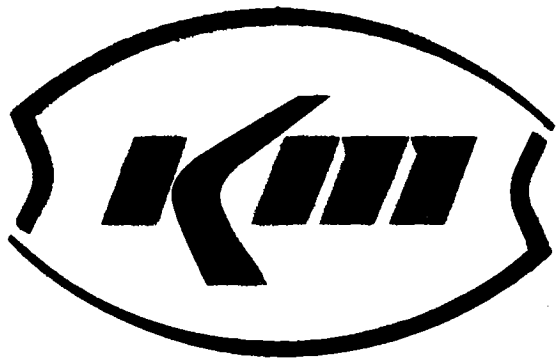
KERR-McGEE CHEMICAL CORPORATION



HENDERSON, NEVADA FACILITY
SAMPLING AND ANALYSIS PLAN

AUGUST 1993

SAMPLING AND ANALYSIS PLAN
KERR-McGEE CHEMICAL CORPORATION
HENDERSON, NEVADA

Prepared By:

Roy K. Widmann
Hydrology Department
Kerr-McGee Corporation

August 16, 1993

TABLE OF CONTENTS

TABLE OF CONTENTS - continued

ILLUSTRATIONS

SAMPLING AND ANALYSIS PLAN
KERR-McGEE CHEMICAL CORPORATION
HENDERSON, NEVADA

1. INTRODUCTION

Kerr-McGee Chemical Corporation (KMCC), has prepared this Sampling and Analysis Plan for the electrolytic facility in Henderson, Nevada. The Sampling and Analysis Plan describes in detail collection protocols for groundwater samples, surface water samples, and surface and sub-surface soil samples. Also included are details on field and laboratory quality assurance/quality control programs, laboratory analyses and monitor well installation and abandonment procedures.

This document is to be used by all facility personnel and consultants responsible for obtaining types of samples described above or who are responsible for monitor well installation/abandonment. A copy of this plan will be kept on file at the facility for the appropriate personnel to review and reference.

2. GROUNDWATER SAMPLING PROTOCOL

Groundwater sampling from wells is required to define and document any potential impacts to native groundwater quality resulting from facility operations. In order to ensure that the analytical data developed for the groundwater is accurate, the sampling personnel must be certain that the collected sample is representative of the groundwater system that exists around the monitoring well.

2.1 SAMPLING TEAM MEMBERS

It is the responsibility of Kerr-McGee Chemical Corporation's environmental personnel to collect or supervise the collection of all routine groundwater monitor well samples at the facility.

2.2 WELL LOCATIONS AND SAMPLING FREQUENCY

All monitoring wells are readily accessible and are readily apparent. Keys for the off-site wells are kept at the facility and are under the control of facility environmental personnel. Most on-site monitor wells are not locked.

Both the frequency of sampling and analytical parameters list are per agreement between KMCC and the regulatory agency. In the event new monitor wells are installed that require sampling as agreed between KMCC and the regulatory agency, sampling of the wells will occur during the next regularly scheduled sampling event.

2.3 STEPS TAKEN PRIOR TO SAMPLE WITHDRAWAL

2.3.1 Initial Observations

Field personnel who sample KMCC groundwater monitor wells make note of the general well and site conditions upon arrival on an appropriate field sampling log (Figure 1). An inspection of all monitor wells is made to ensure their surface and sub-surface integrities. For example, general comments about the weather conditions for each sampling date are recorded. Specific comments on each of the wells are then made, with typical notations to

FIGURE 1:

Kerr McGee Chemical Corporation
Field Sampling Log

Well ID _____ Personel Involved _____
Date _____ _____
Time _____

Weather : _____

Well Condition : _____

Well Information :
Depth to Water _____
Depth of Well _____ (see completion data)
Calculated 3 casing Volumes _____
Well Evacuation Method _____
Final Evacution Volume _____

Equipment Information :
pH meter model # _____ Serial # _____
pH Calib Std _____ Lot # _____ Exp _____
_____ Lot # _____ Exp _____

SC meter model # _____ Serial # _____
SC Calib Std _____ Lot # _____ Exp _____

Field Measurements :

Time	Vol Evac	pH	Temp	SC	Observtions
pH Std					
SC Std					
pH Std					
SC Std					

Sample Apperance : _____

Sample Collection:
Time Started _____ Method _____
Time Finished _____ Bottles _____

include, but not be limited to, whether a well is in a flooded area, ground subsidence, the presence of nearby desiccation cracks, etc.

A notation concerning missing well locks or caps is made if appropriate. Observations related to the physical condition of the well are recorded if it appears the well has been damaged (for example, from vandalism, being struck by a vehicle, etc.). It is the responsibility of the facility environmental personnel to maintain the monitor wells in good repair.

2.3.2 Measurement of Static Water Level and Well Depth

After all general and pertinent observations are recorded, the field technician will measure a static water level in all facility groundwater monitor wells that are sampled. The well cap is removed and laid upside down on the ground or placed in the field vehicle. An electric water level indicator is tested to make sure it is operational. The probe is lowered downhole until the fluid level is detected. The depth to fluid is then recorded (field sampling log) to the nearest 0.01 foot with respect to the reference point (either a mark or a notch) at the top of the casing. All reference points have been measured in relation to mean sea level by a licensed surveyor.

Total well depth is measured with the water level indicator by lowering the probe downhole until it touches the bottom of the well. Total depth measurement is then recorded on the field

sampling log (Figure 1) to the nearest 0.01 foot with respect to the same measuring point from which depth to fluid measurements are made.

The cable on the electric water level indicator is subject to breakage from time to time, particularly when it becomes stuck downhole in wells which have dedicated sampling pumps. When this occurs, the repaired water level indicator often results in lengths of cable which have been cut-off. The marked footage on the cable is no longer accurate, although the meter itself still is operational. It is then necessary for the field technician to correct his depth to water and total well depth measurements by subtracting from his field measurements that length of missing cable. For example, if 40 feet of cable is missing from the cable and the depth to water is 10 feet below grade, the water level indicator would "measure the apparent depth to water" as 50 feet below grade, but the field technician knows to subtract 40 feet from his measurement. All measurements reported to the regulatory agency have been corrected for any missing length of cable.

Following depth to fluid and total well depth measurements, the probe is cleaned and rinsed in distilled/deionized water and wiped with a disposable towel.

2.4 WITHDRAWING A WATER SAMPLE

2.4.1 Calculating Volume of Water to be Evacuated

It is standard practice to evacuate a minimum of three casing

volumes from each well before obtaining a sample. There are instances, however, where well recovery is extremely slow and three casing volumes cannot be removed. When this occurs, the well is evacuated to near dryness and sampled after sufficient volume of water is available to obtain the necessary volume of water required for analyses. Regardless of well capacity, samples for volatile organic analysis (VOA) will be withdrawn from the well within one (1) hour of purging. The volume of water purged from each well before obtaining a sample is recorded (field sampling log) by the field technician.

