_0	9	DB_7
3	DB_1	10	Not used
4	DB_2	11	BUSY
5	DB_3	12	Not used
6	DB_4	13	Not used
7	DB_5	14	GND

This equipment is in conformity with the following directive (s) and standard (s);

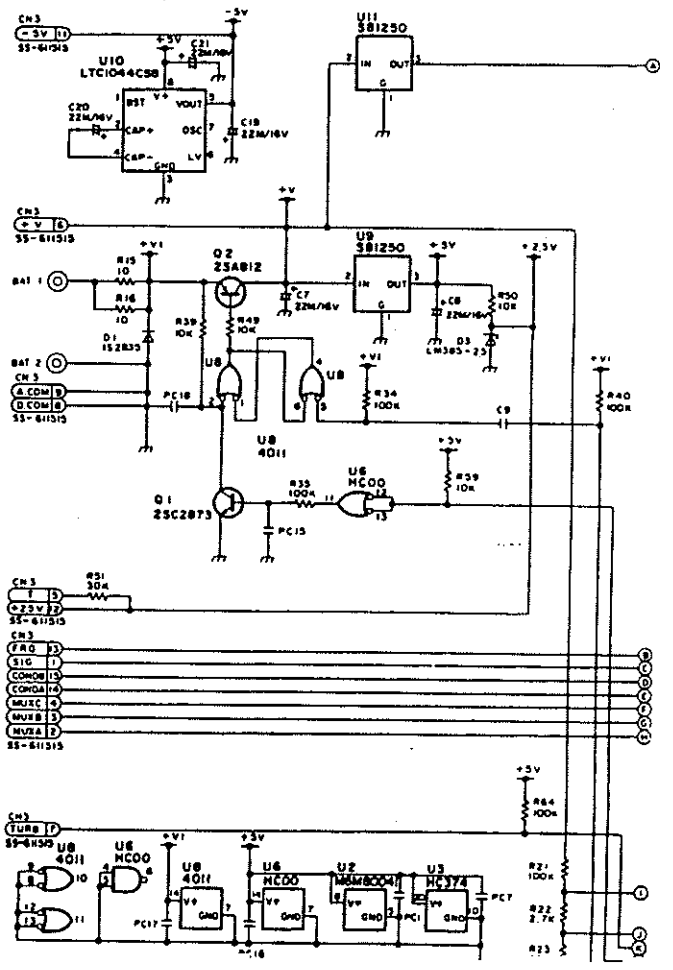
Directive (s) the EMC Directive 89/336/EEC as amended by 91/263/EEC, 92/31/EEC and 93/68/EEC, in accordance with the Article 10 (1) of the Directive

Parts List

The following expendable parts are available for the U-10 Water Checker.

Part name	Model No.	P / N
Probe		9037-0047-00
pH sensor	#7112	9037-0048-00
DO sensor	#7542	9037-0049-00
pH reference sensor		9037-0050-00
Liquid junction (1 pair)	#7210	9037-0051-00
Reference solution	#330	9037-0052-00
pH standard solution pH2	100-2	9003-0015-00
pH standard solution pH4	100-4	9003-0016-00
pH standard solution pH7	100-7	9003-0017-00
pH standard solution pH9	100-9	9003-0018-00
Calibration beaker		9037-0053-00

Circuit Diagram



U-10: ALTERNATIVE MANUAL TURBIDITY CALIBRATION INSTRUCTIONS

As with most analytical techniques, the turbidity span should be calibrated at a concentration close to the turbidity value of the sample to be measured.

In cases where high turbidity is anticipated, such as water run off from mines or cement kilns, a span calibration standard of 400-800 NTU should be utilized. In cases where low turbidity is anticipated, such as samples from lakes, rivers, ponds, streams or oceans, a span calibration standard in the range of 25 to 100 NTU is more appropriate. Below please find instructions on how to prepare 200, 100 & 25 NTU turbidity span calibration standards.

The instruction manual explains how to prepare an 800 NTU span calibration standard (see page 30) from hydrazine sulfate and hexamethylenetetramine.

* To prepare a 200 NTU standard solution:

Pour 50 ml of 800 NTU span calibration solution into a 200 ml volumetric flask. Add distilled or deionized water up to the fill line on the volumetric flask. Mix thoroughly by turning the flask upside down 5-6 times. Pour into plastic calibration beaker (provided) up to the top of the black fill line. Proceed with span calibration as shown on page 31 of U-10 instruction manual.

* To prepare a 100 NTU standard solution:

Pour 25 ml of 800 NTU span calibration solution into a 200 ml volumetric flask. Add distilled or deionized water up to the fill line on the volumetric flask. Mix thoroughly by turning the flask upside down 5-6 times. Pour into plastic calibration beaker (provided) up to the top of the black fill line. Proceed with span calibration.

* To prepare a 25 NTU standard solution:

Pour 50 ml of the 100 NTU span calibration solution into a 200 ml volumetric flask. Add distilled or deionized water up to the fill line on the volumetric flask. Mix thoroughly by turning the flask upside down 5-6 times. Pour into plastic calibration beaker (provided) up to the top of the black fill line. Proceed with span calibration.

Recommended plastic or glassware: 50 ml graduated cylinder, 25 ml graduated cylinder, 200 ml volumetric flask(s).

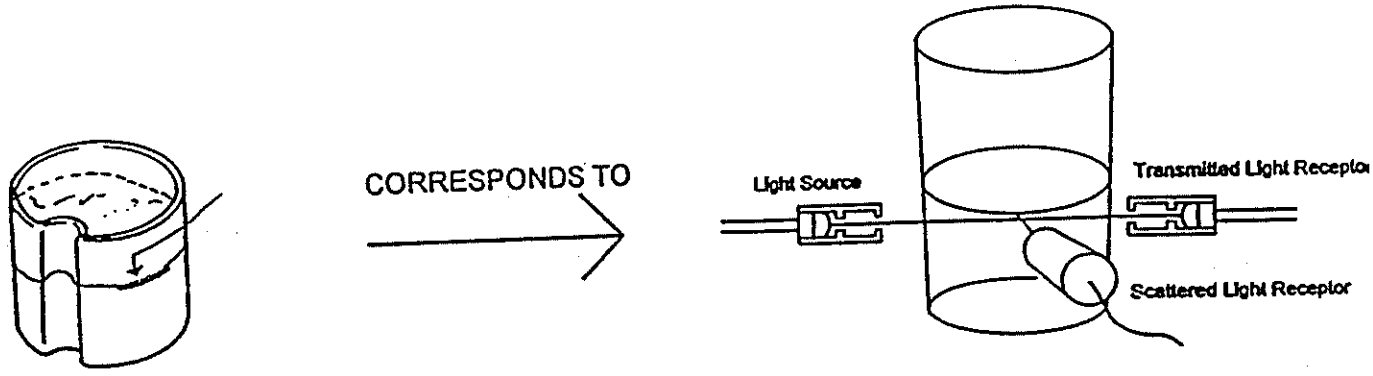
This procedure of choosing a turbidity span calibration standard which has a similar concentration to that of actual water samples leads to improved accuracy of turbidity measurements made in the lower turbidity ranges.

Optimizing The Accuracy Of Turbidity Measurements In The U-10 Water Quality Checker

The accuracy of any measurement by the U-10 turbidity sensor is affected by the calibration. Calibration and measurement are both affected by the height of the solution in the nephelometer tube.

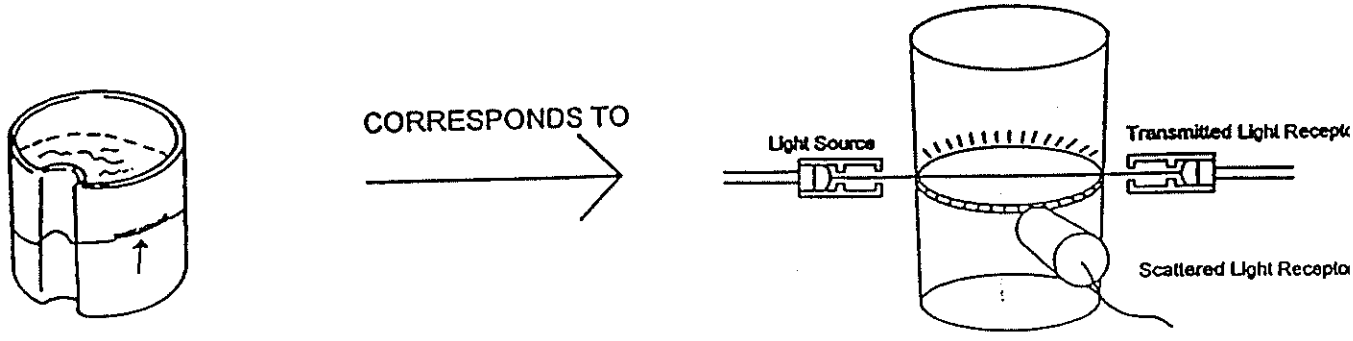
When calibrating, it is crucial that the solution be poured into the special beaker up to the top of the black fill line. This ensures that the surface of water inside the cylindrical turbidity sensor lies above the level of its light source and detectors (See Figure 1).

FIGURE 1



If the standard is filled only to the bottom of the black fill line on the beaker (or below), then there is a high probability that much stray light will be diffracted along the surface of the water by the meniscus. This will cause an altered scattered/transmitted light receptor ratio, and thus a completely different (and incorrect) NTU readout value (See Figure 2).

FIGURE 2



If this occurs during autocal, then subsequent samples are likely to read very low (we have seen examples of readings of -10 NTU). If it occurs during measurement, the measured values are likely to be very high.

So please: while pouring your calibration solutions, pour up to the top of the black fill line. While measuring samples be sure the sensor head is fully immersed.

PRICE LIST
PRODUCTS FOR THE HORIBA U-10

Calitech™ AutoCal and **LevelTwo** Solutions

The AutoCal and **LevelTwo** Solutions are formulated to provide single solutions which provides calibrating standards for pH, Conductivity and Turbidity each in a single solution. AutoCal is used for the auto calibration mode and **LevelTwo** is used for manual two point calibration together with AutoCal..

These levels are:

Parameter	AutoCal	LevelTwo
pH	4.000±0.002 @ 25°C*	6.860±0.002 @ 25°C*
Conductivity	4.49 mSiemens* ±1.0% @ 25°C*	53.7 mSiemens ±1.0% @ 25°C*
Turbidity	0.0 NTU†	Various - see chart below

* Referenced to NIST SRMs. † Referenced to freshly prepared formazin per EPA 180.1.

These solutions are formulated with the finest ingredients including EPA registered broad-spectrum anti-microbial to assure long-life, free of mold and bacterial growth. This solution has no color in order to properly calibrate the turbidity sensor.

Description	Cat. No. Size Price	Cat. No. Size Price	Cat. No. Size Price	Cat. No. Size Price	Cat. No. Size Price
AutoCal Solution Packed in 500 mL, 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-AC00-2 500mL $12.00	2-AC00-3 1 Liter $18.00	2-AC00-4 4 Liters $30.00	2-AC00-8 20 Liters $55.00	2-AC00-P 175 mL(3) $12.00
LevelTwo Solution - Turbidity at 10 NTU Packed in 500 mL 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-LT10-2 500mL $49.00	2-LT10-3 1 Liters $73.00	2-LT10-4 4 Liters $190.00	N/A N/A N/A	2-LT10-P 175 mL(3) $49.00
LevelTwo Solution - Turbidity at 40 NTU Packed in 500 mL 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-LT40-2 500mL $49.00	2-LT40-3 1 Liters $73.00	2-LT40-4 4 Liters $190.00	N/A N/A N/A	2-LT40-P 175 mL(3) $49.00
LevelTwo Solution - Turbidity at 100 NTU Packed in 500 mL 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-LT1C-2 500mL $49.00	2-LT1C-3 1 Liters $73.00	2-LT1C-4 4 Liters $190.00	N/A N/A N/A	2-LT1C-P 175 mL(3) $49.00
LevelTwo Solution - Turbidity at 400 NTU Packed in 500 mL 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-LT4C-2 500mL $49.00	2-LT4C-3 1 Liters $73.00	2-LT4C-4 4 Liters $190.00	N/A N/A N/A	2-LT4C-P 175 mL(3) $49.00
LevelTwo Solution - Turbidity at 800 NTU Packed in 500 mL 1 & 4 Liter Bottles, 20 Liter Cubes and 175mL Pouches-3/Pack	2-LT8C-2 500mL $49.00	2-LT8C-3 1 Liters $73.00	2-LT8C-8 4 Liters $190.00	N/A N/A N/A	2-LT8C-P 175 mL(3) $49.00

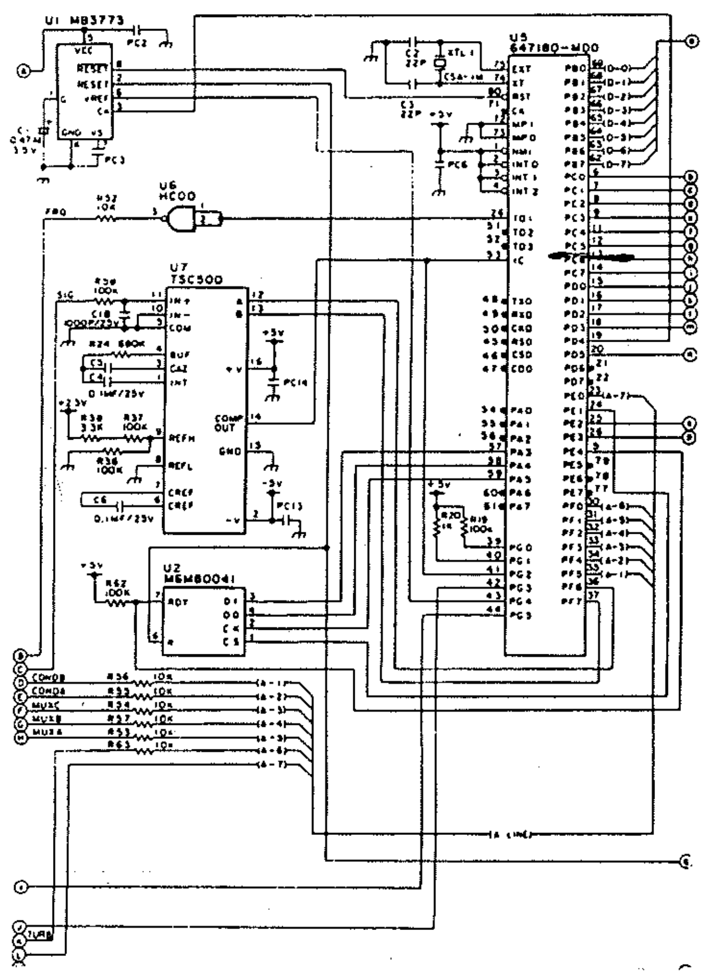
Calitech™ U-10 Specialties and Services

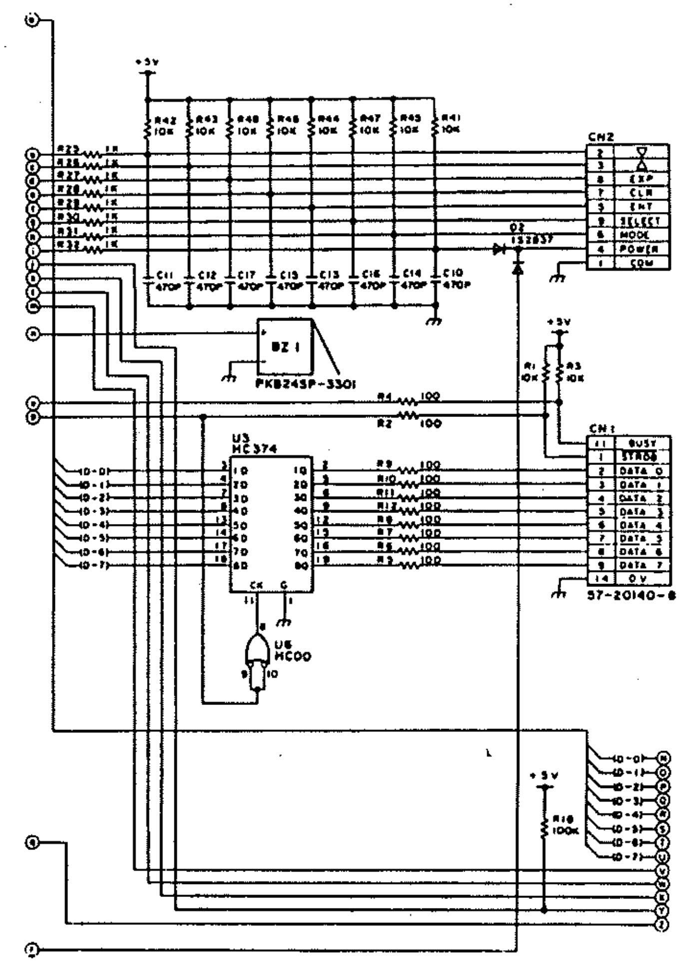
Specialties and Services are provided to enhance the calibration and maintenance of your U-10 tester.

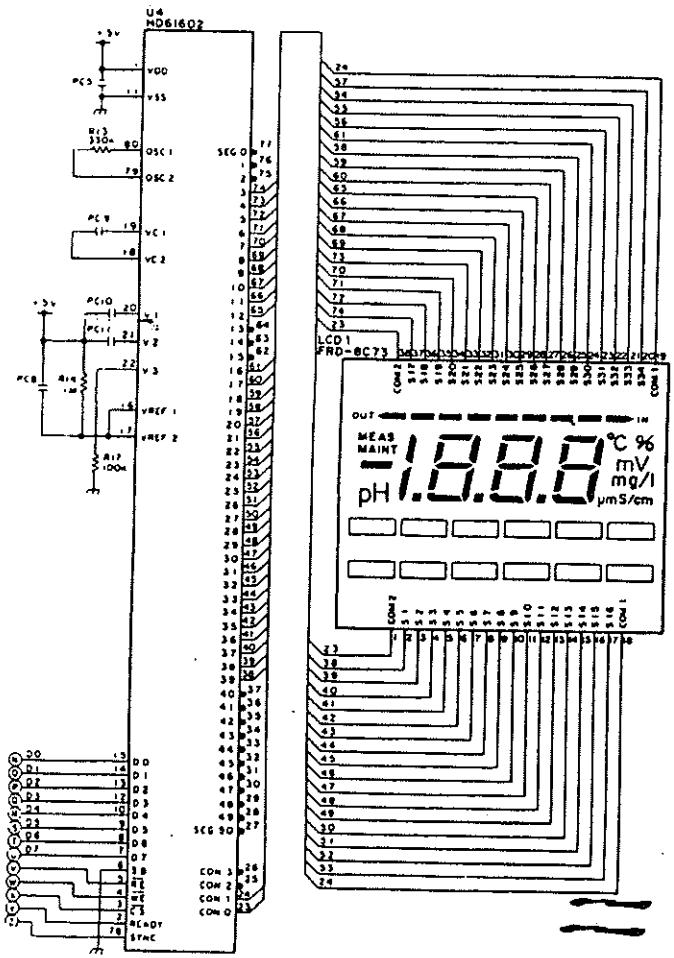
Description	Cat. No.	Price
Oxygen Probe Reconditioning Service includes cleaning, membrane replacement, electrical testing with zero and span testing.	2-510	$90.00
Tonometer to prepare oxygen standards in water or other liquids.	2-550	$350.00
Zero oxygen standard 175 mL/Pouch, 3 Pouches/Pack	2-500-P	$12.00
U-10 Startup Pack: 2 pouches AutoCal & 1 pouch **LevelTwo**	2-ACSU	$25.00

In addition, *Calitech*™ pH Calibrating Buffers. Conductivity Standards, and Turbidity Standards are available in a full range of levels for each parameter. Brochure and prices are available on request. Prices effective May 1, 1997, subject to change without notice and are quoted in U.S. Dollars.

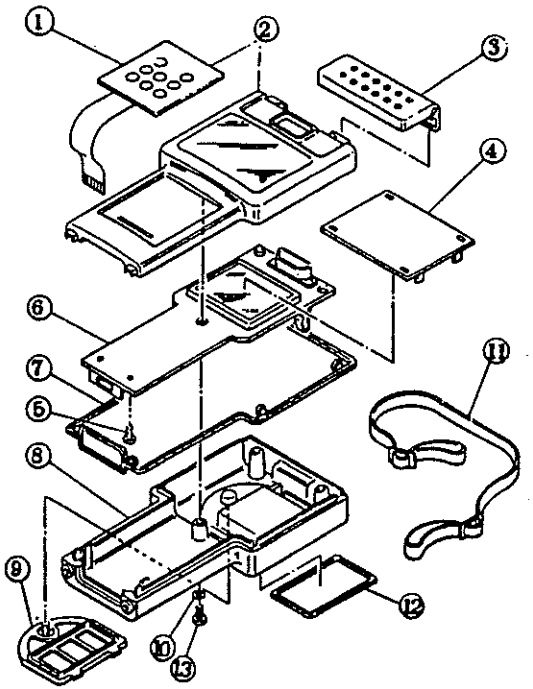
Manufactured by: Compliance Technology Inc. 118 Starlite Street South San Francisco, CA 94080
Telephone: (415) 615-9100 | (800) 492-4046 | Facsimile: (415) 615-0110


U1 MB3773
U6 HC00
U7 TSC500
U2 M6M80041
U5 647180-M00


CN2
CN1
BZ1
PKB24SP-3301
U3 HC374
U6 HC00
57-20140-8

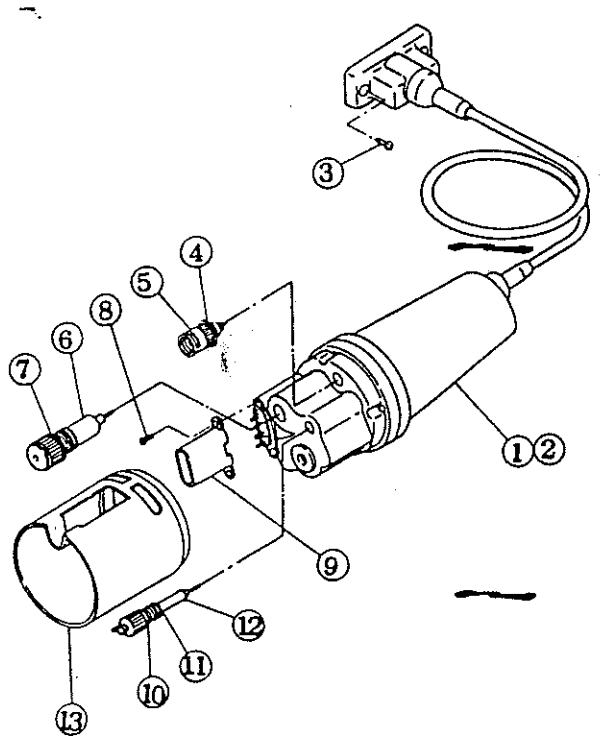


Exploded Views—main unit



NO.	PARTS NO.	PARTS NAME	DESCRIPTION
1	H357911-01	SHEET SWITCH	WATER CHECKER U-10
2	U800842300	CASE ASSY, TOP	U-10 including ①
3	H357944-01	PRT COVER	U-10 METER
4	H542233-01	WINDOW, LCD	U-10 H357887-01
5	F020527500	TAPPING SCREWS	M3X6 (S-ZN3)
6	U800842400	PCB ASSY	U-10
7	H357945-01	CASE PACKING	U-10 METER
8	U800842500	CASE ASSY, BOT	U-10
9	U800842600	COVER ASSY, BAT	U-10
10	H543958-01	SEAR WASHER	U-10 METER
11	H544105-01	METER STRAP	

Exploded Views—prove

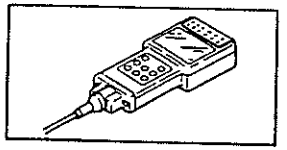


NO.	PARTS NO.	PARTS NAME	DESCRIPTION
3	F020911500	SCREW, PANHEAD	JISB1111 M3×6 (S-ZN3)
4	F020518700	O-RING	NOK S 11.2 (SI)
5	9037004900	DO SENSOR	
6	9037005000	REFERENCE	
7	F020246900	O-RING, S18	NOK S18 FPM
8	F020009500	SCREW, PANHEAD	M3-6L SUS304
9	H542141-01	COND GUARD	
10	F020058000	O-RING, P8	

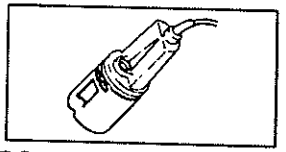
Unpacking the U-10

The following items are included with your U-10 Water Quality Checker.
When you unpack the probe and main unit, confirm that all the other accessories are included as well.

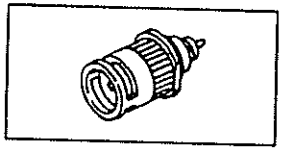
- Main unit



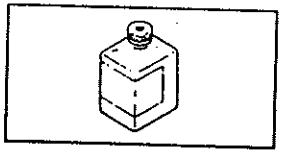
- Probe



- DO sensor

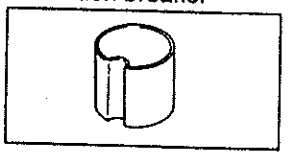


- Standard solution (pH 4 standard solution, 100-4) 500 m*l* bottle

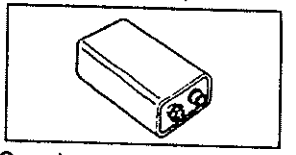


- Reference solution 250m*l* bottle

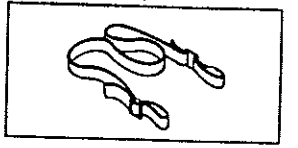
- Calibration breaker



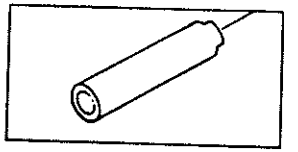
- 9V battery (6F22)



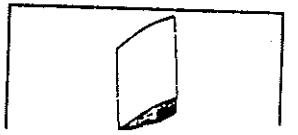
- Carrying strap for main unit



- DO sensor tool

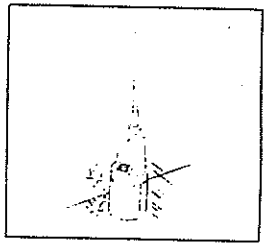


- This Instruction Manual

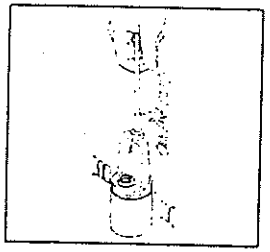


Precautions when using the U-10

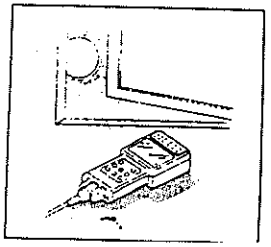
The U-10 Water Quality Checker is carefully designed for trouble-free operation. However, it is a sophisticated electronic instrument, and it can be damaged if used carelessly. Please read the following precautions and observe them when using your U-10 Water Checker.



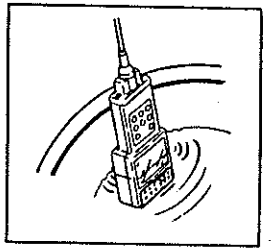
- Do not swing or jerk the probe by its cable.
- Do not subject the cable connector to stress by pulling or stretching it.



- Do not drop either the U-10 probe or main unit. Never subject either component to sudden impact.

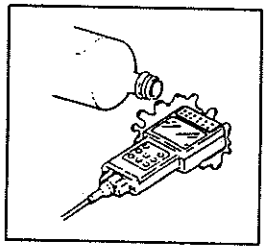


- Do not store the U-10 where it may be exposed to prolonged direct sunlight. Never leave the U-10 inside a vehicle with the windows closed.



- Never immerse the main unit directly in water.

  The main unit is water-resistant and may be safely used in the rain; however, it is not of waterproof construction. Immersing the main unit in water or any other liquid can damage the internal electronic circuits



- Never allow any organic solvent to come in contact with either the probe or the main unit. This includes such organic solvents as methylethyl ketone (MEK) and acetone.

  (The probe is made of polyphenylene ether (PPE); the main unit case is acrylic resin.)

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- CALIBRATION AND MAINTENANCE OF PORTABLE FIELD pH/Eh METER

Applicability: GENERAL Revision No.: ___ Date: _____

Prepared By: THF Date: _____ Approved By: KLB Date: _____

1.0 INTRODUCTION

This guideline presents a method for calibration of a portable pH/Eh meter. The pH/Eh meter measures and provides a log scale reading of the hydrogen ion concentration of a water sample (pH function) or of the oxidation/reduction potential of a water sample (Eh function). In order to ensure an accurate reading, the pH/Eh meter must be calibrated prior to use in the field.

2.0 ACCURACY

The calibrated accuracy of the pH/Eh meter will be:

pH - 0.1 pH unit, over the temperature range of -2°C to 40°C.

Eh - -1 to +1 millivolts over the range of -700 to +700 millivolts.

3.0 CALIBRATION

Calibrate all field test equipment at the beginning of each sampling day and check and recalibrate according to the manufacturer's specifications. Calibrate the pH/Eh meter by immersing the sensing probe in a container of certified pH buffer solution traceable to the National Bureau of Standards, and compare the meter reading to the known value of the buffer solution, which is stirred. If the reading obtained by the meter does not agree with the known value of the buffer solution, adjust the "standardize" control until the desired reading is obtained. In addition,

5.0 DATA VALIDATION

Document all instrument calibrations in the field notebook, indicating the meter readings before and after the meter has been adjusted. Also document the pH buffers used to calibrate the meter. This is important, not only for data validation, but also to establish maintenance schedules and component replacement.

APPENDIX C

Low-Flow Sampling Methodology

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 (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

Cohen, R.M. and J.W. Mercer, 1993, DNAPL Site Evaluation, C.K. Smoley Press, Boca Raton, Florida.

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United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/S-95/504 April 1996

EPA Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls[1] and Michael J. Barcelona[2]

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing units were identified and sampled in keeping with that objective. These were highly productive aquifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic *units.* With time it became apparent that conventional water supply generalizations of *homogeneity* did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

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Director

chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aquifer heterogeneity and colloidal transport. Aquifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry, hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third *phase* as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria. These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling

objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

1) Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;

2) Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and

3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term *representativeness* applies to chemical and hydrogeologic data collected via wells, borings, piezometers, geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

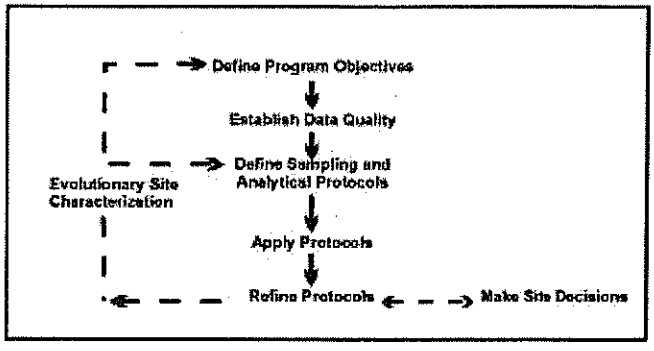

Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

1) Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-

flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the *mobile* load of contaminants present (dissolved and colloid-associated);
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water;
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- higher initial capital costs,
- greater set-up time in the field,
- need to transport additional equipment to and from the site,
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a *change in conditions* and trigger an *action.*

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). High-quality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and *fresh* screen waters during insertion of the sampling device or ground-water level measurement device; disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g. , pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- maximize tubing wall thickness, minimize tubing length;
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are ill-suited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a *fix* for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally *dissolved* [i.e., samples filtered with 0.45 µm filters]) concentrations of major ions and trace metals, 0.1 µm filters are recommended although 0.45 µm filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO_2 composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and non-disposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality

indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon™ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C.

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

(1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.

(2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.