KMCC has prepared a table (Table 1) used by sampling personnel in determining the amount of fluid to be evacuated from various size monitor wells. In instances where the table is not useful, the field technician will calculate the volume of fluid he should remove by using the conversion factors of 0.16, 0.37, 0.65, 1.02 and 1.47 gallons per foot of water in well for 2, 3, 4, 5 and 6 inch diameter wells, respectively. For example, given a 2 inch well with 40 feet of standing fluid:

40 ft. x 0.16 gals/ft = 6.4 gals. per casing volume

-therefore, 19.2 gallons of fluid would need to be evacuated before a sample is taken (3 casing volumes)

TABLE 1: VOLUME OF WATER TO BE PURGED FROM VARIOUS SIZE MONITOR WELLS

AMOUNT (FEET) OF FLUID IN WELL	# Gals to Evacuate One Casing Volume					# Gals to Evacuate Two Casing Volumes					# Gals to Evacuate Three Casing Volumes				
	2"	3"	4"	5"	6"	2"	3"	4"	5"	6"	2"	3"	4"	5"	6"
1.0	0.16	0.37	0.65	1.02	1.47	0.32	0.74	1.30	2.04	2.94	0.48	1.11	1.95	3.06	4.41
2.0	0.32	0.74	1.30	2.04	2.94	0.64	1.48	2.60	4.08	5.88	0.96	2.22	3.90	6.12	8.82
3.0	0.48	1.11	1.95	3.06	4.41	0.96	2.22	3.90	6.12	8.82	1.44	3.33	5.85	9.18	13.23
4.0	0.64	1.48	2.60	4.08	5.88	1.28	2.96	5.20	8.16	11.76	1.92	4.44	7.80	12.24	17.64
5.0	0.80	1.85	3.25	5.10	7.35	1.60	3.70	6.50	10.20	14.70	2.40	5.55	9.75	15.30	22.05
6.0	0.96	2.22	3.90	6.12	8.82	1.92	4.44	7.80	12.24	17.64	2.88	6.66	11.70	18.36	26.46
7.0	1.12	2.59	4.55	7.14	10.29	2.24	5.18	9.10	14.28	20.58	3.36	7.77	13.65	21.42	30.87
8.0	1.28	2.96	5.20	8.16	11.76	2.56	5.92	10.40	16.32	23.52	3.84	8.88	15.60	24.48	35.28
9.0	1.44	3.33	5.85	9.18	13.23	2.88	6.66	11.70	18.36	26.46	4.32	9.99	17.55	27.54	39.69
10.	1.60	3.70	6.50	10.20	14.70	3.20	7.40	13.00	20.40	29.40	4.80	11.10	19.50	30.60	44.10
15.	2.40	5.55	9.75	15.30	22.05	4.80	11.10	19.50	30.60	44.10	7.20	16.65	29.25	45.90	66.15
20.	3.20	7.40	13.00	20.40	29.40	6.40	14.80	26.00	40.80	58.80	9.60	22.20	39.00	61.20	88.20
25.	4.00	9.25	16.25	25.50	36.75	8.00	18.50	32.50	51.00	73.50	12.00	27.75	48.75	76.50	110
30.	4.80	11.10	19.50	30.60	44.10	9.60	22.20	39.00	61.20	88.20	14.40	33.30	58.50	91.80	132

2.4.2 Well Evacuation

Well evacuation is performed with the use of teflon or stainless steel bailers and attached polyethylene rope or with dedicated pneumatic bladder pumping systems (i.e, Well Wizard by QED Groundwater Specialists). Purging/sampling equipment is inspected for damage prior to each use, and either repaired (if possible) or replaced.

When well purging is performed with bailers, a clean plastic sheet or a 30 gallon trash can lined with clean plastic is placed adjacent to the monitor well to keep the bailer and rope from coming in contact with the ground. This procedure is done to prevent the bailer and rope from possibly becoming contaminated from touching the ground before, during and after the bailing and sampling process.

Well evacuation with a bailer is performed by gently lowering the bailer downhole to prevent de-gassing of the fluid column. The bailer is allowed to fill and is then retrieved from the well. All purged water is disposed of at the discretion of the property owner.

In case of poorly yielding wells where three casing evacuations cannot be made, the well is allowed to recover one hour before collecting VOA samples. The well is then allowed to recover further until enough sample volume can be removed for the remaining

necessary analyses. This may require going back to a well several hours after it was initially bailed to dryness or returning the following day to obtain the remaining samples.

For wells equipped with a dedicated pneumatic bladder pumping system, purging is performed according to the manufacturer's recommendations, using the manufacturer's-supplied pump controller panel and power source.

2.4.3 Field Measurements and Field QA/QC Procedures

A minimum of four (4) separate groundwater samples will be collected in inert containers (i.e, plastic beakers or glass bottles) during the purging process for the field determination of pH, specific conductivity and temperature. The data will be recorded on the field sampling log.

Before the pH measurements are performed, the pH meter is calibrated following manufacturer's recommendation in pH 7 and pH 4 or pH 7 and pH 10 buffer solutions. Calibration notes are recorded in a field calibration notebook.

Following standardization, the pH probe is rinsed in distilled or deionized water and then immersed in the first field sample for a pH determination. The pH of the sample is allowed to equilibrate before the reading is recorded (field sampling log).

Following equilibration and recording, the probe is rinsed with deionized water and placed in the second field sample. This method of equilibration, recording and rinsing is followed until the four pH measurements are made. The samples are then discarded and the containers are rinsed with deionized water.

Conductivity measurements are made on four samples following calibration of the meter according to manufacturer's recommendations. Following calibration, the meter is checked in a solution of 10,000 umhos/cm^3. Again, calibration notes are recorded in a field calibration notebook.

The conductivity probe is then rinsed with deionized water and placed in one of the field samples. Allowing 2-3 minutes for equilibration, the conductivity and temperature of the samples is then recorded (field sampling log) followed by a thorough rinsing of the probe in deionized water. The remaining three samples are treated in the same manner until the four conductivity measurements have been recorded. The samples are then discarded and the containers are rinsed with deionized water.

2.4.3.1 Field Blanks - Field blanks are not generally collected. When field blanks are collected, however, they are prepared by contacting deionized water with the sampling equipment, followed by filling the appropriate bottles and submitting them to the laboratory with the rest of the samples. This action serves as a measure of decontamination effectiveness.

2.4.3.2 Trip Blanks - Trip blanks are provided by the laboratory only when sampling events include analysis for volatile organic compounds. Contaminants found in the analysis of trip blanks may be attributed to 1) an interaction between the sample and container or 2) a handling/storage procedure. Trip blank procedures would be required under conditions in which volatiles are present in the groundwater samples so that possible sample contaminant sources could be identified. Analytical requirements of the facility are not directed toward volatiles, and therefore trip blanks are not ordinarily sent.

2.4.4 Sample Collection

Following well purging and field measurement determinations, sample containers are filled in the following order: 1) volatile organics (collected within one (1) hour of well purging), 2) volatile organic halogens, 3) total organic halogens, 4) total organic carbon, 5) extractable organics, 6) total metals, 7) dissolved metals, 8) phenols, 9) cyanide, 10) sulfate and chloride, 11) turbidity, 12) nitrate and ammonia, 13) radionuclides. KMCC has contracted with Environmental Technologies (ET) of North Las Vegas, Nevada to do the laboratory analyses.

All sample bottles, "blue ice" and labels are shipped or delivered to the KMCC facility by ET. The bottles provided have been pre-cleaned according to SW-846 methodology, and if requested by KMCC, may already contain preservatives upon arrival at the facility.