(3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of

the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

   a. "portable or non-dedicated mode" - Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.

   b. "dedicated mode" - Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

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VIII. References

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Figure 2. **Ground Water Sampling Log**

Project _____ **Site** _____ **Well No.** _____ **Date** _____

Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____

Sampling Device _____ **Tubing type** _____ **Water Level** _____

Measuring Point _____ **Other Infor** _____

Sampling Personnel _____

Time	pH	Temp	Cond.	Dis.O_2	Turb.	[ ]Conc			Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project _____ **Site** _____ **Well No.** _____ **Date** _____
Well Depth _____ **Screen Length** _____ **Well Diameter** _____ **Casing Type** _____
Sampling Device _____ **Tubing type** _____ **Water Level** _____
Measuring Point _____ **Other Infor** _____

Sampling Personnel _____

Time	Pump Rate	Turbidity	Alkalinity	[ ] Conc	Notes

Type of Samples Collected

_____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

APPENDIX D

Laboratory SOPs

SOUTHWEST LABORATORY OF OKLAHOMA, INC. and
AMERICAN ANALYTICAL & TECHNICAL SERVICES, INC.

Standard Operating Procedure

Extraction and Analysis of TEPHs by GC, SW-846, Modified Method 8015B

Document No.: SWL-OP-416

Rev No. / Date: Rev. 4.1 — 06/22/99

OFFICIAL COPY RED STAMP INDICATES ORIGINAL

APPROVALS	DATES
Procedure Prepared By	6-22-99 Date
Program Manager or Section Supervisor	7-7-99 Date
Laboratory Safety Officer	7/8/99 Date
Laboratory QA/QC Officer	7/8/99 Date

(Effective Date is 5 calendar days after the last signature above - QA/QC Officer)

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[✓] Official Copy OC No.: 2441 Issued to: Daria Navon Date: 12/19/00 QA: CFH

EXTRACTION AND ANALYSIS OF TEPH'S BY GC, SW-846, MODIFIED METHOD 8015B

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to determine the concentrations of total extractable petroleum hydrocarbons in extracts from solid and liquid matrices. The method is based on EPA SW-846 methods 8000B and 8015B for analysis and methods 3500B, 3510C, 3550B, and 3580A for extraction. The method can be used to determine extractable fuel concentrations in the mid parts-per-million range in water and soil matrices. Test codes encompassed by this method include but are not limited to GC300, GC320, GC330, GC340 and GC399.

1.2 Tables 1, 2, 3, and 4 represent the compounds that may be analyzed by this method.

Table 1
Target Compound List (GC300)

ANALYTE
Gasoline
Naphtha
Kerosene
JP-4
Diesel #2
Fuel Oil #6

Table 2
Target Compound List (GC320 and GC330)

ANALYTE
Naphtha
Kerosene
JP-4
Diesel #2
Fuel Oil #6

Table 3
Target Compound List (GC340)

ANALYTE
DRH (C10-C28)

TABLE 4
Extended Target Compound List

ANALYTE
Mineral Spirits
Standard Solvent
Fuel Oil #2
JP-5
SAE 10W

1.3 This method utilizes wide bore capillary columns (0.53 mm ID) or narrow bore capillary (0.32 mm ID) columns.

1.4 See the Redbook for most current quantitation limits (QLs).

2.0 METHOD SUMMARY

2.1 Separatory funnel extraction is employed for the extraction of aqueous samples. Sonication extraction or Shaking (California method) is required for soil/sediment samples. Both neat and diluted organic liquids may be analyzed by direct injection (Method 3580A, Waste Dilution).

2.2 Columns are calibrated using the external calibration procedure with 5 concentrations of the analytes covering the working linear range of the FID detectors beginning from the level of quantitation or below. Calibration criteria specified in method 8000B are followed (unless otherwise specified).

2.3 Calibration verification standards are analyzed each 12-hour shift and before the start of an analysis sequence so that they bracket the samples.

2.4 A method blank, laboratory control spike, and a matrix spike/matrix spike duplicate must be prepared for all batches of 20 samples or less.

3.0 HEALTH AND SAFETY

3.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in chemical analysis.

3.2 Caution should be taken when working with all sample extracts and calibration standards. Samples are of unknown origin and should be considered hazardous. Many of the spiking solutions used, along with chlorinated solvents, are considered carcinogens. Concentrated acids and bases, if not handled properly, can cause severe burns.

3.3 Gloves should be used for the manipulation of all sample extracts and calibration standards and during the preparation of all acid and base solutions. Wear personal protective equipment (PPE) and goggles or face shield when warranted. See the standard operating procedure for "*Laboratory Safety Plan*", SWL-GA-111 for detailed safety procedures.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

4.1 Sample Extraction

4.1.1 See Section 15.0 for specific state holding time requirements. When holding times are not specified aqueous and solid samples must be extracted within 14 days of collection.

4.1.2 Extracts must be stored under refrigeration at 4°C (±2°C) and analyzed within 40 days of extraction.

4.2 Sample Storage

4.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery to the client of a complete, reconciled sample data package. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

4.2.2 The sample must be stored in an atmosphere demonstrated to be free of all potential contaminants.

4.2.3 Samples, sample extracts, and standards must be stored separately.

4.3 Sample Extract Storage

4.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery to the client of a complete data package.

4.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

4.3.3 Samples, sample extracts, and standards must be stored separately.

4.4 All containers should be glass jars or bottles with Teflon lids. A minimum of one liter is required for aqueous samples. A minimum of 100 g is required for soil samples (125-mL glass jar).

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

5.1 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of co-eluting compounds in the sample matrix; the FID is a non-selective detector, hence there is a potential for many interfering non-target compounds. Knowledge of good laboratory practices is assumed, including steps to be followed in routine testing and cleanup of solvents, reagents and sample processing hardware/glassware, and instrument maintenance.

5.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with all plastic materials and checking all solvents and reagents for phthalate contamination.

6.0 EQUIPMENT/APPARATUS

6.1 Separatory funnel - 2 liter, with Teflon stopcock.

6.2 Glass funnel with sodium sulfate.

6.3 Apparatus for grinding dry waste samples.

6.4 Ultrasonic preparation - A horn type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

6.4.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturer's instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

6.4.2 Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

6.5 Sonabox or equivalent- Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

6.6 Horizontal shaker – Eberbach Tabletop shaker, or equivalent.

6.7 Apparatus for determining percent dry weight:

6.7.1 Oven - Drying.

6.7.2 Desiccator.

6.7.3 Crucibles - Porcelain or disposable aluminum.

6.8 Pasteur glass pipettes - 1 mL, disposable.

6.9 Beakers - 400 mL.

6.10 Vacuum or pressure filtration apparatus.

6.10.1 Buchner funnel.

6.10.2 Filter paper - S&S #595 (size 18.5 cm) or equivalent.

6.11 Kuderna-Danish (K-D) apparatus.

6.11.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

6.11.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs or clips.

6.11.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

6.11.4 Springs – ½ inch (Kontes K-662750 or equivalent).

6.12 Solvent vapor recovery system (Kontes K-545000-1006 or K547300-0000, Ace Glass 6614-30, or equivalent).

6.13 Boiling chips - Solvent extracted and oven baked; approximately 10/40 mesh (silicon carbide or equivalent).

6.14 Water bath - Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

6.15 Balance - Top loading, capable of accurately weighing to the nearest 0.01 g to 100g.

6.16 Vials - Glass, 2-mL capacity with Teflon lined screw caps or crimp tops.

6.17 Glass scintillation vials - 20 mL, with aluminum lined screw caps.

6.18 Syringe - 1.0, 2.5, and 10.0 mL.

6.19 Micro pipettor – Drummond, various sizes.

6.20 Micro Syringes – 10 µL and larger.

6.21 Graduated cylinder - 1 liter.

6.22 Spatula - Stainless steel or Teflon.

6.23 Glass funnel.

6.24 Erlenmeyer flask – 250 mL

6.25 Automated 8-place Glascol shaker or equivalent.

6.26 Turbovap extract concentrator.

6.27 Test tube rack.

6.28 Pyrex glass wool.

6.29 Volumetric flasks, Class A – various sizes.

6.30 VOA vials – 40-mL with Teflon septa.

6.31 Gas chromatograph — Analytical system complete with gas chromatograph suitable for on-column, direct, and split-splitless injection and all required accessories including syringes, analytical columns, gases, flame ionization detector, and recorder/integrator or data system.

6.31.1 HP 5890 Gas Chromatograph with FID detector(s) and a 7673 autosampler. The autosampler must be capable of 2 µL to 5 µL injections. The carrier gas should be ultra pure helium or hydrogen, and the makeup gas (detector gas) should be ultra pure nitrogen.

6.31.2 Wide-bore columns:

6.31.2.1 Column 1 — 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 5 percent phenyl methylpolysiloxane (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

6.31.2.2 Wide-bore columns should be installed with deactivated liners designed specifically for use with these columns.

6.31.3 Narrow-bore columns (optional):

6.31.3.1 Column 1 — 30m x 0.32 mm ID fused silica capillary column (DB-5, RTX-5, etc.), 0.25, 0.5, or 1.0 µm film thickness.

6.31.3.2 All columns should be equipped with megabore (0.53 mm) deactivated guard columns.

7.0 REAGENTS

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

7.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water.

7.3 Solvents and reagents as appropriate for Method 3510C and 3550B: methylene chloride. All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free.

7.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by pre-cleaning the Na_2SO_4 with methylene chloride. If the Na_2SO_4 is cleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the Na_2SO_4.

7.5 All gases (i.e., carrier, auxiliary, etc.) should be at least high purity grade.

7.6 Gasoline (Restek 30096), Naphtha (Supelco 4-8265), JP-4 (Restek 31219), Mineral Spirits (Restek 31225), Kerosene (Restek 31256), Diesel (Restek 31258), Fuel #6 (Restek 31248), p-terphenyl (Aldrich 25,738-9).

7.7 Standards preparation:

Prepare individual stock standard solutions in methylene chloride every six months, or sooner, if the solution has degraded or concentrated. Assign log numbers to each of the solutions and log them into the Standards Log Book; see Standard Operating Procedure for "Standards Receipt, Traceability, and Preparation", SWL-OP-202.

7.7.1 Stock Standard Solutions

7.7.1.1 Concentrated and certified standard mixtures can be obtained from several sources. For example, Restek and Supelco supply the fuel mixtures. It is recommended that these be used for traceability purposes. Stock standard solutions can then be diluted directly from the concentrates.

7.7.1.2 The surrogate standard p-terphenyl is added to all standards, samples and blanks.

7.7.1.3 Stock standard solutions must be kept refrigerated at 4°C (±2°C) for no longer than 6 months.

7.7.2 Calibration Standards - A minimum of five calibration standards for each parameter of interest should be prepared through dilution of the highest level standard with methylene chloride. One of the concentrations should be at or below the PQL. The remaining concentrations should bracket the expected range of concentrations found in real samples or should define the working range of the GC/FID.

7.7.2.1 Calibration standards must be remade at least every six months, or verified against new standards before use.

TABLE 5
Calibration Standards — Low Point Concentration ug/mL

Fuel Mixtures – Low Point Concentration ug/mL	
Gasoline	20
Kerosene	20
Naphtha	20
JP-4	20
Diesel #2	20
Fuel Oil #6	100

TABLE 6
GC320 and GC330 Mixture — Low Point Concentration ug/mL

GC320 & GC330 Mixture – Low Point Concentration ug/mL	
Kerosene	20
Naphtha	20
JP-4	20
Diesel #2	20
Fuel Oil #6	100

TABLE 7
Extended List Mixture — Low Point Concentration ug/mL

Extended Mixture – Low Point Concentration ug/mL	
Mineral Spirits	20
Stoddard Solvent	20
JP-5	20
SAE 10W Oil	20
Fuel Oil #2	20

Note: The low-level calibration standard may vary as long as it is at or below the reporting limit. The 5-level calibration range may vary.

Prepare all solutions in methylene chloride. Keep stored at 4°C (±2°C) no longer than 6 months.

7.7.3 Spiking Solutions:

7.7.3.1 Surrogate Solution

7.7.3.1.1 The surrogate, p-terphenyl, is added to all samples, matrix spikes, and blanks. Prepare a surrogate spiking solution at 5000 µg/mL in methylene chloride. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner, if comparison with a quality control check sample indicates a problem.

CAUTION: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

7.7.3.2 Matrix Spiking Solution

7.7.3.2.1 Prepare a spiking solution in methylene chloride that contains Diesel #2 in the concentration specified in Tables 8 and 9. Diesel purchased from a local filling station is used to prepare this standard.

Table 8
Matrix Spiking Solution (µg/mL)

Analyte	Concentration (ug/mL)
Diesel #2	50,000

Table 9
DRH Matrix Spiking Solution (µg/mL)

Analyte	Concentration (ug/mL)
DRH (C10-C28)	20,000

7.7.3.2.2 The solution must be prepared every six months or sooner if the solution has degraded or concentrated.

8.0 PROCEDURE

8.1 Extraction Procedure

8.1.1 Upon receiving a copy of the LIMS (Laboratory Information Management System) sample log, the samples are retrieved from storage and logged out for extraction by the technician according to the chain-of-custody procedure.

8.1.2 The technician now initiates the automated extraction logsheet (See Attachment 1 for Extraction Log example). The pertinent extraction information is keyed into the Extraction Laboratory Database, which is updated as the extraction procedure progresses.

8.1.3 After the samples are extracted and are ready for departmental transfer, the database-generated extraction log is reviewed and submitted with the sample extracts to the appropriate laboratory for analysis.

8.1.4 Aqueous Sample Procedure: Aqueous samples are extracted by the Separatory Funnel method.

8.1.4.1 Aqueous samples should be examined for substantial amounts of undissolved petroleum products before extraction. Undissolved product is evident by the presence of layers in the liquid. If organic layers are present, the phases may need to be processed separately. See Supervisor before proceeding with extraction.

8.1.4.2 Rinse all glassware with methylene chloride before proceeding with extraction.

8.1.4.3 Mark the liquid meniscus on the outside of the sample container. Decant the sample into a 2-liter separatory funnel. Using a 1-liter graduated cylinder, pour tapwater into the sample container to the level previously marked. Record the volume used as the sample volume. If high concentrations are anticipated, a smaller volume of sample may be used and then diluted with organic-free reagent water to 1 liter. Add 100 µL of the surrogate standard to all samples, spikes, and blanks and mix well. For the sample in each analytical batch selected for spiking, add 100 µL of the matrix-spiking standard and mix well.

8.1.4.4 Add 60-100 mL of methylene chloride to the separatory funnel. Record the solvent lot on the Extraction Log.

8.1.4.5 Seal and shake the separatory funnel vigorously for 3 minutes with periodic venting to release excess pressure. This process can be performed manually or by an automated 8-place Glascol shaker.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to solvent vapors.

8.1.4.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Decant the solvent layer into an Erlenmeyer flask.

8.1.4.7 Repeat the extraction two more times using fresh portions of solvent (Sections 8.1.4.1.1.3-8.1.4.1.1.5). Combine the three solvent extracts.

8.1.4.8 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10mL concentrator tube to the 500-mL evaporation flask.

8.1.4.9 Dry the extract by passing it through a funnel containing about 100 g of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

8.1.4.10 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 45-60 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 3 mL, allow to cool for approximately 10 minutes.

8.1.4.11 Rinse the Snyder column into the sample extract with just enough solvent to bring the extract to a final volume of 5 mL.

8.1.4.12 The extract obtained may now be analyzed for analyte content using GC/FID analysis. Transfer the extract to a vial with a Teflon lined screw-cap or crimp top, and label appropriately.

8.1.5 Solid Sample Procedure:

Solid samples are extracted based on method 3550B, Ultrasonic Extraction, or by the Shaker method (California Method).

8.1.5.1 Sample Handling:

8.1.5.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

8.1.5.1.2 Determine the dry weight of the sample remaining after decanting.

8.1.5.1.3 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two of SW-846 before extraction. This procedure is for solids only.

8.1.5.1.4 Dry waste samples amenable to grinding; grind or otherwise subdivide the waste.

8.1.5.1.5 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices. The

addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

8.1.5.1.6 Determination of percent moisture: weigh out a portion of sample for this determination at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample. However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be over-dried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay oven-drying of the weighed-out portion until other analytical results are available.

8.1.5.2 Ultrasonic Extraction (3550B):

8.1.5.2.1 Rinse all glassware with methylene chloride before proceeding with extraction.

8.1.5.2.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 20 g of well-mixed sample into a 400-mL beaker. Record the weight to the nearest 0.1 g (DO NOT TARGET WEIGHTS). Nonporous or wet samples (gummy or clay type) that do not have a free flowing sandy texture must be mixed with approximately 60 g of anhydrous sodium sulfate, using a spatula. After addition of sodium sulfate, the sample should be free flowing. Add 50 µL of surrogate standards to all samples, spikes, standards, and blanks. For the sample in each analytical batch selected for spiking, add 50 µL of the matrix-spiking standard. Immediately add 60-100 mL of methylene chloride.

8.1.5.2.3 Place the bottom surface of the tip of the disrupter horn about 1/8 to 1/4 inch below the surface of the solvent, but above the sediment layer. Be sure that the horn is properly tuned according the manufacturer's instructions.

8.1.5.2.4 Extract ultrasonically for 3 minutes, with output control knob set at 7-9 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50%-80%. Do not use microtip probe.

8.1.5.2.5 Decant the extract and filter it through S&S 595 size 18.5 cm filter paper (or equivalent) in a glass funnel filled with sodium sulfate.

8.1.5.2.6 Repeat the extraction two more times with two additional 60-100 mL portions of the solvent. Decant off the solvent after each ultrasonic extraction.

8.1.5.2.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Transfer filtered extract to a 500-mL evaporator flask and proceed to the next section.

8.1.5.2.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-75°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 45-60 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 3 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

8.1.5.2.9 Rinse and remove the Snyder column with just enough methylene chloride to bring the extract volume to 5 mL. Transfer the extract to a scintillation vial.

8.1.5.2.10 The extract obtained may now be analyzed for analyte content using GC/FID analysis. Transfer the extract to a vial with Teflon lined screw caps or crimp the top, and label appropriately.

8.1.5.3 California Extraction Method:

8.1.5.3.1 Rinse all glassware with methylene chloride before proceeding with extraction.

8.1.5.3.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 20 g of well-mixed sample into a 250-mL glass jar with a Teflon-lined lid. Record the weight to the nearest 0.1 g (DO NOT TARGET WEIGHTS). Add 50 µL of surrogate standards to all samples, spikes, standards, and blanks. For the sample in each analytical batch selected for spiking, add 50 µL of the matrix-spiking standard. Immediately add 80 mL of methylene chloride.

8.1.5.3.3 Shake for four hours on a reciprocal shaker.

8.1.5.3.4 Decant the methylene chloride extract through sodium sulfate into a K-D flask. Rinse the sodium sulfate twice and proceed to the concentration step in Section 8.5.2.7.

8.1.5.4 Waste Dilution

8.1.5.4.1 This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals at a concentration greater than 20,000 mg/Kg and that are soluble in the dilution solvent.

8.1.5.4.2 Samples consisting of multiphases must be prepared by the phase separation method before extraction.

8.1.5.4.3 The sample dilution may be performed in a 10-mL volumetric flask. If disposable glassware is preferred, the 20-mL scintillation vial may be calibrated for use. Pipette 10.0 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

8.1.5.4.4 Transfer approximately 1 g of each phase of the sample to separate 20mL vials or 10-mL volumetric flasks (record weight to the nearest 0.1 g). Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

8.1.5.4.5 Add 50 µL surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 50 µL of the matrix-spiking standard.

8.1.5.4.6 Immediately dilute to 10 mL with methylene chloride.

8.1.5.4.7 Add 2.0 g of anhydrous sodium sulfate to the sample.

8.1.5.4.8 Cap and shake the sample for 2 min.

8.1.5.4.9 Loosely pack disposable Pasteur pipettes with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

8.1.5.4.10 The extract obtained may now be analyzed for analyte content using GC/FID analysis. Transfer the extract to a vial with Teflon lined screw-caps or crimp the top, and label appropriately.

8.1.5.4.11 Any reagent blanks and matrix spike samples must be subjected to exactly the same analytical procedures as those used on actual samples.

8.1.6 Direct Injection for Volatile Organics (including gasoline):

8.1.6.1 This may involve injection of an aqueous sample containing a very high concentration of analytes and injection of an organic solvent waste.

8.2 GC Analysis Procedures

8.2.1 Gas chromatography conditions:

These conditions are only recommended starting conditions. Each instrument may vary and require changes to be optimized.

8.2.1.1 Columns: column phases may be varied as long as equivalency is established.

8.2.1.2 Column 1:

Carrier gas (He or H_2)	5-7 mL/minute
Makeup gas (N_2)	90 mL/min
Injector temperature	250°C
Detector temperature	300°C
Initial temperature	35°C for 1 minute; 10°C/min. ramp
Final temperature	300°C.

8.2.2 Calibration

8.2.2.1 Refer to Method 8000B for proper calibration techniques. Percent relative standard deviation must be ≤ 20 for all analytes over the five-point calibration range to assume linearity through the origin (and use the mean calibration factor or response factor for quantitation).

Linear fit calibration or non-linear (quadratic) calibration may be used if % RSD is > 20 as long as the correlation coefficient or coefficient of determination (for quadratic) are 0.99 or greater.

Note: the low-point calibration curve must be at or below the PQL.

8.2.2.2 Calculation of retention time windows following method 8000B's method yields extremely small windows (to the 1/100th of a minute) for all compounds (when using the 72/72+ hour method). This is due to highly stable chromatographic systems. The use of such retention time windows for "real-world" samples may result in numerous false negatives, therefore, the windows of ±0.10 have been adopted. 72-hour retention time studies (Form 9Es) are maintained for each instrument and column per method 8000B to prove the stability of the instruments.

8.2.2.3 The retention time range for DROs is defined during initial calibration. The range is established from the retention times of the C_{10} and C_{28} alkanes. The retention time range is calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

8.2.2.4 The procedure of external calibration is used. Quantitation using the mean calibration factor/response factor is preferred, however, linear least squares and quadratic fit may be used. If a quadratic fit is to be used, six levels of standards must be analyzed for the initial calibration.

8.2.2.5 All confirmed values above the practical quantitation limit must be reported. Values below the PQL should not be reported unless the client specifies.

8.2.3 Gas chromatographic analysis:

8.2.3.1 Following acceptable initial calibration and calibration verification standards, samples may be analyzed. Analysis of a mid-concentration standard every 10 samples is recommended for dirty samples. Relatively clean samples may allow for an extended sequence (not to exceed a 12-hour period per Method 8000B) based on analyst judgment. Each sample must be bracketed with an acceptable initial calibration or calibration verification standards interspersed between the sample analyses. When a calibration verification standard fails to meet the ± 15% difference criteria, re-inject a calibration verification standard. If it still exceeds the criteria, all samples that were injected after the last standard that last met the criteria must be re-injected. An exception to this rule follows:

If the ending calibration verification bracket fails with percent differences > 15% above the initial calibration response and no "hits" are present in the samples, then the samples may be reported.

8.2.3.2 Analysis of a mid-concentration standard every 12-hour shift (not to exceed 20 samples) is required. –

8.2.3.3 The hydrocarbon retention time standard is also analyzed every 12-hour shift. The C_{10} through C_{28} n-alkanes must fall within the RT windows for the sample analysis to be reported.

8.2.3.4 Examples of GC/FID chromatograms generated by instruments with capillary columns are presented in Attachments 2-9.

8.2.3.5 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted by the context in which the result is to be used.

8.2.3.6 If the peak response exceeds the range of the highest standard, quantitatively dilute the extract and reanalyze.

8.2.3.7 Verification of the identity of the contaminant must be established by comparison of sample chromatograms with high-quality commercial products used as standards. Petroleum products are complex mixtures of compounds derived from crude petroleum, and different products may have overlapping boiling ranges and chromatograms; care must be taken to distinguish closely related products and to account for possible degradation in the environment. If the identity of the product is not known, identification is performed by comparison of the chromatograms of samples and various commercial products. Guidance for this comparison process is contained in references such as ASTM Standard Method 3328-78; such comparison is greatly aided by overlaying sample and standard chromatograms utilizing a computer data system. The standard most nearly matching the sample chromatogram(s) is selected and used for quantitation.

If the sample chromatogram exhibits peaks in the range of interest, but no pattern is recognizable, the peaks are quantitated using the response factor of the product with the closest elution range. The TPH is labeled as miscellaneous and the approximate carbon range is specified in the report. The entire carbon range, approximately through C_{28}, is integrated unless otherwise specified by the client. The baseline-to-baseline technique is used for integration of petroleum hydrocarbon mixtures. Valley-to valley integration is used for single-response analytes (i.e., DRH).

8.2.3.8 Identify single responding compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. Make sure to take into account the variance caused by matrix interference and environmental degradation. Second column confirmation is not required.

8.2.3.9 Identification of fuels, especially gasoline, is complicated by their inherent volatility. The early eluting compounds in fuels are obviously the most volatile and the most likely to have weathered unless sampled immediately following a spill. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is least likely to be present in an environmental sample or present in only very low concentration in relation to the remainder of a gasoline chromatogram. Second column confirmation is not required.

8.2.3.10 Quantitation of the compound(s) of interest is premised on: 1) a linear response of the FID to the ranges of concentrations of the compound(s) of interest encountered in the sample extract and the corresponding calibration extract; and 2) a direct linear proportionality between the magnitude of response of the FID over the width(s) of the retention window(s) (the area under the characteristic or "fingerprint" peak[s]) in the sample and calibration extracts. Proper quantitation requires the appropriate selection of a baseline from which the area under the characteristic peak(s) can be calculated.

8.2.3.10.1 Since most of the compounds in this method are mixtures, the concentration of samples is obtained by averaging the concentrations determined using the area of all integrated peaks (minus the surrogate if it interferes).

8.2.3.10.2 A comment should be made, in the final data report, noting which commercial product was used as the standard for calibration. In addition, note whether the chromatographic pattern of the sample generally matched that of the standard chromatogram.

8.2.4 See the standard operating procedure for the "Preventive Maintenance of Hewlett-Packard and Fisons Gas Chromatographs", SWL-OP-201, for specific GC maintenance procedures.

9.0 CALCULATIONS

9.1 Calibration Factor = $\frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected}}$

9.2 Response Factor = $\frac{\text{Mass of the Compound Injected}}{\text{Peak Area of the Compound in the Standard}}$

9.3 Mean CF = $\frac{\text{Sum of CF for each level}}{\text{Number of levels}}$

9.4 SD = Square root $\left[\frac{\text{Sum of (CF of each individual level - Mean CF)}^2}{\text{(Number of levels - 1)}}\right]$

9.5 RSD = $\frac{\text{SD}}{\text{Mean CF}}$ x100

9.6 See SW-846, Revision 2, January 1995, page 8000B - 20 through 22 for linear and higher order fit equations.

9.7 % Difference = $\frac{\text{Mean CF - CF from the calibration verification standard}}{\text{Mean CF}}$ x 100

NOTE: CF and RF may be interchanged in the formulas in Sections 9.3 through 9.7, depending on which one is being used for sample calculation.

9.8 % Drift (used for linear and higher order fits) = $\frac{\text{Calculated conc. - Nominal conc.}}{\text{Theoretical conc.}}$ x100

9.9 Determine the concentration of individual compounds in the sample.

9.9.1 Sample Concentration Calculation:

9.9.1.1 Aqueous Samples using Mean RF

Concentration (µg/L)=[As] [V(t)][D] [Mean RF] [1000mL/L] / [V(s)]

Where:
As = Area (or height) of the peak for the analyte in the sample.
V(t) = Total volume of concentrated extract (mL).
D = Dilution factor.
Mean RF = Mean response factor.
V(s) = Volume of aqueous sample extracted (mL).

9.9.1.2 Aqueous Samples using Mean CF

Concentration (µg/L)=[As] [V(t)][D][1000mL/L] / [Mean CF] [V(s)]

Where:
As = Area (or height) of the peak for the analyte in the sample.
V(t) = Total volume of concentrated extract (mL).
D = Dilution factor.
Mean CF = Mean calibration factor.
V(s) = Volume of aqueous sample extracted (mL).

9.9.1.3 Non-aqueous Samples using Mean RF

Concentration (mg/Kg)=[As] [V(t)][D] [Mean RF] / [W(s)]

Where:
As = Area (or height) of the peak for the analyte in the sample.
V(t) = Total volume of concentrated extract (mL).
D = Dilution factor.
Mean RF = Mean response factor.
W(s) = Weight of sample extracted (g).

9.9.1.4 Non-aqueous Samples using Mean CF

Concentration (mg/Kg)=[As] [V(t)][D] / [Mean CF] [W(s)]

Where:
As = Area (or height) of the peak for the analyte in the sample.
V(t) = Total volume of concentrated extract (mL).
D = Dilution factor.
Mean CF = Mean calibration factor.
W(s) = Weight of sample extracted (g).

9.10 For multi-component mixtures, match retention times and patterns (relative ratios) of peaks in the standards with peaks in the sample.

9.11 Report results in µg/L for water samples and mg/Kg for solid samples without correction for recovery data. All QC data obtained should be reported with the sample results.

9.12 Dry weight calculation (from data gathered during step 8.1.5.1.6):

$$\% \text{ Moisture} = \frac{\text{grams of sample - grams of dried sample}}{\text{grams of sample}} \times 100$$

10.0 QUALITY ASSURANCE / QUALITY CONTROL

10.1 Refer to Chapter One of SW-846 for specific quality control (QC) procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized.

10.2 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits established. If recovery is not within limits, the following are required:

10.2.1 Check to be sure that there are no errors in calculations and surrogate solutions. Also, check instrument performance.

10.2.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

10.2.3 If both method blank surrogate recoveries are outside of control limits, reanalyze the sample to rule out instrument problems. Re-extract and reanalyze the samples if none of the above are a problem.

10.3 If the spike recoveries are outside of laboratory control limits in both the LCS and LCSD, the LCS/LCSD and associated samples must be re-analyzed and/or re-extracted/reanalyzed. If out-of-control analytes are out high and those analytes are not present in the samples, then no corrective action is required. Control limits will be those annually updated from in-house generated data. See "Blue Book" for SWLO's current control limits.

10.4 If spike recoveries in the MS/MSD are outside of control limits but the combined LCS/LCSD are within control limits, the poor MS/MSD recoveries may be attributed to matrix effect. If both LCS/LCSD and MS/MSD have spiked compounds outside of control limits, the samples and associated QC must be re-analyzed and/or re-extracted/reanalyzed. Control limits will be those annually updated from in-house generated data. See "Blue Book" for SWLO's current control limits.

10.5 If RPDs for the LCS/LCSD pair are outside of acceptance limits, repeat one or both spikes. If the control spike is still outside of control limits, correct the problem, then re-extract and reanalyze the associated samples and QC.

10.6 Include a mid-concentration calibration standard every 10 or more samples (not to exceed a 12-hour period) in the analysis sequence as a calibration check. The response factors for the mid-concentration calibration should be within 15 percent of the average values for the multi-concentration calibration. When a calibration verification standard fails to meet the ± 15% difference criteria, re-inject a calibration verification standard. If it still exceeds the criteria, all samples that were injected after the last standard that last met the criteria must be re-injected.

An exception to this rule follows: If the ending calibration verification bracket fails with percent differences > 15% above the initial calibration response and no "hits" are present in the samples, then the samples may be reported.

10.7 If any of the target analytes in the calibration verification fall outside of the retention time window established during initial calibration, the system is considered out of control. All samples analyzed after the last compliant calibration verification must be re-analyzed after instrument maintenance and re-calibration is successfully performed.

10.8 Instrument blanks and method blanks must not contain any confirmed target analyte greater than the reporting limit for the associated samples. If contamination is noted, stop all analyses, determine the source of the contamination, remove the source, and confirm the source is gone by reanalyzing an instrument blank and/or method blank as appropriate. QC and associated samples will be re-extracted and reanalyzed if the blank contamination is present > PQL in the samples.

10.9 If a sample contains an analyte at >2X the high calibration standard and the subsequent sample contains low levels of that analyte, the subsequent sample must be re-analyzed to

ensure that the low-level hit was not carryover.

10.10 Significant peak tailing must be corrected, as it indicates a problem with the chromatographic system. Check for active sites on the column, detector operation, and for leaks in the system.

11.0 WASTE DISPOSAL.

See the Standard Operating Procedure for *"Hazardous Waste Management Plan"*, SWL-GA-114.

12.0 METHOD PERFORMANCE

12.1 The MDL concentrations are updated annually and are obtained using organic-free reagent water and sandy loam soil. The QA Department maintains MDL results in SWLO's "Red book". Details for determining MDLs are given in Chapter One of SW-846 and the SOP for the "*Definition and Determination of Detection Limits*", SWL-GA-113.