Water samples for laboratory analyses are taken from the dedicated pump discharge line or poured from the stainless steel bailer into appropriate clean containers. Sample containers for organic analyses are amber glass bottles with teflon-lined caps. Samples requiring volatile organic analyses are small glass vials with teflon septa. Samples for inorganic metal analyses are collected in either glass or plastic containers. All sample containers, particularly those which are to be used for organic analyses are filled to the top to eliminate any headspace and therefore the possible change in certain volatile constituents. Preservation methods and holding times for each analytical parameter, as well as the sample container type are included on Table 2.

2.4.5 Sample Filtering

Samples that require dissolved metals analyses are field filtered through a 0.45u filter before being preserved with nitric acid. In the event excessive suspended sediment is present in the samples that greatly hinders the ability to field filter, the samples will be sent to the laboratory for filtration before any further preservatives are added. KMCC reserves the right to collect samples for dissolved metals anytime samples requiring total metals analyses are collected.

2.4.6 Split Sampling Events

In the event an authorized regulatory agency wishes to obtain split samples, it is the agency's responsibility to supply their own

TABLE 2: SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

VOLATILE ORGANICS

Matrix	Container	Minimum Sample Size	Preservative	Holding Time (from date sampled)
Residual Cl-not present	3 vials with Teflon lined septum	40 ml/vial	4 drops conc. HCl, 4°C	14 days
Residual Cl-present	3 vials with Teflon lined	40 ml/vial	4 drops of 10% $Na_2O_3S_2$, 4 drops conc. HCl, 4°C	14 days
Acrolein & Acrylonitrile.	3 vials with Teflon lined	40 ml/vial	adjust pH 4-5, 4°C	14 days
Soil/Sediments & Sludges	Glass jar with Teflon liner or core tube	50 g	4°C	14 days
Concentrated waste samples	Glass jar with Teflon liner or core tube	50 g	none	14 days

The above information applies to the following parameters and methods:

Parameter	Method
Volatile Halocarbons	601/8010 (GC)
Volatile Aromatics	602/8020 (GC)
Volatile Organics	624/8240/8260 (GC/MS)
Acrolein/Acrylonitrile	603/8030 (GC)

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

SEMI-VOLATILE ORGANICS

Matrix	Container	Minimum Sample Size	Preservative	Holding Time (from date sampled)
Residual Cl-not present	1 liter glass with Teflon liner	2 liter	4°C	Samples must be extracted w/in 7 days and analyzed w/in 40 days of extraction.
Residual Cl-present	1 liter glass jar with lined septum caps	2 liter	3 ml of 10% $Na_2O_3S_2$ 4°C	Samples must be extracted w/in 7 days and analyzed w/in 40 days of extraction.
Soil/Sediments & sludges	Glass jar with Teflon liner or core tube	100 g	4°C	Samples must be extracted w/in 14 days and analyzed w/in 40 days of extraction.
Concentrated waste samples	Glass jar with Teflon liner or core tube	100 g	none	Samples must be extracted w/in 14 days and analyzed w/in 40 days of extraction.

The above information applies to the following parameters and methods:

Parameter	Method
Phenols	604/8040 (GC)
Phthalate Esters	606/8060 (GC)
Organochlorine Pesticides/PCB's	608/8080 (GC)
Polynuclear aromatic hydrocarbons	610/8310 (HPLC)
Organophosphorus Pesticides	614/8140 (GC)
Phenoxy acid Herbicides	615/8150 (GC)
Semi-Volatile Organics	625/8270 (GC/MS)
Carbamate & urea Pesticides	632 (HPLC)

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

MISCELLANEOUS ORGANICS

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative	Min Sample Size
Dioxins/ Furans	8280	Water	30 days extn. 45 days anal. (b)	1 liter glass jar	4°C	1000 ml
		Soil/Waste	30 days extn 45 days anal. (b)	Core tube or glass jar		50 g
Petroleum Hydrocarbons as gas	TPH-Gas Purge/trap (LUFT manual)	Water	14 days	3 vials w/teflon liners	4°c,HCL to pH<2	40 ml/vial
		Soil/Waste	14 days	Core tube/glass jar	4°C	100 g
Petroleum Hydrocarbons as gas	TPH-Gas Extractable (LUFT manual)	Water	14 days extn. 40 days anal.	2 liter glass	4°C,HCL	500 ml to pH<2
		Soil/waste	14 days extn. 40 days anal.	Core tube or glass jar	4°C	50 g
Petroleum Hydrocarbons as Diesel	TPH-Diesel Extractable (LUFT)	Water	14 days extn. 40 days anal.	2 liter glass	4°C jar	500 ml
		Soil/waste	14 days extn. 40 days anal.	Core tube or glass jar	4°C	100 g
Petroleum Hydrocarbons (TPH)	TPH-IR (418.1)	Water	28 days	1 liter glass	4°C, H_2SO_4 to pH<2	1000 ml

(a) extn: extraction anal: analysis
(b) from date of collection

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

METALS

Parameter	Method#	Matrix	Holding Time (from date sampled)	Container	Preservative (a)	Min Sample Size
Metals (ICP)	200.7/6010	Water	6 months	Poly	HNO_3 to pH <2.0	100 ml
		Soil/Waste	6 months	Core tube	4°C	10 g
Arsenic (GF-AA)	206.2/7060	Water	6 months	Poly	HNO_3 to pH <2,	100 ml
		Soil/Waste	6 months	Core tube glass jar	4°C	10 g
Mercury (CV-AA)	245.1/7470	Water	28 days	Poly	HNO_3 to pH <2.0,	100 ml
		Soil/Waste	28 days	Core tube	4°C	10 g
Selenium (GF-AA)	270.2/7740	Water	6 months	Poly	HNO_3 to pH <2.0,	100 ml
		Soil/Waste	6 months	Core tube glass jar	4°C	10 g
Silica	200.7/6010	Water	28 days	Poly	4°C	100 ml
		Soil/Waste	28 days	Core tube glass jar	4°C	10 g

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

METALS - CON'T

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Thallium (GF-AA)	279.2/7841	Water	6 months	Poly	HNO_3 to pH <2.0, 4°C	100 ml
		Soil/Waste	6 months	Core tube glass jar		10 g
Lead (GF-AA)	239.2/7421	Water	6 months	Poly	HNO_3 to pH <2.0, 4°C	100 ml
		Soil/Waste	6 months	Core tube glass jar		10 g
Chromium (III, VI)	220.7, 218.4 312B,7197	Water	24 hours	Poly	4°C	100 ml
		Soil/Waste	24 hours extn.	Core tube glass jar	4°C	10 g

(a) Listed preservative is for total metals. Dissolved or suspended metals require filtration prior to pH.

(b) extn: extraction

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

CONVENTIONAL ANALYSES

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Color	110.2	Water	48 hours	Poly	4°C	100 ml
Oil & Grease	413.1/413.2	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	1 liter
Specific	120.1	Water	28 days	Poly	4°C	50 ml
Acidity	305.1	Water	14 days	Poly	4°C	50 ml
pH	150.1	Water	ASAP	Poly	4°C	50 ml
Alkalinity	310.1	Water	14 days	Poly	4°C	50 ml
Hardness	200.7	Water	6 months	Poly	HNO_3 to pH<2	50 ml
Surfactants	425.1	Water	48 hours	Poly	4°C	100 ml
Gross Alpha, Beta & Radium	9310/9315	Water	6 months	Poly	HNO_3 to pH<2	2 liters
Odor	140.1	Water	ASAP	Glass	4°C	1 liter

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

CONVENTIONAL ANALYSES - con't

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Sulfite	377.1	Water	ASAP	Poly	4°C	100 ml
Sulfide	376.2	Water	7 days	Poly	4°C, NaOH to pH<9, $Zn(C_2H_3O_3)_2$	100 ml
Cyanide	335.1/335.2 335.3	Water	14 days	Poly	4°C, NaOH to pH<12	250 ml
Coliform Total & Fecal	909A, 909C	Water	6 hours	Sterile Poly	4°C, $Na_2S_2O_3$	100 ml
Bromide	Dionex	Water	28 days	Poly	4°C	50 ml
Chloride	300.0	Water	28 days	Poly	4°C	50 ml
Chlorine, Residual	330.1	Water	ASAP	Poly	4°C	100 ml
Fluoride	340.2	Water	28 days	Poly	4°C	50 ml
Iodine	Dionex	Water	28 days	Poly	4°C	50 ml
Total Organic Halogen (TOX)	9020	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	200 ml
Phenolics	420.1/420.2	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml

TABLE 2 - (con't): SAMPLE CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES
(from Environmental Technologies of Nevada, Inc., 1993)

CONVENTIONAL ANALYSES - con't

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Biochemical Oxygen Demand	405.1	Water	48 hours	Poly	4°C	100 ml
Chemical Oxygen Demand	410.4	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml
Total Organic Carbon (TOC)	415.1	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml
Ortho-phosphate	365.3	Water	48hours	Poly	4°C	100 ml
Phosphorous (Total)	365.3	Water	28 days	Glass	H_2SO_4 to pH<2	100 ml
Total Kjeldahl Nitrogen	351.2	Water	28 days	Glass	4°C, H_2SO_4 pH<2	100 ml
Ammonia	350.1	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	50 ml
Nitrite	354.1	Water	48 hours	Poly	4°C	50 ml
Nitrate	353.2/0 300.0	Water	48 hours	Poly	4°C	50 ml
Sulfate	300.0	Water	28 days	Poly	4°C	50 ml

collection containers and preservatives. Well purging will be done according to this Sampling and Analysis Plan, and sample containers will be filled alternately between KMCC and the regulatory agency.

2.4.7 Sample Preservation and Shipment

Immediately after collection, all samples are stored in an insulated sample shuttle (chest) and cooled to $4^{o}C$ with ice. Those samples to be analyzed for phenols or total organic carbon are additionally preserved with 1-2 ml of ultrapure sulfuric acid. Samples collected for total metals analyses are preserved with ultrapure nitric acid.

Samples are packed in ice and delivered to the contract laboratory within 24 hours of collection. Chain of custody forms accompany all samples.

2.4.8 Contaminated Equipment Disposal

All contaminated field equipment will be disposed of in accordance with applicable local, state and federal regulations.

2.5 FIELD CHAIN OF CUSTODY

Following sample collection, the field technician will prepare the shuttles for delivery to ET. The shuttles are packed with bottles, ice (or "blue ice"), and chain of custody forms (Figure 2). The shuttles are delivered to ET where they are inspected on arrival for evidence of breakage or tampering. The shuttle is then opened,

FIGURE 2:

CHAIN OF CUSTODY RECORD— ENVIRONMENTAL SAMPLES KM-4775

KERR-McGEE CORPORATION

FACILITY	SAMPLING FIRM	SAMPLE
NAME	NAME	☐ Effluent ☐ Groundwater
ADDRESS	ADDRESS	☐ Solid ☐ Surface Water
	SIGNATURE	☐

NO.	LOCATION	DATE	TIME	WEATHER		SAMPLE TYPE AND METHOD				TIMES CASING CLEARED	NO. OF CONTAINERS	ANALYSIS REQUIRED	REMARKS
				TEMP.	PREC.	COMP.	GRAB	MECH	MAN.				

RELINQUISHED BY (SIGNATURE) | RECEIVED BY (SIGNATURE) | DATE | TIME

RELINQUISHED BY (SIGNATURE) | RECEIVED BY (SIGNATURE) | DATE | TIME

RELINQUISHED BY (SIGNATURE) | RECEIVED BY (SIGNATURE) | DATE | TIME

DISPATCHED BY (SIGNATURE) | DATE | TIME | RECEIVED FOR LABORATORY (SIGNATURE) | DATE | TIME

CARRIER | LABORATORY

ADDRESS | ADDRESS

METHOD OF SHIPMENT

ADDITIONAL REMARKS

ALL ANALYSIS PERFORMED BY EPA APPROVED PROCEDURES

☐ Yes ☐ No, explain above

the chain of custody form signed as to the date and time opening occurred, and the samples are logged into the ET sample management computer.

2.6 DATA REPORTING

All analytical data is reported to the facility contact designated on the chain of custody form.

3. SURFACE WATER SAMPLING PROTOCOL

3.1 INTRODUCTION

Surface water sampling is an important part of the overall facility sampling program. The potential impact(s) to surface water quality from groundwater discharges or facility operations must be defined and documented. All sampling procedures listed below must be followed to ensure the collection and analysis of representative surface water samples. Surface water samples in this text generally refer to streams, but may also included springs, seeps, and impoundments.

3.2 STEPS TAKEN PRIOR TO OBTAINING WATER SAMPLE

3.2.1 Initial Observations

Field personnel who obtain surface water samples for KMCC record site weather conditions for the sampling date on the field sampling log (Figure 1, page 3). A notation is made for unusual weather events just prior to sampling (for example, drought, heavy rain previous week, etc.). For stream samples, an elevation measurement

is taken relative to a staff gauge and recorded to the nearest 0.1 foot. Other observations are recorded if deemed appropriate.

3.3 OBTAINING A WATER SAMPLE

3.3.1 Sample Collection

Grab samples are taken from surface water bodies from either the shore or by wading into the water. When sampling streams, the field sampler turns toward the upstream direction and dips the sample bottles to just below the water surface. Filling and capping the bottles under water eliminates the potential of headspace in the bottles, particularly important where the measurement of organics is concerned.

For those bottles that have already been prepared with preservatives (for example, TOC bottles with sulfuric acid) by the contract laboratory, the bottles are not dipped under water, but rather are filled with sample which is poured from one of the other bottles. This eliminates the loss of preservative that may otherwise occur if such bottles were filled under water. Any sample transfer between bottles is done slowly and in a manner to prevent the loss of volatiles.

3.3.2 Field Measurements and Field QA/QC Procedures

The identical field measurements and field QA/QC procedures as described for groundwater samples (see p. 9) pertains to surface water samples. Reference is made to that section for complete details.

3.3.3 Sample Preservation and Shipment

The sample preservation and shipment procedures described in the groundwater sampling section (see p. 21) pertain to samples collected from surface waters. Reference is made to that section for complete details.