The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics, and matrix effects.

12.2 The accuracy and precision obtainable following this method will be determined by the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

12.3 The laboratory should maintain control charts of LCS, MS, and MSD recoveries and relative percent deviations between MS and MSD recovery for accuracy and precision data. Surrogate recovery is also plotted. The control charts are monitored monthly for LCS and quarterly for MS and are maintained on file in the laboratory.

Control limits are updated on an annual basis (See SOP "*Control Charts*", SWL-GA-112 for more details). See "Blue Book" for SWLO's most current control limits.

12.4 QLs are calculated by multiplying the MDL value for an analyte by a number ranging from 5-10. In no instance will the QL be less than the MDL. See "Red Book" for SWLO's QLs.

13.0 REFERENCES

13.1 "Method for Total Petroleum Hydrocarbons and Total Organic Lead." Hazardous Materials Laboratory. California Department of Health Services. February 1988.

13.2 "OA-2" University of Hygienic Laboratory, Iowa City, Iowa. July 1991.

13.3 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 3500B. Organic Extraction and Sample Preparation" Revision 2, December 1996.

13.4 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 3510C. Separatory Liquid-Liquid Extraction" Revision 3, December 1996.

13.5 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 3550B. Sonication Extraction" Revision 2, December 1996.

13.6 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 3580A. Waste Dilution" Revision 1, July 1992.

13.7 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 8000B. Determinative Chromatographic Separations" Revision 2, December 1996.

13.8 U.S.EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: "Method 8015B. Nonhalogenated Organics Using GC/FID" Revision 2, December 1996.

13.9 Standard Operating Procedure, "Preventative Maintenance of Hewlett-Packard and Fisons Gas Chromatographs", SWL-OP-201.

13.10 Standard Operating Procedure, "Standards Receipt, Traceability, and Preparation", SWL-OP-202.

13.11 Standard Operating Procedure, "Laboratory Safety Plan", SWL-GA-111.

13.12 Standard Operating Procedure, "Control Charts", SWL-GA-112.

13.13 Standard Operating Procedure, "Definition and Determination of Detection Limits", SWL-GA-113.

13.14 Standard Operating Procedure, "Hazardous Waste Management Plan", SWL-GA-114.

13.15 Headquarters Air Force Center for Environmental Excellence Quality Assurance Project Plan. Version 2.0, January 1997.

13.16 U.S.EPA, Statement of Work OLM03.2, "Organic Analysis: Multi-media, Multi-concentration".

14.0 DEFINITIONS

PQL ..... Practical Quantitation Limit.

N/A .....Not applicable.

(MSDS) Material Safety Data Sheet: Information provided by commercial vendors for the chemical products prepared by their company. The information on the MSDS includes but is not limited to composition, physical properties, hazard identification, first aid measures, emergency clean-up and/or response, exposure, and storage.

SDG.....The Sample Delivery Group; a unit within a single case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer field samples within a case, received over a period of up to 14 calendar days (7 calendar days for 14-day turns). Data from all samples in a SDG are due concurrently.

15.0 VARIANCES AND SPECIAL INSTRUCTIONS

15.1 SW-846, 8015B VARIANCES — Several variances from the strictest interpretation of SW-846, method 8015B are noted in this section.

15.1.1 Section 8.1.4.4 notes using 60-100 mL of methylene chloride for extraction of water samples. SW-846, method 3510C notes using 60 mL.

15.1.2 Section 8.1.5.2.2 notes using 20 grams of sample for extraction of solid samples. SW-846, method 3550B notes using 30 grams.

15.1.3 Sections 8.1.4.11 and 8.1.5.2.9 note bringing the final extract volume to 5 mL. The appropriate SW-846 extraction methods note bringing the final extract volume to 10 mL.

15.1.4 Section 8.2.2.2 notes that calculation of retention time windows following method 8000B's method yields extremely small windows (to the 1/100th of a minute) for all compounds (when using the 72/72+ hour method). This is due to highly stable chromatographic systems. The use of such retention time windows for "real-world" samples may result in numerous false negatives, therefore, the windows of ±0.10 have been adopted. 72-hour retention time studies (Form 9Es) are maintained for each instrument and column per method 8000B to prove the stability of the instruments.

15.2 California Method VARIANCES -- Several variances from the strictest interpretation of California's method are noted in this section.

15.2.1 Detection limits noted in California's method are noted as 500 ppb for water samples and 10 ppm for soil samples. SWLO's reporting limits are adjusted based on annual MDLs.

15.2.2 Section 8.1.4.4 notes using 60-100 mL of methylene chloride for extraction of water samples. The California method notes using 60 mL.

15.2.3 See Section 8.1.5.3 for the California method of extraction soil samples. Do not proceed according to Section 8.1.5.2.

15.2.4 Section notes that calibration verification standards must be with ± 15% of the initial calibration response. The California method notes using ± 10% as the calibration verification criteria.

15.3 Iowa Method VARIANCES -- Variances from the strictest interpretation of Iowa's method are noted in this section.

15.3.1 SWLO's sample holding times are 14 days for waters and soils. OA-2 notes using a 7-day holding time for water samples.

15.4 Oklahoma Department of Environmental Quality (ODEQ) Method VARIANCES and SPECIAL INSTRUCTIONS -- Several variances from the strictest interpretation of Iowa's method and special method instructions are noted in this section.

15.4.1 The following must be applied to sample analyzed based on the ODEQ protocol. The retention time window for total DRO is defined as beginning approximately 0.1 minutes before the retention time of n-decane and ending 0.1 minutes after the retention time of n-octacosane in the calibration run. Retention time windows for the individual components are established as ± 0.1 minutes of the retention times in the calibration run.

15.4.2 SWLO uses at least 1000 mL of water for extraction of aqueous samples. ODEQ notes using 800 – 900 mL.

15.4.3 Section 8.1.4.4 notes using 60-100 mL of methylene chloride for extraction of water samples. The ODEQ method notes using 50 mL.

15.4.4 SWLO soil/sediment samples are extracted 3 times for 3 minutes by sonication using 60-100 mL of methylene chloride each time according to Section 8.1.5.2.2 8.1.5.2.6. The ODEQ method notes using equal volumes of sample and solvent (mLs of solvent to grams of sample) and extracting three times for 2-5 minutes.

15.4.5 SWLO prepares and analyzes a LCS/LCSD set for every 20 or fewer samples. The ODEQ method notes to analyze a duplicate diesel component spike ever batch of 10 or less samples.

15.4.6 Samples extracted and analyzed based on the ODEQ method must be extracted within the following time ranges: water samples must be extracted within 7 days of collection; soil samples must at least be placed under solvent within 7 days of collection.

15.4.7 SWLO reporting limits are calculated based on annual MDL results. ODEQ reporting limits are noted as follows: DRH water = 0.1 ppm; DRH soil = 10 ppm.

16.0 ATTACHMENTS

16.1 Attachment 1: Sample Extraction Log / For Example Only

16.2 Attachment 2: Chromatogram 1 – Gasoline / For Example Only

16.3 Attachment 3: Chromatogram 2 –Kerosene / For Example Only

16.4 Attachment 4: Chromatogram 3 –Naphtha / For Example Only

16.5 Attachment 5: Chromatogram 4 / JP-4 / For Example Only

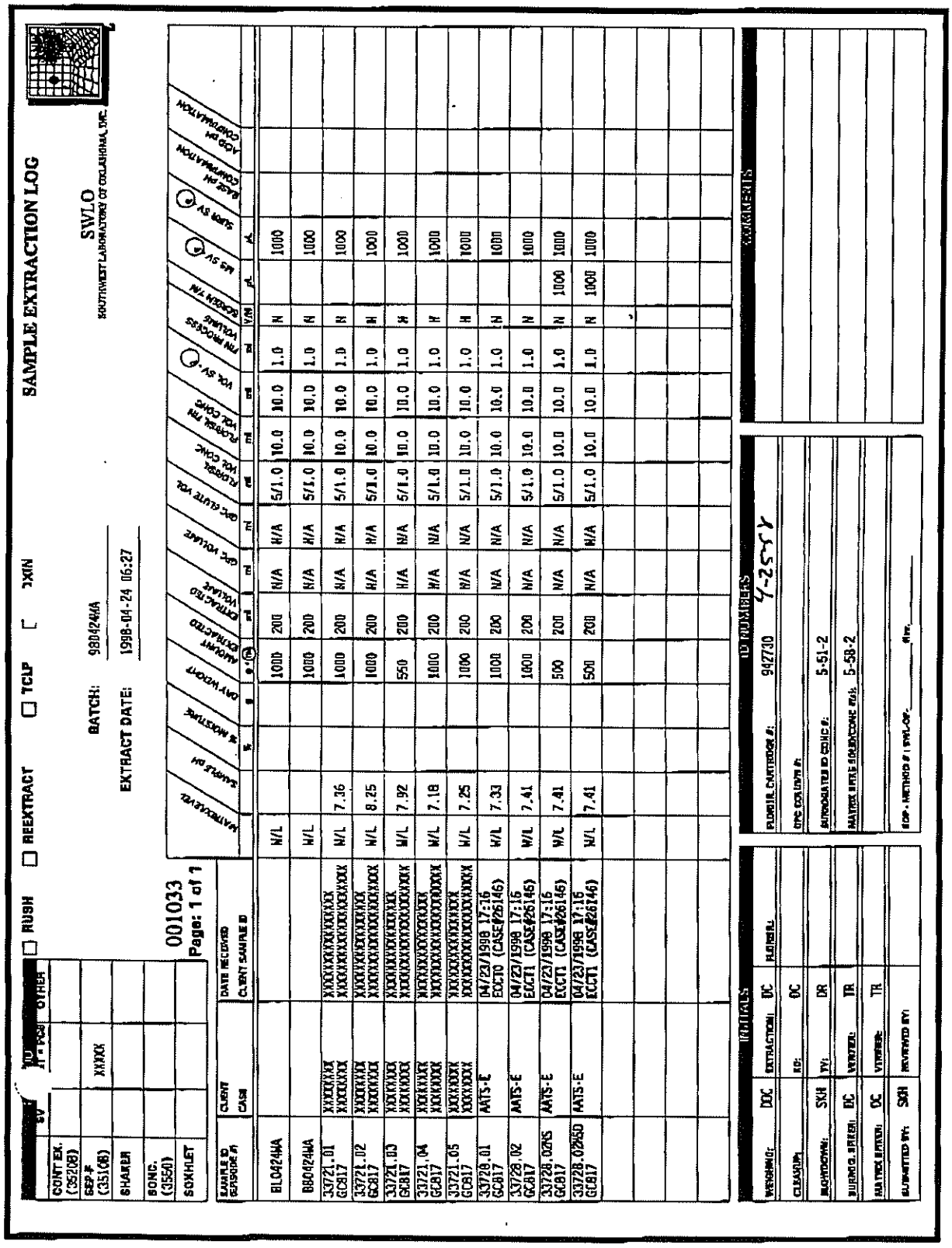
16.6 Attachment 6: Chromatogram 5 / Diesel #2 / For Example Only

16.7 Attachment 7: Chromatogram 6 / Fuel Oil #6 / For Example Only

16.8 Attachment 8: Chromatogram 7 / Mineral Spirits / For Example Only

16.9 Attachment 9: Chromatogram 8 / DRH (C10-C28) / For Example Only

ATTACHMENT 1
Sample Extraction Log



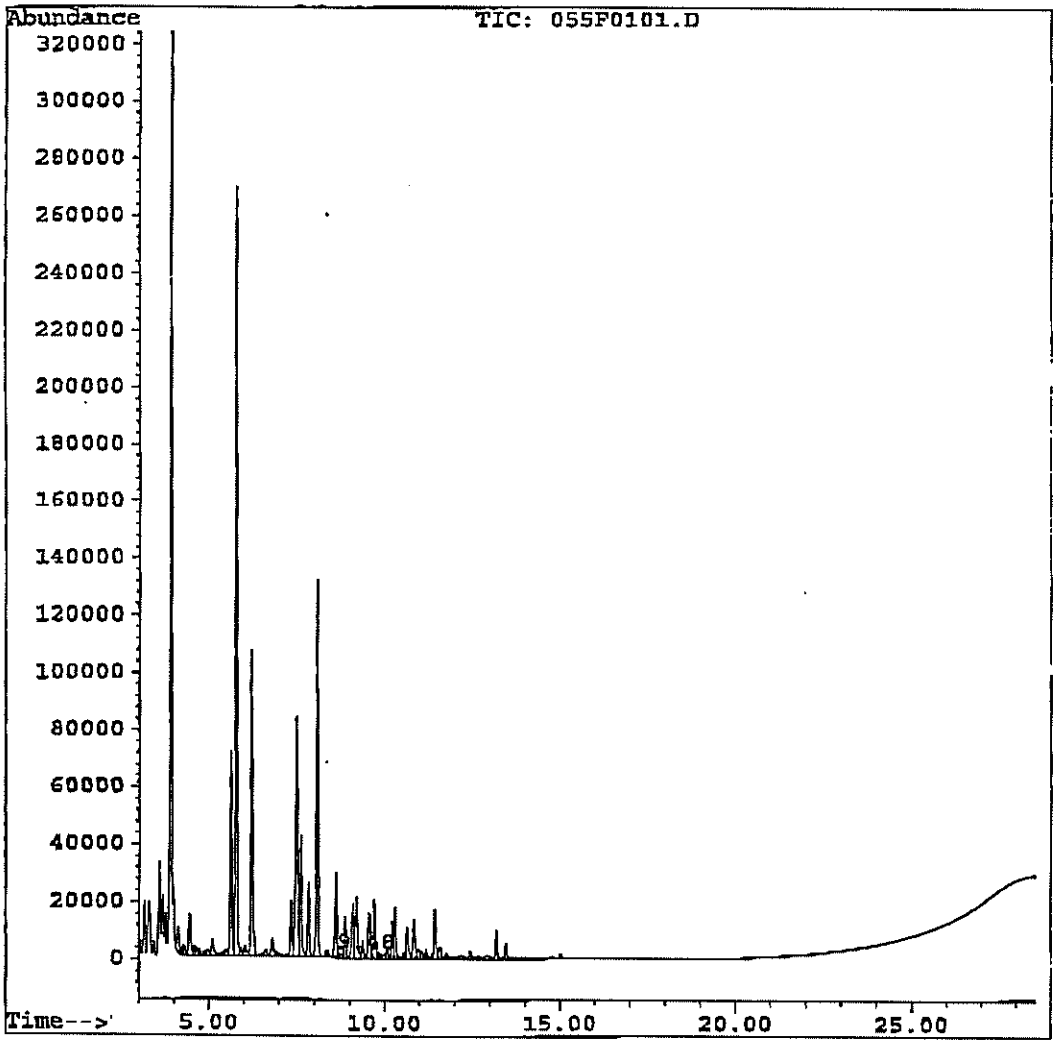
ATTACHMENT 2
Chromatogram 1: Gasoline

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\055F0101.D Vial: 55
Acq On : 12 Jan 98 04:01 Operator: [GC].D\DAT
Sample : 500 GAS 53061 Inst : HP_17
Misc : Multiplr: 1.0000
Quant Time: Apr 17 11:15 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\GASA10.M
Title : SW-846, METHOD 8080
Last Update : Fri Apr 17 11:01:42 1998
Response via : Single Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