3.4 FIELD CHAIN OF CUSTODY

Field chain of custody protocol for surface water samples in no way differs from that described in the groundwater sampling section (see p. 21). Refer to that section for complete details.

3.5 DATA REPORTING

All analytical data is reported to the facility contact designated on the chain of custody form.

4. SURFACE AND NEAR SURFACE SOIL SAMPLING PROTOCOL

Surface and near surface soil samples (depth: 0 to 1 meter) will be collected following procedures described in "Preparation of Soil Sampling Protocol: Techniques and Strategies," an EPA document prepared by Benjamin J. Mason (May, 1983). (A copy of an appropriate section of this document is contained in Appendix A). Generally, the procedures allow for the use of soil punches, scoops and shovels, soil probes and augers, and power augers.

4.1 INITIAL OBSERVATIONS

Soil sampling locations will be marked in the field and referenced on field sample log and chain of custody forms so as to enable re-

sampling of that exact location at a later date, if necessary. Weather conditions on the sampling date will be described as will any unusual weather events (for example, drought) just prior to the sampling. Other appropriate notes will be made as deemed necessary.

4.2 OBTAINING SOIL SAMPLES

Depending upon the required laboratory analyses, soil samples will be collected using various methods. Surface and near surface samples that require chemical testing (for example, wet analyses) will be collected with soil punches, scoops, shovels, probes or augers and stored in glass jars. Those samples to be tested for physical parameters (for example, permeability, Atterburg Limits, etc.) will be collected using dedicated Shelby (thin walled) tubes advanced by a drill rig. Both ends of the Shelby tube will be capped and secured upon retrieval from the hole so as to create no disturbance to the sample.

Soil samples collected with scoops, shovels, probes and augers will be described according to ASTM Method D2488, Description and Identification of Soils (Visual Manual Procedures).

4.2.1 Field Compositing

Where composite samples must be taken, compositing will be done with large dedicated plastic sheets (one time use only) or with stainless steel mixing bowls. In each case, clods of soil will be

broken up before being mixed with hand tools. Following mixing, the soil will be placed in a pile, sectioned into four quarters, and a small sample from each quarter will be taken and mixed together to form the composite. The composite will then be placed in a glass jar and shipped with the rest of the samples to the laboratory. The excess soil will be discarded.

4.2.2 Sample Preservation

Soil samples collected in jars for wet chemistry analyses will be stored at $4^{o}C$ in the sample shuttle pack and delivered to the laboratory within 24 hours of sampling. Other than capping both ends of a Shelby tube, no special preservation procedures will occur for these type samples.

4.2.3 Decontamination Procedures

All sampling implements will be decontaminated between use with a steam cleaner or in a detergent solution (i.e., Alconox or similar), followed by rinsing with clean water.

4.3 FIELD CHAIN OF CUSTODY

Chain of custody forms will accompany all soil samples collected and shipped for analyses. (See page 21).

4.4 DATA REPORTING

All analytical data is reported to the facility contact designated on the chain of custody form.

5. SUBSURFACE SAMPLING PROTOCOL

Subsurface soil sampling refers to those procedures used to obtain soil samples from a depth of greater than 1 meter. In some instances, small portable power augers may be useful to slightly greater depths, but generally the procedures require the use of a drill rig and Shelby tube (thin wall) or split-barrel (split-spoon) devices.

5.1 INITIAL OBSERVATIONS

Borehole locations will be referenced on field sampling logs and chain of custody forms to permanent/semi-permanent structures and located on facility site drawings. (In some cases, it may be necessary to survey exact location of the borings). Weather conditions on the sampling date will be described as will any unusual weather conditions leading up to the sampling date. Other appropriate notes may be made as necessary.

5.2 OBTAINING SUB-SURFACE SOIL SAMPLES

Some borings will require either continuous or intermittent sampling from grade level to total depth. Such samples will be collected by either the use of dedicated Shelby (thin walled) tubes or split-barrel (split-spoon) devices. Shelby tube samples will be collected following the method described in ASTM Method D1587 and split-barrel samples will be collected following ASTM Method D1586.

All boreholes will be visually logged from grade level to the target depth. Soil and formation description will follow ASTM Method D2488, with notes also made as to water level and visual or olfactory evidence of contamination. A photoionization detector or comparable instrument will be used in the field to screen logged samples for volatile constituents.

Borings not completed as monitor wells will be grouted back to the surface using a tremie line and Type I Portland cement with 5% bentonite (see section 7, page 31 of this document).

5.2.1 Field Compositing

Where composite samples must be taken, compositing will be done with large dedicated plastic sheets (one time use only) or with stainless steel mixing bowls. In each case, clods of soil will be broken up before being mixed with hand tools. Following mixing, the soil will be placed in a pile, sectioned into four quarters, and a small sample from each quarter will be taken and mixed together to form the composite. The composite will then be placed in a glass jar and shipped with the rest of the samples to the laboratory. The excess soil will be discarded.

5.2.2 Sample Preservation

Soil samples collected off auger flights or from the split barrel for wet chemistry analyses will be stored in glass jars and kept at $4^{o}C$ until delivered to the laboratory by the next day. No special

preservation will be done on the Shelby tube samples other than capping both ends of the tube after removal from the borehole.

5.2.3 Decontamination Procedures

All sampling implements will be decontaminated between use with a steam cleaner or in a detergent solution (i.e. Alconox or similar), followed by rinsing with clean water.

5.3 FIELD CHAIN OF CUSTODY

Chain of custody forms will accompany all soil samples collected and shipped for analyses (see page 21 for complete details).

5.4 DATA REPORTING

All analytical data is reported to the facility contact designated on the chain of custody form.

6. ANALYSES OF ALL WATER AND SOIL SAMPLES

6.1 LABORATORY QA/QC PROGRAM

All water and soil samples submitted to the contract analytical laboratory for analyses will be handled and analyzed according to the highest standards. Most analytical methodologies originate from USEPA SW-846. Appendix B contains the contract laboratory Quality Assurance Program Plan and Standard Operating Procedures.

6.2 PHYSICAL (SOIL) TESTING

Some soil samples may be submitted to a soils-testing laboratory for the determination of physical properties of that sample. As

yet, testing parameters have not been specified, but may include such parameters as 1) particle size analysis (ASTM Method D421/D422); 2) permeability-constant head (ASTM Method D2434); 3) Atterberg Limits (ASTM Method D4318). Any other physical testing that may be required will also comply with ASTM specifications.

7. WELL INSTALLATION/ABANDONMENT PROCEDURES

All groundwater monitor wells have been installed so as to yield representative groundwater quality data. Installation methods will include the use of hollow stem auger or rotary wash drilling techniques with minimal introduction of drilling fluid into the borehole.

Temporary wells may remain open-hole or PVC completed if all that is required is a water level elevation measurement or a grab sample for chemical analysis. Temporary wells will be plugged within two days after being drilled by cementing them with a tremie line from total depth to grade using a neat Portland Type I cement with 5% bentonite.

Any permanent monitor wells needing to be abandoned or replaced will be drilled out or casing pulled out in its entirety. If borehole collapse occurs or casing/screen remains in the hole, the borehole will be drilled out before plugging with a tremie line and neat cement/bentonite grout. If the casing or screen cannot be removed or drilled out, the casing is cut at ground surface and

is filled using a tremie line with cement mixed with 5% bentonite. Well abandonment/plugging report forms will be filed, as appropriate, with the regulatory agency within 30 days of decommissioning.

Wells installed for longer term monitoring will be 2 inches or larger in diameter and constructed of PVC, stainless steel or teflon material, as agreed upon between KMCC and the regulatory agency. All joints will be flush threaded without the use of cementing compounds.

Monitor well completion will be in accordance with the guidelines contained in the "RCRA Groundwater Monitoring Technical Enforcement Guidance Document" (US EPA, 1986). Specifically, the annular space between the screen and borehole will be filled with a filter pack of proper gradation to provide mechanical retention of the formation sand and silt. The filter pack will extend no more than two feet above the top of the well screen. At the bottom of the screen will be a 0.5 foot or longer dense phase sampling cup.

A minimum of two feet of bentonite pellets will be placed immediately above the filter pack in the annular space between the well casing and borehole. Above the bentonite seal will be a cement/bentonite grout mixture consisting of 3 to 5 pounds of bentonite per 94 pound sack of cement with approximately 6.5

gallons of water. A tremie line will be used to place the grout from depth to three feet below grade level. Following a suitable amount of time to allow grout settlement, the annular space from three feet below grade to grade level will be sealed with concrete, blending into a cement apron extending three feet from the outer edge of the borehole. Figure 3 has been reproduced and modified from the "RCRA Groundwater Monitoring Technical Enforcement Guidance Document" (US EPA, 1986) to show how the wells will be constructed.

Following well completion, well development will be initiated to remove any fluids used during drilling and to remove fines from the natural formation to provide a particulate free discharge.

Development will be done by reversing flow direction or surging the well. No fluids other than natural formation water will be added during development, and any collected water remaining from the development process will be put into the facility wastewater treatment system. A locking cap will be placed on all wells.

A record of drilling (Figures 4 and 5) and well construction details (Figure 6) will be completed and be kept on site. The record will include:

- date/time of construction
- drilling method/fluid use
- well location ($\pm$0.5 ft.)
- borehole diameter and well casing diameter
- well depth ($\pm$0.1 ft.)
- drilling and lithologic logs

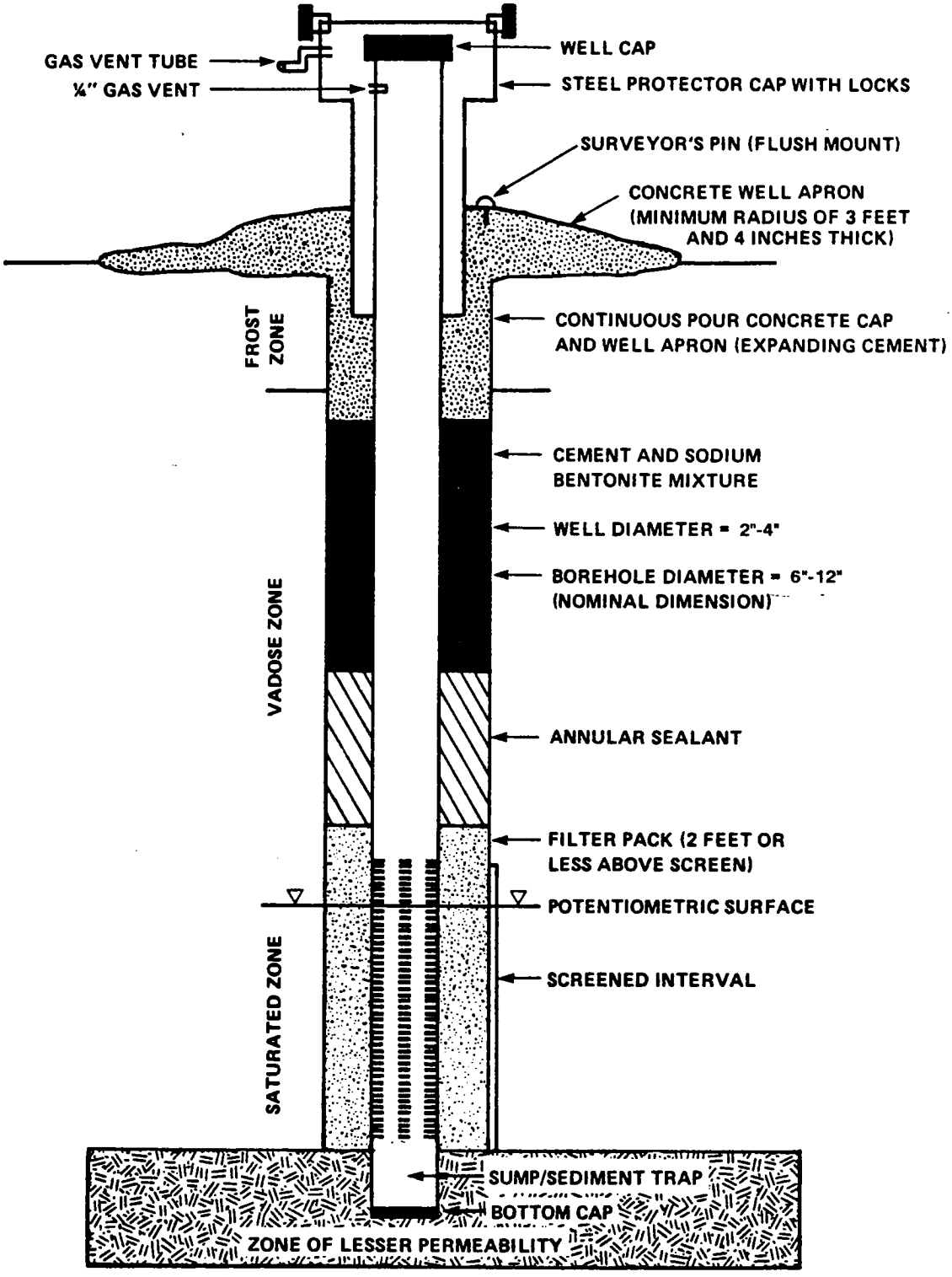


FIGURE 3: GENERAL MONITORING WELL CROSS-SECTION
(modified from USEPA, 1986)

FIGURE 4:
SOIL BORING LOG KM—5655-A

KERR-McGEE CORPORATION Hydrology Dept. Engineering Services	KM SUBSIDIARY	LOCATION	BORING NUMBER

DEPTH IN FEET	LITHOLOGIC DESCRIPTION	GRAPHIC LOG	UNIFIED SOIL FIELD CLASS.	BLOWS PER FOOT	PID (ppm)	SOIL SAMPLE NO.	SOIL SAMPLE TYPE	SOIL SAMPLE DEPTH	SOIL SAMPLE REC.	REMARKS OR FIELD OBSERVATIONS

EXPLANATION

- Water Table (24 Hour)
- Water Table (Time of Boring)
- PID — Photoionization Detection (ppm)
- NO. — Identifies Sample by Number
- TYPE — Sample Collection Method
- SPLIT-BARREL
- AUGER
- ROCK CORE
- THIN-WALLED TUBE
- CONTINUOUS SAMPLER
- NO RECOVERY
- DEPTH — Depth Top and Bottom of Sample
- REC. — Actual Length of Recovered Sample in Feet