055F0101.D GASA10.M Fri Apr 17 11:15:23 1998 Page 2

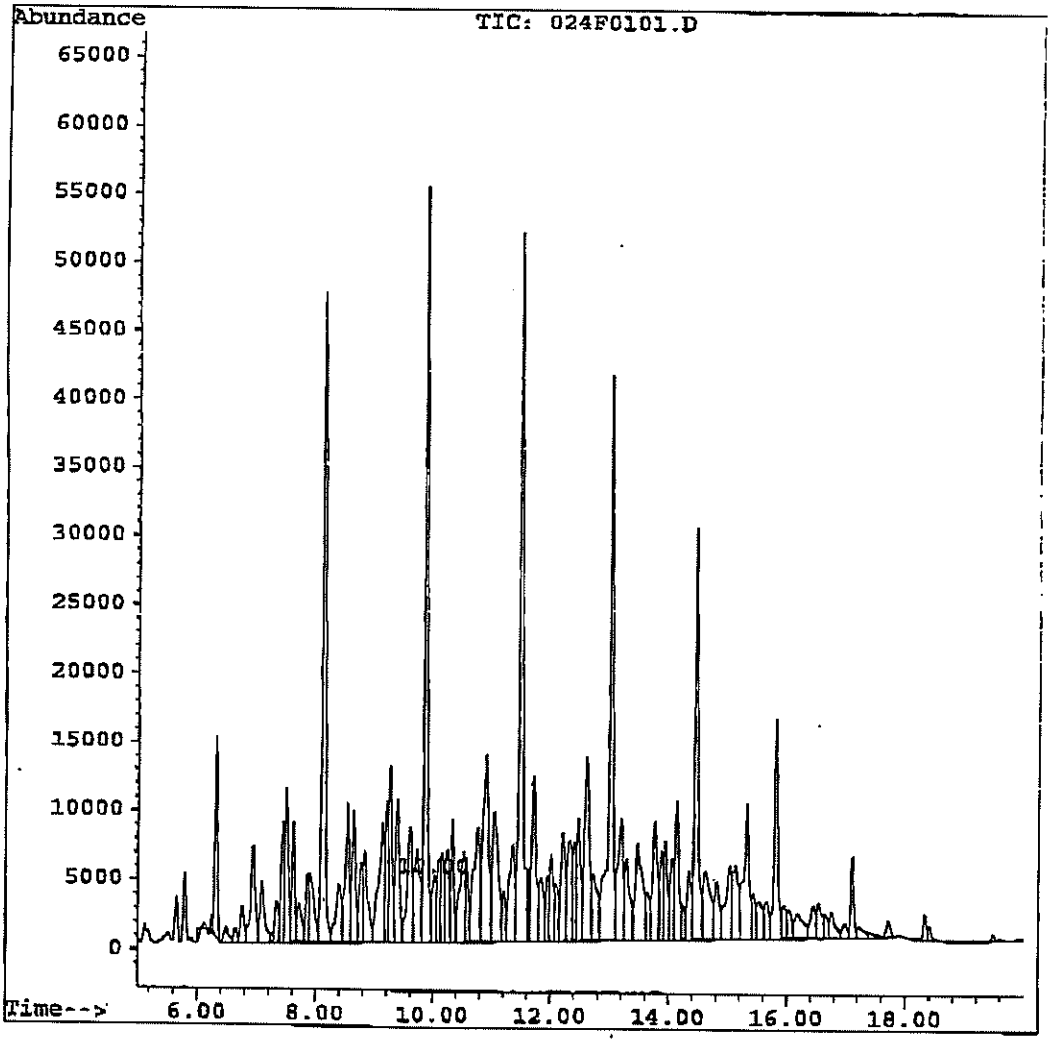
ATTACHMENT 3
Chromatogram 2: Kerosene

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\024F0101.D Vial: 24
Acq On : 11 Jan 98 04:43 Operator: AJS
Sample : KEROL3 Inst : HP_17
Misc : 53001 Multiplr: 1.0000
Quant Time: Apr 20 15:39 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\KERA10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Mon Apr 20 15:39:17 1998
Response via : Single Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



024F0101.D KERA10.M Mon Apr 20 15:39:24 1998 Page 2

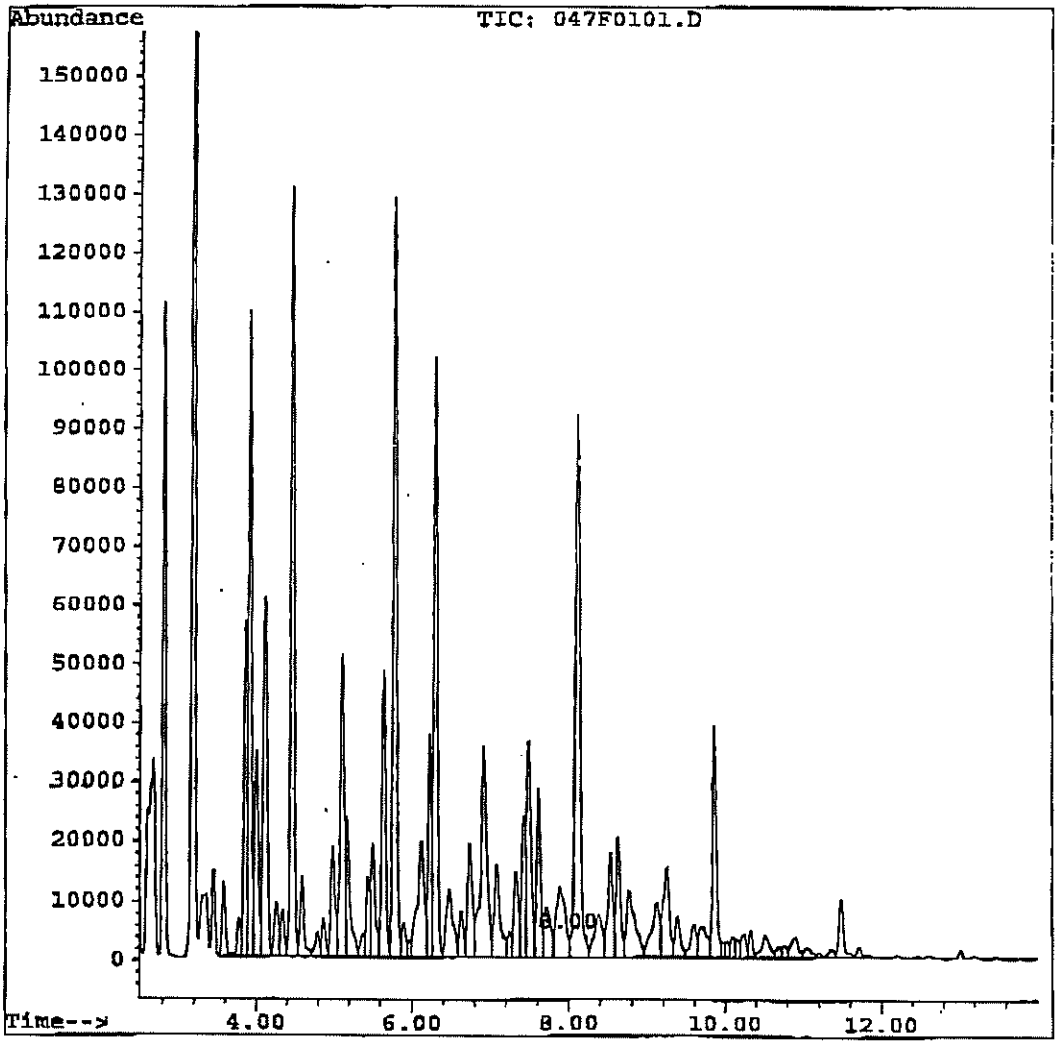
ATTACHMENT 4
Chromatogram 3: Naphtha

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\047F0101.D Vial: 47
Acq On : 11 Jan 98 22:00 Operator: AJS
Sample : NAPHL3 Inst : HP_17
Misc : 5-328-1 500PPM Multiplr: 1.0000
Quant Time: Apr 21 11:05 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\NAPHA10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Tue Apr 21 11:05:30 1998
Response via : Multiple Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



047F0101.D NAPHA10.M Tue Apr 21 11:05:37 1998 Page 2

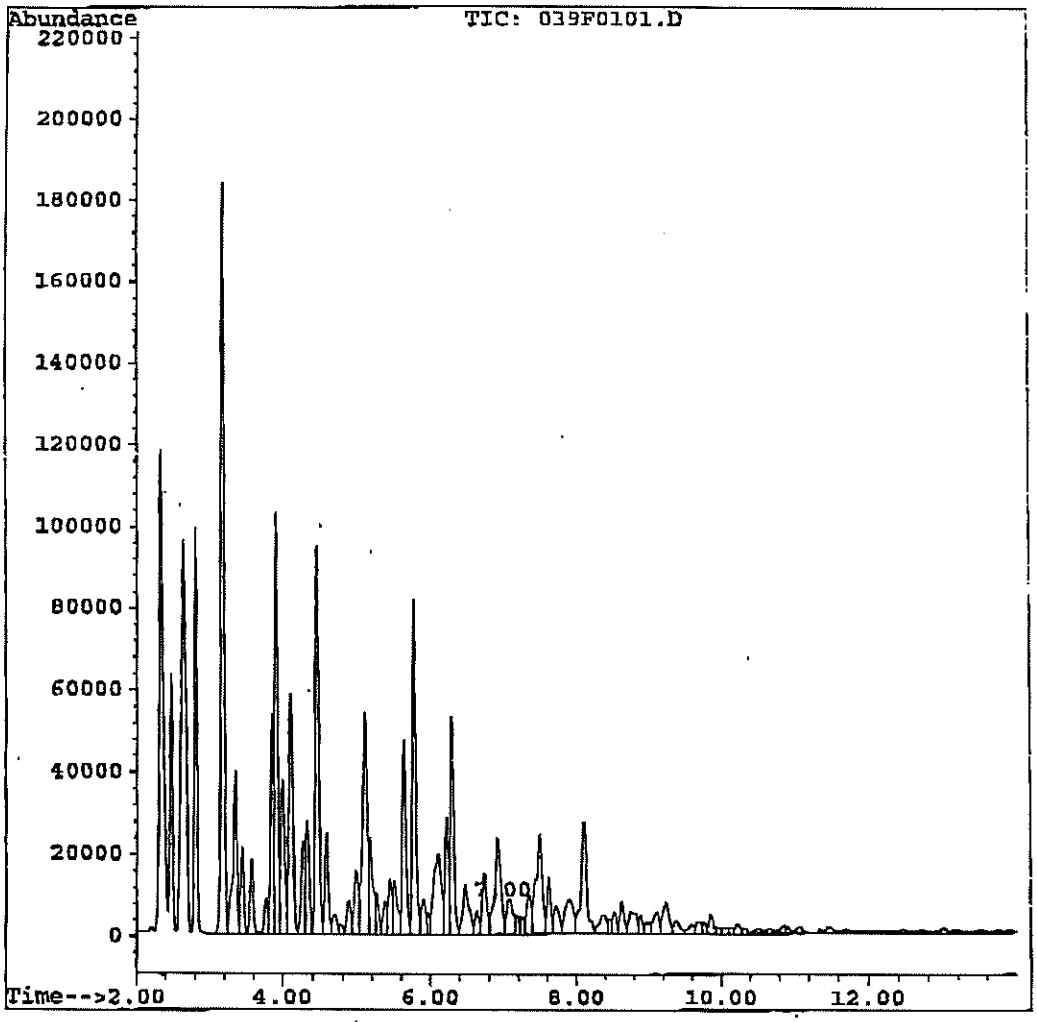
ATTACMENT 5
Chromatogram 4: JP-4

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\039F0101.D Vial: 39
Acq On : 11 Jan 98 15:59 Operator: AJS
Sample : JP4_L3 Inst : HP_17
Misc : 5-320-1 500PPM Multiplr: 1.0000
Quant Time: Apr 21 11:48 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\JP4_A10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Tue Apr 21 11:48:52 1998
Response via : Multiple Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



039F0101.D JP4_A10.M Tue Apr 21 11:49:00 1998 Page 2

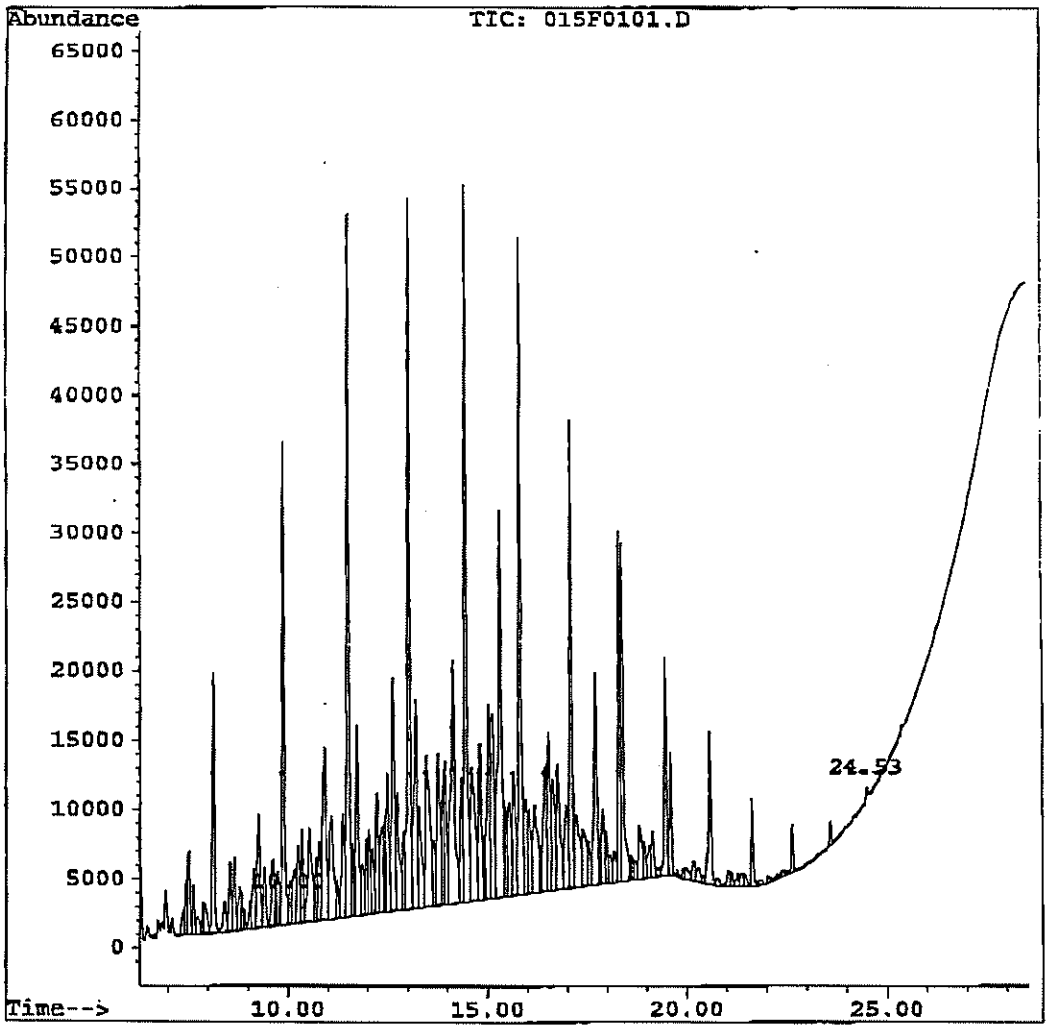
ATTACHMENT 6
Chromatogram 5: Diesel #2

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\015F0101.D Vial: 15
Acq On : 10 Jan 98 22:08 Operator: AJS
Sample : DIESL4 Inst : HP_17
Misc : 52791 Multiplr: 1.0000
Quant Time: Apr 17 14:14 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\DIEA10.M
Title : SW-846, METHOD 8015 TPH
Last Update : Fri Apr 17 14:15:50 1998
Response via : Single Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