GRAPHIC LOG LEGEND

- CLAY
- SILT
- SAND
- GRAVEL
- SILTY CLAY
- CLAYEY SILT
- DEBRIS FILL
- HIGHLY ORGANIC (PEAT)
- SANDY CLAY
- CLAYEY SAND
- ☐ _____
- ☐ _____

DATE DRILLED	PAGE of
DRILLING METHOD	
DRILLED BY	
LOGGED BY	
EXISTING GRADE ELEVATION (FT. AMSL)	
LOCATION OR GRID COORDINATES	

FIGURE 5: **KERR-McGEE CORPORATION**
HYDROLOGY DEPARTMENT

DRILLER'S LOG SUMMARY

Bore Hole Number: _____ **Rig Number:** _____

Date Bore Hole Started: _____ **Ground Elevation:** _____

Time Bore Hole Started: _____ **Weather:** _____

Date Bore Hole Completed: _____

Time Bore Hole Completed: _____

Driller's Name: _____

Helper's Name: _____

Technician's Name: _____

Auger Drilling: From _____ **feet to** _____ **feet, and**

Rotary Wash Drilling: From _____ **feet to** _____ **feet, and**

Completed Bore Hole Depth: _____

Bottom Sample Depth: From _____ **to** _____ **feet**

Groundwater First Noted: _____ **feet @** _____ **hours (date:** _____**)**

Depth to Groundwater _____ **hours/minutes after bore hole completion:** _____ **(date:** _____**)**

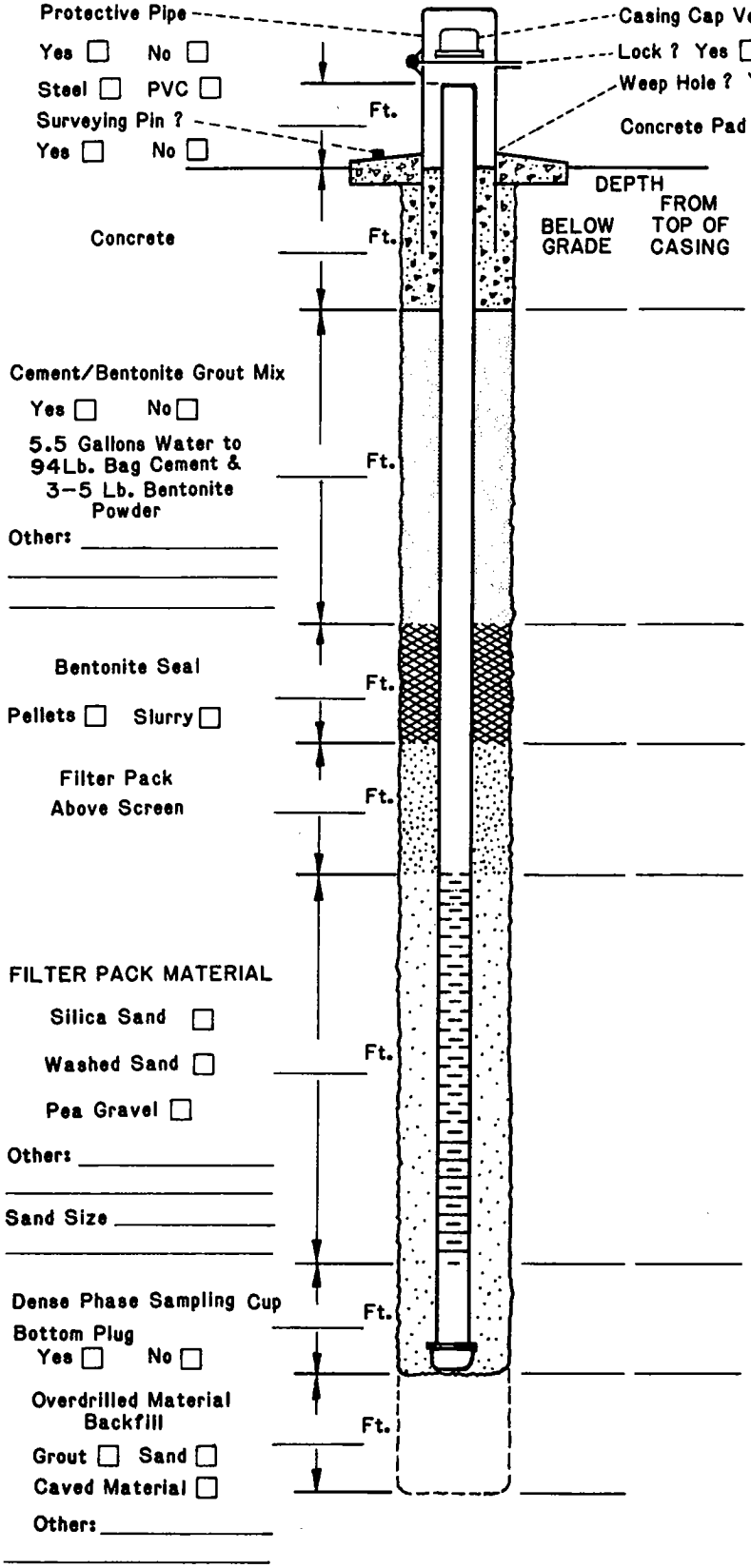
Number and Type of Samples Collected: (Please List)

Number _____ Type of Sample

LOCATION: _____

KERR-McGEE CORPORATION
HYDROLOGY DEPARTMENT

FIGURE 6: *MONITORING WELL INSTALLATION DIAGRAM*



DRILLING INFORMATION:

1. Borehole Diameter= _____ Inches.
2. Were Drilling Additives Used ? Yes ☐ No ☐
   Revert ☐ Bentonite ☐ Water ☐
   Solid Auger ☐ Hollow Stem Auger ☐
3. Was Outer Steel Casing Used ? Yes ☐ No ☐
   Depth= _____ to _____ Feet.
4. Borehole Diameter for Outer Casing _____ Inches.

WELL CONSTRUCTION INFORMATION:

1. Type of Casing: PVC ☐ Galvanized ☐ Teflon ☐
   Stainless ☐ Other _____
2. Type of Casing Joints: Screw–Couple ☐ Glue–Couple ☐ Other _____
3. Type of Well Screen: PVC ☐ Galvanized ☐
   Stainless ☐ Teflon ☐ Other _____
4. Diameter of Casing and Well Screen:
   Casing _____ Inches, Screen _____ Inches.
5. Slot Size of Screen:
6. Type of Screen Perforation: Factory Slotted ☐
   Hacksaw ☐ Drilled ☐ Other _____
7. Installed Protector Pipe w/Lock: Yes ☐ No ☐

WELL DEVELOPMENT INFORMATION:

1. How was Well Developed ? Bailing ☐ Pumping ☐
   Air Surging (Air or Nitrogen) ☐ Other _____
2. Time Spent on Well Development ?
   _____ / _____ Minutes/Hours
3. Approximate Water Volume Removed ? _____ Gallons
4. Water Clarity Before Development ? Clear ☐
   Turbid ☐ Opaque ☐
5. Water Clarity After Development ? Clear ☐
   Turbid ☐ Opaque ☐
6. Did Water have Odor ? Yes ☐ No ☐
   If Yes, Describe _____
7. Did Water have any Color ? Yes ☐ No ☐
   If Yes , Describe _____