015F0101.D DIEA10.M Fri Apr 17 14:16:58 1998 Page 2

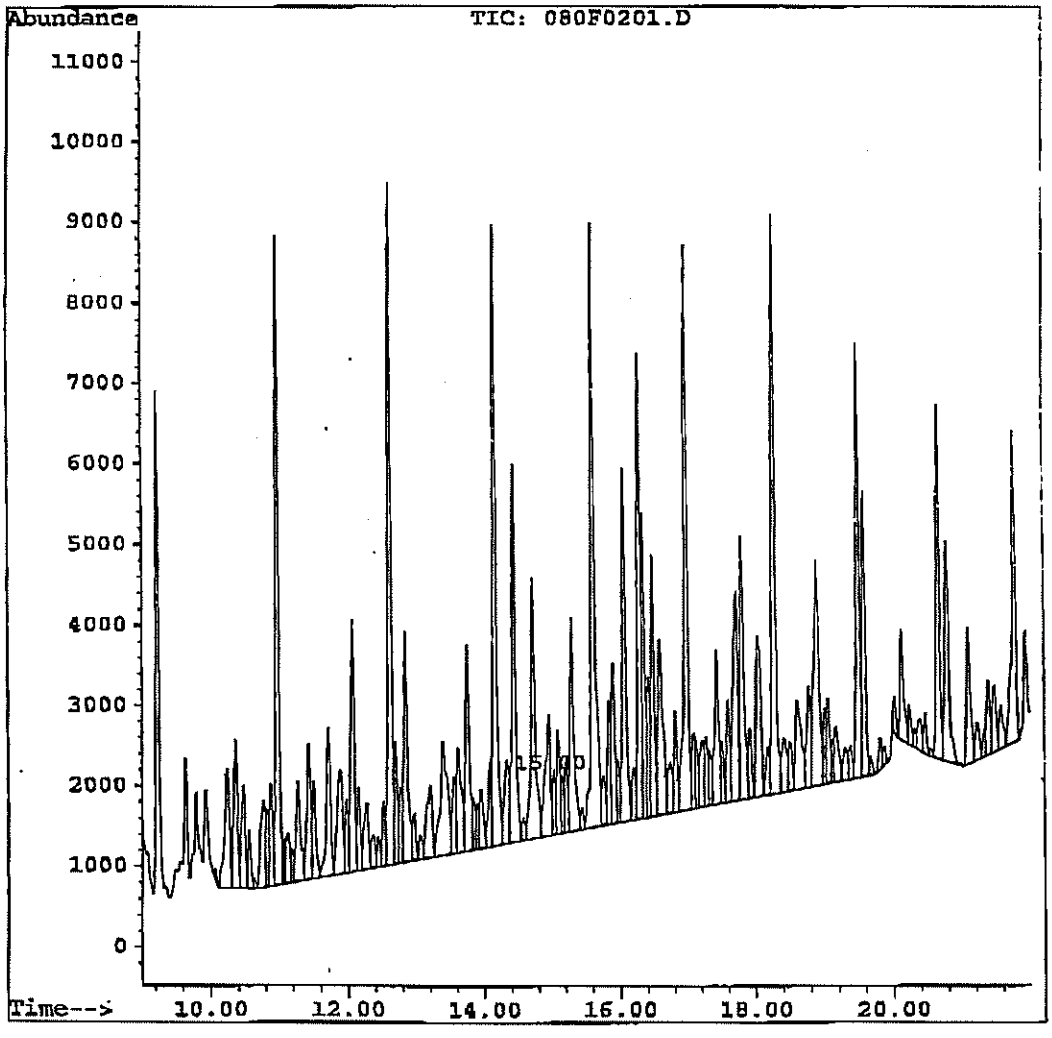
ATTACHMENT 7
Chromatogram 6: Fuel Oil #6

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\080F0201.D Vial: 80
Acq On : 12 Jan 98 23:23 Operator: AJS
Sample : FO6_L3 Inst : HP_17
Misc : 5-266-1 500PPM Multiplr: 1.0000
Quant Time: Apr 21 11:30 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\FO6_A10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Tue Apr 21 11:30:23 1998
Response via : Multiple Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



080F0201.D FO6_A10.M Tue Apr 21 11:30:31 1998 Page 2

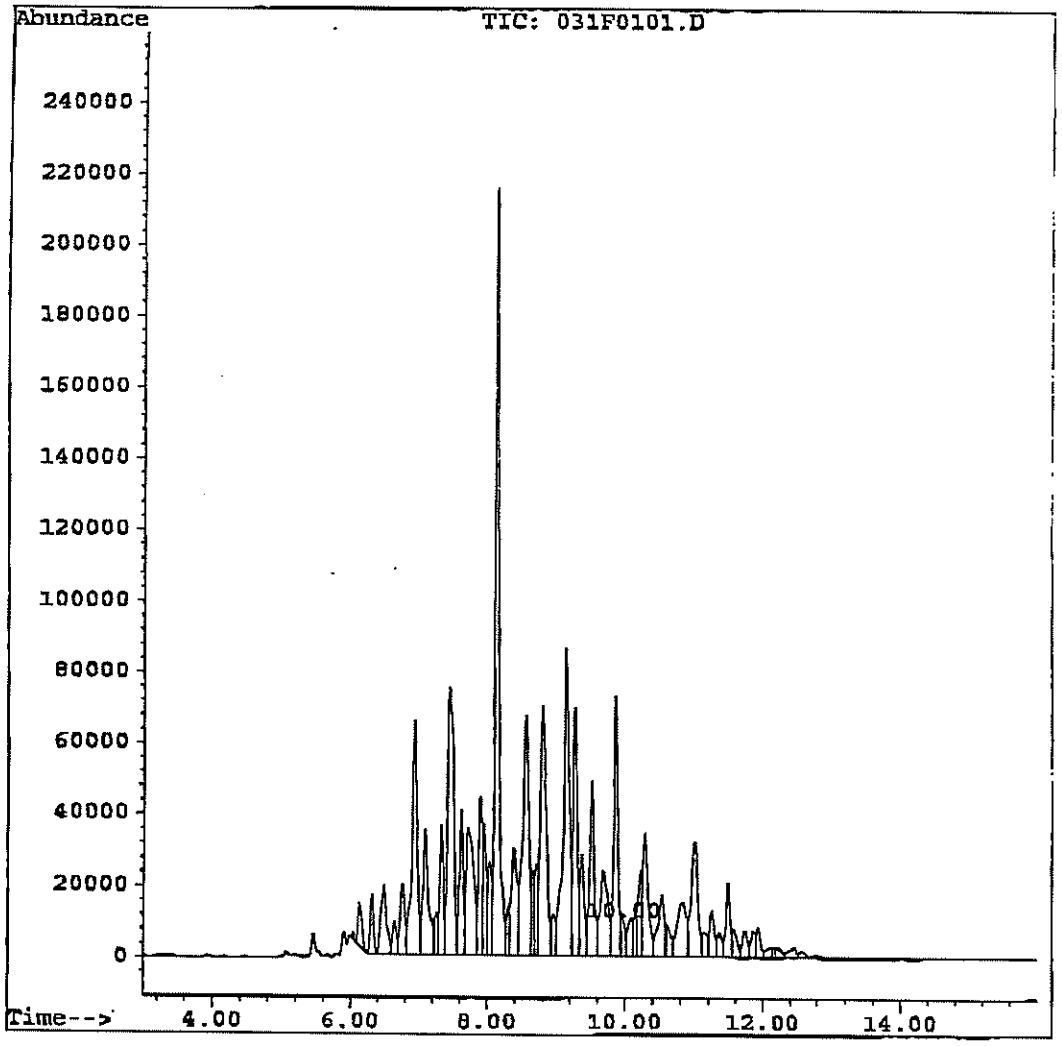
ATTACHMENT 8
Chromatogram 9: Mineral Spirits

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\031F0101.D Vial: 31
Acq On : 11 Jan 98 10:02 Operator: AJS
Sample : MINSL4 Inst : HP_17
Misc : 5-313-1 Multiplr: 1.0000
Quant Time: Apr 21 8:00 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\MINSA10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Tue Apr 21 08:00:25 1998
Response via : Multiple Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



031F0101.D MINSA10.M Tue Apr 21 08:00:31 1998 Page 2

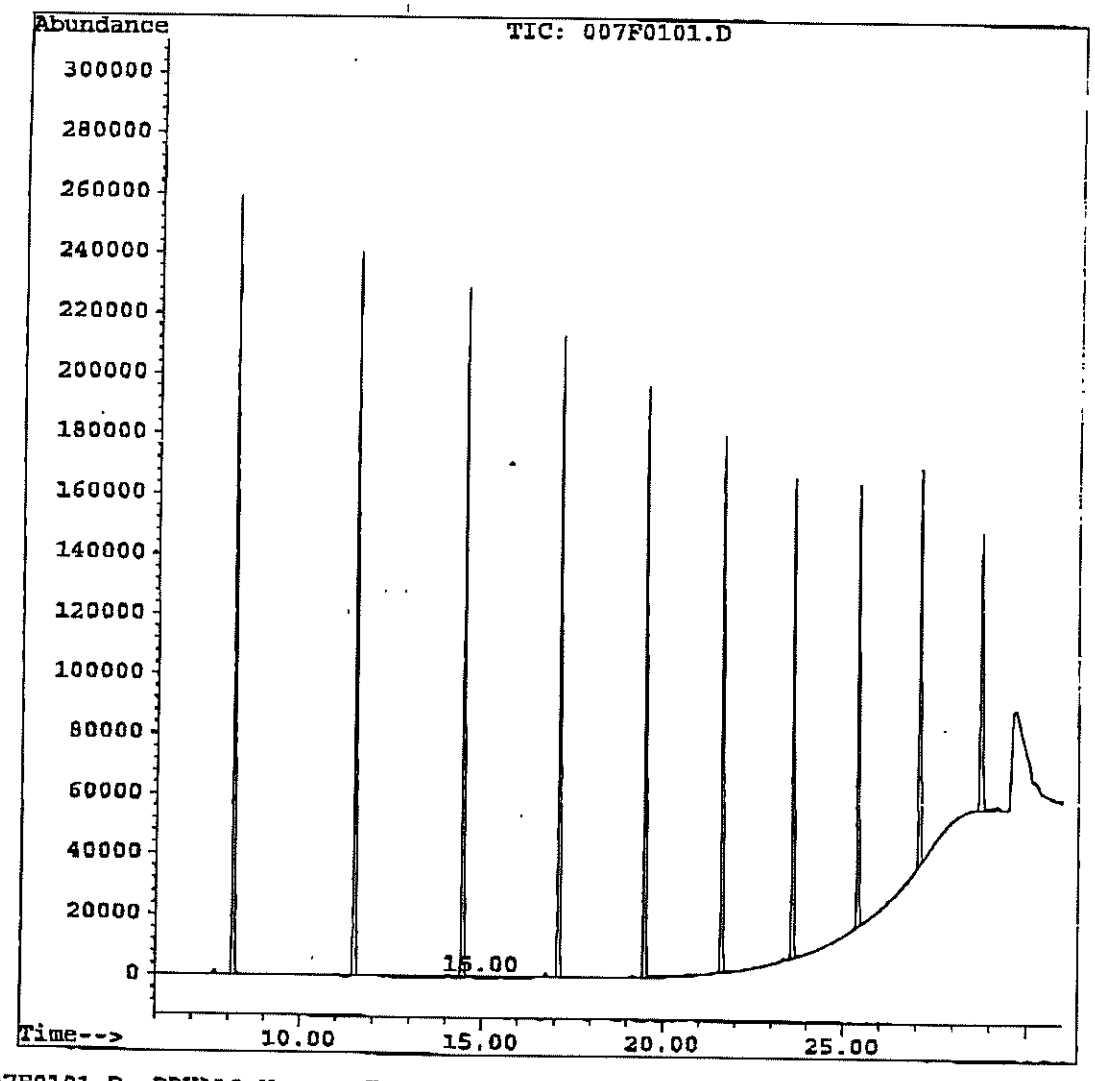
ATTACHMENT 9
Chromatogram 10: DRH (C10-C28)

Chromatographic Report

Data File : F:\HPCHEM\HP\17_ENV\DATA\17011098\007F0101.D Vial: 7
Acq On : 10 Jan 98 16:09 Operator: AJS
Sample : DRH_L4 Inst : HP_17
Misc : 5-272-1 500PPM Multiplr: 1.0000
Quant Time: Apr 21 15:15 1998

Method : F:\HPCHEM\HP\17_ENV\METHODS\DRHA10.M
Title : SW-846, METHOD 8015 Mod.
Last Update : Tue Apr 21 15:15:25 1998
Response via : Multiple Level Calibration

Volume Inj. : 1uL
Signal Phase : DB-5
Signal Info : .53 mm



007F0101.D DRHA10.M Tue Apr 21 15:15:33 1998 Page 2

SOUTHWEST LABORATORY OF OKLAHOMA, INC.

Standard Operating Procedure

Ammonia as Nitrogen (Titrimetric with Distillation)

Document No.: SWL-IN-504

Rev No. / Date: Rev. 2.2 — 05/17/00

OFFICIAL COPY RED STAMP INDICATES ORIGINAL

APPROVALS	DATES
Procedure Prepared By	5-18-00
Program Manager or Section Supervisor	5-18-00
Laboratory Safety Officer	5/19/2000
Laboratory QA/QC Officer	5/18/00

(Effective Date is 5 calendar days after the last signature above - QA/QC Officer)

Document Status

[ ] Controlled DC No. _____ Issued to: _____ Date: _____ QA: _____

[✓] Official Copy OC No.: 2441 Issued to: Darla Mavon Date: 12/19/00 QA: CFH

AMMONIA AS NITROGEN (TITRIMETRIC WITH DISTILLATION)

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of Ammonia as Nitrogen in drinking, surface, and saline waters, soils, sediments, and sludges. It coveres USEPA method 350.2 and Standard Methods 4500-NH_3A-C. All QC requirements of each are covered using the stricter requirement where applicable.

1.2 After distillation, the Ammonia is determined by the titrimetric method which is applicable to concentrations above 1 mgN/L (waters) and 10 mgN/Kg (soils).

2.0 METHOD SUMMARY — This method is based on the distillation of ammonia in a borate buffer at pH 9.5 and subsequent reaction of the distillate with indicating boric acid solution, which is then titrated with sulfuric acid.

3.0 HEALTH AND SAFETY

3.1 Refer to the current version of the "Laboratory Safety Plan" SOP.

3.2 Each chemical and sample should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. This may be done by wearing gloves, eye protection, and laboratory coat during distillation and analysis.

3.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS: Sulfuric Acid, Sodium Hydroxide.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING & STORAGE

4.1 Samples may be preserved by H_2SO_4 at pH between 1.5 and 2 and stored at 4°C.

4.2 Samples should be collected in plastic or glass bottles. All containers must be thoroughly cleared and rinsed with reagent water.

5.0 INTERFERENCES — Volatile alkaline compounds such as hydrazine and amines will influence titrimetric results.

6.0 APPARATUS

6.1 Distillation Apparatus

6.1.1 500 mL borosilicate boiling flask

6.1.2 Vertical condenser

6.1.3 500 mL receiving beakers

6.1.4 Boiling flask heating mantel

6.1.5 pH paper

6.2 Titration apparatus

6.2.1 50 mL Class A T-buret with Teflon stopcock

6.2.2 Buret support

7.0 REAGENTS

7.1 ASTM Type II Water (ASTMD 1193): Water should be monitored to be Ammonia free.

7.2 Sulfuric Acid, H_2SO_4: Concentrated, Tracepur.

7.3 Borate buffer solution: Add 88 mL 0.1 N NaOH solution to 500 mL approximately 0.025 M sodium tetraborate ($Na_2B_4O_7$) solution (9.5 g $Na_2B_4O_7$ • 10 H_2O/L) and dilute to 1 liter.

7.4 Sodium Hydroxide. 6N: Dissolve 240 g NaOH in beaker and dilute to 1 L.

7.5 Mixed indicator solution: Mix 2 volumes of 0.2% methylene in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol.

7.6 Indicating boric acid solution: Dissolve 20 g H_3BO_3 in water. Add 10 mL mixed indicator solution and dilute to 1 L.

7.7 Standard sulfuric acid titrant, 0.02N: Standardize with Na_2CO_3.

8.0 PROCEDURE

8.1 Distillation

8.1.1 The distillation apparatus should be precleaned before use to make sure it is Ammonia free.

8.1.2 Place 100 mL (water) or 10 g (soils) of sample into distillation boiling flask with 20 mL of borate buffer solution and 100 mL of distilled H_2O. Adjust pH to 9.5 with NaOH solution. Attach to condenser.

8.1.3 Put 50 mL of indicating boric acid solution into receiving beaker, and put tip of the delivery tube below the surface of acid solution.

8.1.4 Distill at a rate of 6-10 mL/min. until about 100 mL of distillate has been collected.

8.1.5 Remove delivery tube from collection beaker and titrate.

8.2 Titration

8.2.1 Titrate Ammonia in distillate with standard 0.02 N H_2SO_4. Titrate until indicator turns a pale lavender.

8.2.2 Carry a blank through all steps of the procedure and apply the necessary correction to the results.

9.0 CALCULATION

9.1 Liquid Samples

$$\text{mg } NH_3 \text{ - N/L} = \frac{(A-B) \times 280}{\text{mL sample}}$$

9.2 Soil Samples

$$\text{mg } NH_3 \text{ - N/Kg} = \frac{(A-B) \times 280}{\text{g weight sample}}$$

where:

A = Volume of H_2SO_4 titrated for sample (mL)
B = Volume of H_2SO_4 titrated for blank (mL)

10.0 QUALITY ASSURANCE/QUALITY CONTROL

10.1 Ensure all quality control documentation is readily available.

10.2 Analyze one standard at the detection limit (PQL) with each batch of samples.

10.3 Analyze at least one method blank carried through the whole procedure (PBW).

10.4 Analyze a laboratory control sample (LCW) and laboratory control sample duplicate (LDW) with each batch of samples.

10.5 At the client's request a matrix spike (MS) and matrix spike duplicate (MSD) will be analyzed with each batch of samples.

11.0 WASTE DISPOSAL / POLLUTION PREVENTION— All samples and chemicals will be disposed of as per instruction in SOP SWL-GA-114 "Hazardous Waste Management Plan".

12.0 METHOD PERFORMANCE

12.1 The result of the method blank must be below the reporting limit.

12.2 The control limit of the laboratory control sample is 20% RPD and 80-120% recovery.

12.3 The control limits for MS-MSD are 75-125% recoveries and 25% RPD: Measurements outside these limits are flagged.

13.0 REFERENCES

13.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, APHA-AWWA-WPCF, Method 4500-NH_3-A – C.

13.2 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-010, March 1983, Method 350.2.

14.0 DEFINITIONS

14.1 Material Safety Data Sheet (MSDS):..... Information provided by vendors for the chemical products prepared by their company. The information on the MSDS includes but is not limited to composition, physical properties, hazards identification, first aid measures, emergency clean-up and/or response, exposure and storage.

14.2 Sample Batch: ..... Consists of a maximum of twenty samples per matrix.

14.3 Method Blank: ..... A distilled water sample carried through the entire preparation and analysis procedure to check for contamination.

14.4 Laboratory Control Sample: ..... A spiked sample taken through distillation and analysis to check the methods accuracy.

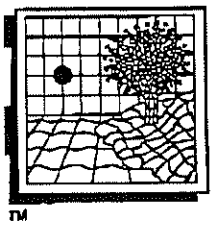
14.5 Matrix Spike (MS): ..... A spiked sample taken through the distillation and analysis to check the effect of the matrix on the accuracy of the method.

14.6 Matrix Spike Duplicate (MSD):..... A spiked sample taken through the distillation and analysis to check the effect of the matrix on the precision and accuracy of the method.

15.0 ATTACHMENTS

15.1 Ammonia as Nitrogen Standard Batch Form

ATTACHMENT 1
Ammonia as Nitrogen Standard Batch Form



AMMONIA AS NITROGEN STANDARD BATCH FORM

INORGANICS DEPARTMENT

AMMONIA AS NITROGEN STD. BATCH FORM (IN504F1.DOC) SWL-IN-504 REV. 2.2 PAGE _____

Analyst: _____ **Date:** _____ **Reagent (Standards) Batch ID:** _____

REAGENTS FOR AMMONIA AS NITROGEN

REAGENT	*LOT #*
Sulfuric Acid	_____
NaOH	_____
M Sodium Tetraborate	_____
Methylene	_____
Ethanol	_____
Boric Acid	_____
Na_2CO_3	_____

STANDARD PREPARATION

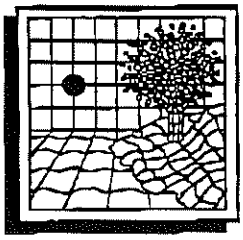
Stock solution ID: _____

Standard Ammonia as Nitrogen solution:

100ml (Stock NH_3-N solution) ⟹ 1000ml

Analyst:_____

NOTE: The above standard was brought to volume with DI water and has a final conc. of **1.00ml = 10.00ug Ammonia as Nitrogen.**



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SOUTHWEST LABORATORY OF OKLAHOMA, INC. *and*
AMERICAN ANALYTICAL & TECHNICAL SERVICES, INC.

Standard Operating Procedure

Anions in Water by Ion Chromatography

Document No.: SWL-IN-301

Rev No. / Date: Rev. 4.0 — 07/19/00

OFFICIAL COPY RED STAMP INDICATES ORIGINAL

APPROVALS	DATES
Procedure Prepared By	8-29-00 Date
Program Manager or Section Supervisor	8-29-00 Date
Laboratory Safety Officer	9/6/2000 Date
Laboratory QA/QC Officer	9/6/00 Date

(Effective Date is 5 calendar days after the last signature above - QA/QC Officer)

Document Status

[ ] Controlled DC No. _____ Issued to: _____ Date: _____ QA: _____

[✓] Official Copy OC No.: 2441 Issued to: Daria Navon Date: 12/19/00 QA: SFH

ANIONS IN WATER BY ION CHROMATOGRAPHY

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions; Bromide, Chloride, Nitrate-N, Nitrite-N, Ortho-Phosphate-P, Sulfate, and Fluoride. This procedure covers EPA methods 300.0 and 9056. All QC requirements of each method are covered using the stricter requirement where applicable.

1.2 This method is applicable to the determination of the above anions in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, and solids (after extraction).

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of sample matrix spikes covering the anions of interest.

2.0 METHOD SUMMARY

2.1 A 1.0 milliliter volume of sample is introduced into the ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

2.2 In order to use this method for solids, an extraction procedure must be performed.

3.0 HEALTH AND SAFETY

See Standard Operating Procedure "*Laboratory Safety Plan*", SWL-GA-111.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING & STORAGE

4.1 Samples should be collected in scrupulously clean glass or polyethylene bottles.

4.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
NO_3-NO_2	Cool to 4°C	28 days
O-Phosphate-P	Cool to 4°C	24 hours
Sulfate	Cool to 4°C	28 days
Fluoride	Cool to 4°C	28 days

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

5.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

5.2 Method interferences may be caused by contaminants in the reagents water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

5.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

6.0 EQUIPMENT / APPARATUS

6.1 Balance – M ettler/H80, capable of accurately weighting to the nearest 0.0001g.

6.2 Ion Chromatograph – Dionex Model 2010i or DX100 with required accessories including syringes, analytical columns, compressed gases, and detectors.

6.3 Anion guard column – Dionex Ion Pac AG14-4mm.

6.4 Anion separator column – Dionex Ion Pac AS14-4mm

6.5 Anion suppressor device –Dionex Anion Micro-Membrane Suppressor (P/N 43074).

6.6 Detector – Dionex Conductivity Cell.

6.7 VG Chromatography server and mini-chrom data system.

7.0 REAGENTS

7.1 Reagent water – Deionized water, free of the anions of interest. The water must be filtered through a 0.20-micron filter.

7.2 Eluent Solution – Sodium bicarbonate 0.5 M, sodium carbonate 0.5 M. Dissolve 26.5g of sodium carbonate (Na_2CO_3) per 500 ml reagent DI water. Dissolve 21.25g sodium bicarbonate ($NaHCO_3$) per 500 ml reagent water. Use 14ml of the sodium carbonate 0.5 M solution and 4 ml of the sodium bicarbonate 0.5 M solution in a 2000ml volumetric flask and bring up to volume with reagent water.

7.3 Regeneration solution – Sulfuric acid, 0.025 N. Dilute 2.8ml conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

7.4 Stock Standard solutions, 10,000 mg/l – Certified stock standards for all anions are purchased from SPEX Industries, Inc. (or another NIST-certified manufacturer), and are the bases for all working standards.

7.5 Intermediate Standard – Dilute the 10000ppm stock standards to 500ml according to the following schedule: 2.5ml Br^- (50ppm), 2.5ml Cl^- (50ppm), 12.5mls NO_3^- (25ppm), 1.0ml NO_2^- (20ppm), 1.0mls PO_4^- (20ppm), 1ml F^- (20ppm), and 5.0ml SO_4^- (100ppm).

7.6 Working Standards (Method 2010i):

7.6.1 Number 1 Standard – Dilute 125ml of the Intermediate Standard (Section 7.5) to 250ml in reagent water to obtain the following concentrations: 25ppm Br^-, 25ppm Cl^-, 12.5ppm NO_3^-, 10ppm NO_2^-, 10ppm PO_4^-, 10ppm F^-, and 50ppm SO_4^-.

7.6.2 Number 2 Standard – Dilute 25ml of the Intermediate Standard (Section 7.5) to 25ml in reagent water to obtain the following concentrations: 5ppm Br^-, 5ppm Cl^-, 2.5ppm NO_3^-, 2ppm NO_2^-, 2ppm PO_4^-, 2ppm F^-, and 10ppm SO_4^-.

7.6.3 Number 3 Standard – Dilute 5ml of the Intermediate Standard (Section 7.5) to 100ml in reagent water to obtain the following concentrations: 2.5ppm Br^-, 2.5ppm Cl^-, 1.25ppm NO_3^-, 1.0ppm NO_2^-, 1.0ppm PO_4^-, 1.0ppm F^-, and 5.0ppm SO_4^-.

7.6.4 Number 4 Standard – Dilute 2ml of the Intermediate Standard (Section 7.5) to 100ml in reagent water to obtain the following concentrations: 1.0ppm Br^-, 1.0ppm CL^-, 0.5ppm NO_3^-, 0.4ppm NO_2^-, 0.4ppm PO_4^-, 0.4ppm F^-, and 2.0ppm SO_4^-.

7.6.5 Number 5 Standard – Dilute 0.5ml of the Intermediate Standard (Section 7.5) to 100ml in reagent water to obtain the following concentrations: 0.25ppm Br^-, 0.25ppm Cl^-, 0.125ppm NO_3^-, 0.10ppm NO_2^-, 0.10ppm PO_4^-, 0.10ppm F^-, and 0.5ppm SO_4^-.

7.7 Initial Calibration Verification – A certified premixed standard is purchased from SPEX Industries, Inc. (or another NIST-certified manufacturer) and should have the following approximate concentrations: 10ppm Br^-, 25ppm Cl^-, 10ppm NO_3^-, 5ppm NO_2^-, 10ppm PO_4^-, 5ppm F^-, and 25ppm SO_4^-.

8.0 PROCEDURE

8.1 Instrument analysis – Refer to the procedure as listed in the instrument manual.

8.2 Calibration and Standardization

8.2.1 Inject 1.0ml of the mid-range calibration standard.

8.2.2 Using the retention times from this standard, build your calibration table entering the concentrations for each standard, in Calibration Menu of Dionex Mini-chrome software.

8.2.3 Using injection of 1.0ml of each calibration standard, tabulate peak area against the concentration. The results will be used to prepare a calibration curve for each

analyte. The coefficient for each anion should be 0.995 or better in the Cal Plot Menu of the mini-chrome software.

8.2.4 A minimum of three calibration standards must be used. A calibration is required at a minimum of once a month.

8.2.5 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 10 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that anlayte.

8.3 Analysis

8.3.1 Start the system and prime the column by injecting a standard. Then check the calibration as described in Section 8.2.

8.3.2 Load and inject 1.0 – 2.0ml of well mixed samples. Flush the injection loop thoroughly, using each new sample. Use the same size loop for standards and samples.

8.3.3 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards.

8.3.4 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

8.3.5 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

8.3.6 The following extraction should be use for solid materials. Weigh 10.0g of sample into a plastic 4oz sample container. Add 100ml of deionized water. Shake for 10-20 minutes in a mechanical shaker. Pour slurry into a 40ml VOA vial, and centrifuge for 30min. Filter the supernatant through a 0.2 micron I.C. filter, and load autosampler as normal.

8.4 Write-up and review

8.4.1 Transfer electronic data to the inorganic database, print out run log, complete write-up, and upload data to LIMS. Refer to Inorganic Database SOP SWL-IN-108 for procedure and forms.

8.4.2 Review data according to the guidelines in Section 10.0 and 12.0 of this SOP and "1st and 2nd Data Review for Wet Chemistry" SOP SWL-IN-107.

9.0 CALCULATIONS

9.1 Results are printed in mg/l. No calculations are necessary for waters.

9.2 For Soils:

$$mg/kg = \frac{(R \times V)}{g}$$

Where: R = result in mg/l
V = Volume of reagent water added for the extraction (milliliters)
g = the grams of the sample used in the extraction

10.0 QUALITY ASSURANCE / QUALITY CONTROL

10.1 Immediately after the calibration has been established, the calibration must be verified for every analyte by the analysis of an Independent Standard (ICV). When measurements exceed the 90-110% confidence interval, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

10.2 A Calibration Verification (CCV) and a Calibration Blank (CCB) must be ran every 10 analytical samples and after the last sample. The CCV must agree within 90-110% recovery of the expected value with less than a 5% variation from the previous or subsequent CCV, and the CCB must be below the reporting limit. If they are not, terminate the analysis, correct the problem, and recalibrate the instrument.

10.3 The following QC samples must be analyzed with every batch of 20 samples per matrix:

10.3.1 Preparation Blank – result must be below the Reporting limit for the analyte of interest, or the analysis must be terminated and samples re-prepared.

10.3.2 Laboratory Control Sample and Laboratory Control Sample Duplicate – Measurements must be within 90-110% recovery, or the analysis must be terminated and samples re-prepared.

10.3.3 Matrix Spike and Matrix Spike Duplicate – If Measurements fall outside of 80-120% R the data will be flagged. The following procedure will be followed for matrix spikes:

10.3.3.1 Waters – Add 10µl of a 10,000mg/l stock standard for each analyte and bring up to a final volume of 5ml with the sample, giving a spike value of 20 mg/l.

10.3.3.2 Soils – Add 0.2ml of 10,000 mg/l stock standard for each analyte to 10g of sample. Follow the soil extraction procedure in Section 8.3.6, thus giving a 20 mg/l or 200 mg/kg spike value.

10.4 Reprocessing of QC integrations should be avoided. When performed, they must be printed out, signed by the analyst attached to a Non-Conformance Report and reviewed by the supervisor. The Non-Conformance is to be discussed in the case Narrative and a copy of the report is to be included with the data to the client.

11.0 WASTE DISPOSAL/POLLUTION PREVENTION

Refer to the current version of the "*Hazardous Waste Management Plan*", SWL-GA-114.

12.0 METHOD PERFORMANCE

12.1 Preparation Blank – result must be below the Reporting limit for the analyte of interest, or the analysis must be terminated and samples re-prepared.

12.2 Laboratory Control Sample and Laboratory Control Sample Duplicate – Measurements must be within 90-110% recovery, or the analysis must be terminated and samples re-prepared.

12.3 Matrix Spike and Matrix Spike Duplicate – If Measurements fall outside of 80-120% R the data will be flagged. The following procedure will be followed for matrix spikes:

12.3.1 Waters – Add 10µl of a 10,000mg/l stock standard for each analyte and bring up to a final volume of 5ml with the sample, giving a spike value of 20 mg/l.

12.3.2 Soils – Add 0.2ml of 10,000 mg/l stock standard for each analyte to 10g of sample. Follow the soil extraction procedure in Section 8.3.6, thus giving a 20 mg/l or 200 mg/kg spike value.

13.0 REFERENCES

13.1 U.S. Environmental Protection Agency, Methods for the Determination of Inorganic Substances in Environmental Samples, August 1993, Method 300.0.

13.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition, APHA-AWWA-WPCF, Method 4110, pp. 4-1 to 4-5.

13.3 SW846 Method 9056 Rev. 0, September 1994.

13.4 Southwest Laboratory Standard Operating Procedures listed in text.

14.0 DEFINITIONS

None required. Terminology is explained in text.

15.0 ATTACHMENTS

Attachment 1: Anions in Water Standard Batch Form

ATTACHMENT 1
Anions in Water Standard Batch Form

ANIONS IN WATER STANDARD BATCH FORM

INORGANICS DEPARTMENT

ANIONS STD. BATCH FORM (IN301F1.DOC) SWL-IN-301, REV. 4.0

Analyst: _____ Date: _____ Reagent (Standards) Batch ID: _____

REAGENTS FOR ANIONS IN WATER

REAGENT	LOT #
Sodium Bicarbonate ($NaHCO_3$)	
Sodium Carbonate (Na_2CO_3)	
Sulfuric Acid	

SOLUTION ID

Solution	Solution ID #
ICV	
CRI/Low STD	
CCV/Mid STD	
Matrix Spike	
Intermediate Standard 1	
Intermediate Standard 2	
High Standard	

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