WATER LEVEL INFORMATION:

Water Level Summary (From Top of Casing)

During Drilling _____ Ft. Date _____
Before Development _____ Ft. Date _____
After Development _____ Ft. Date _____

Driller/Firm _____ Drill Rig Type _____ Date Installed _____

Drill Crew _____ Well No. _____ Kerr–McGee Hydrologist _____

- depth to first saturated zone
- casing material
- screen material and design
- casing and screen joint type
- screen slot size length
- filter pack material/size
- filter pack volume
- filter pack placement method
- sealant materials
- sealant volume
- sealant placement method
- surface seal design/construction
- well development procedure
- type of protective well cap
- ground surface elevation
- top of casing elevation (to 0.01 ft MSL)
- detailed drawing of well (including dimensions)

Following well construction, a certification report will be prepared by a qualified geologist or geotechnical engineer which includes an accurate log of the soil boring and depicts the location, elevations, material specifications, construction details and soil conditions encountered in the boring of the well.

All wells will be permanently numbered and surveyed by a licensed surveyor as to location ($\pm$0.5 ft) and elevation (MSL) of the top of each well casing ($\pm$0.01 ft). Well locations will be plotted on the facility base map.

REFERENCES

American Society for Testing and Materials, 1990a, Standard practice for dry preparation of soil samples for particle size analysis and determination of soil constants: D421-85, p. 114.

American Society for Testing and Materials, 1990b, Standard method for particle size analysis of soils: D422-63, p. 116.

American Society for Testing and Materials, 1990c, Standard method for penetration test and split-barrel sampling of soils: D1586-84, p. 298.

American Society for Testing and Materials, 1990d, Standard practice for thin-walled tube sampling of soils: D1587-83, p. 304.

American Society for Testing and Materials, 1990e Standard test method for permeability of granular soils (constant head): D2434-68, p. 383.

American Society for Testing and Materials, 1990f, Standard practice for description and identification of soils (visual-manual procedure): D2488-84, p. 411.

American Society for Testing and Materials, 1990g, Standard test method for liquid limit, plastic limit and plasticity index of soils: D4318-84, p. 769.

AOHA-AWWA-WPCF, 1980, Standard methods for the examination of water and wastewater - 15th edition, Washington, D.C.

EMSL/US EPA, 1979, Methods for chemical analysis of water and wastes, Cincinnati, Ohio, EPA-600/4-79-020.

Environmental Technologies of Nevada, Inc., 1993, Quality assurance program plan for environmental chemical monitoring, Revision no.5.

Mason, Benjamin J., 1983, Preparation of soil sampling protocol: techniques and strategies, EMSL/US EPA, Las Vegas, NV, EPA-600/4-83-020.

State of California - Leaking Underground Fuel Tank Task Force, 1987, Leaking underground fuel tank field manual: guidelines for site assessment, cleanup and underground storage tank closure, 115 p.

US Environmental Protection Agency, 1979, National enforcement investigation center policies and procedures manual, Washington, D.C., EPA-330/9/79/001-R

REFERENCES- cont'd

US Environmental Protection Agency, 1982, Test methods for evaluating solid waste - physical/chemical methods, SW-846, 2nd edition, Washington, D.C.

US Environmental Protection Agency, 1986, RCRA groundwater monitoring technical enforcement guidance document, OSWER-9950.1.

US Environmental Protection Agency, 1990, Field measurements: dependable data when you need it, Washington, D.C., EPA/530/UST-90-003.

EPA-600/4-83-020
May 1983

FB83-206979

PREPARATION OF SOIL SAMPLING PROTOCOL: TECHNIQUES AND STRATEGIES

by

Benjamin J. Mason
ETHURA
McLean, Virginia 22101

under subcontract
to

Environmental Research Center
University of Nevada, Las Vegas
Las Vegas, Nevada 89154

Cooperative Agreement Number: CR808529-01-2

Project Office

Robert D. Schonbrod
Exposure Assessment Research Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89114

Environmental Monitoring Systems Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Las Vegas, Nevada 89114

7.1 Surface Sampling

Surface soil sampling can be divided into two categories -- the upper 15 cm and the upper meter. The very shallow pollution such as that found downwind from a new source or at sites of recent spills of relatively insoluble chemicals can be sampled by use of one of the methods listed in Section 7.1.1. The deeper pollutants found in the top meter are the more soluble, recent pollutants or those that were deposited on the surface a number of years ago. These have begun to move downward into the deeper soil layers. One of the methods in 7.2 should be used in those cases.

7.1.1 Sampling with a Soil Punch

A number of studies of surface soil have made use of a punch or thin walled steel tube that is 15 to 20 cm long to extract short cores from the soil. The tube is driven into the soil with a wooden mallet; the core and the tube are extracted; the soil is pushed out of the tube into a stainless steel mixing bowl and composited with other cores. Two alternates are the short King-tube samplers or the tube type density samplers used by the Corps of Engineers. (These sampling devices can be supplied by any field equipment company or by agricultural equipment companies.) The latter sampler is machined to a predetermined volume and is designed to be handled and shipped as a soil-tube unit. A number of similar devices are available for collecting short cores from surface soils.

The soil punch is fast and can be adapted to a number of analytical schemes provided precautions are taken to avoid contamination during shipping and in the laboratory. An example of how this method can be adapted would be to use the system to collect samples for volatile organic chemical analysis. The tubes could be sealed with a Teflon plug and coated with a vapor sealant such as paraffin or, better yet, some non-reactive sealant. These tubes could then be decontaminated on the outside and shipped to the laboratory for analyses.

7.1.2 Ring Sampler

Soil engineers have a tool that can be purchased from any engineering equipment supply house that can be used to collect larger surface samples. A seamless steel ring, approximately 15 to 30 cm in diameter, is driven into the soil to a depth of 15 to 20 cm. The ring is extracted as a soil-ring unit and the soil removed for analysis. These large cores should be used where the results are going to be expressed on a per unit area basis. This allows a constant area of wale to be collected each time. Removal of these cores is often difficult in very loose sandy soil and in very tight clayey soils. The loose soil will not stay in the ring. The clayey soil is often difficult to break loose from the underlying soil layers thus the ring must be removed with a shovel.

This device has not been used extensively for collecting samples for chemical analysis but the technique should offer a useful method for collecting samples either for area contamination measurements or for taking large volume samples.

7.1.3 Scoop or Shovel Sampling

Perhaps the most undesirable sample collection device is the shovel or scoop. This technique is often used in agriculture but where samples are being taken for chemical pollutants, the inconsistencies are too great. Samples can be collected using a shovel or trowel if area and/or volume are not critical. Usually the shovel is used to mark out a boundary of soil to be sampled. The soil scientist attempts to take a constant depth of soil but the reproducibility of sample sizes is poor; thus the variation is often considerably greater than with one of the methods listed above.

7.2 Shallow Subsurface Sampling

Precipitation may move surface pollutants into the lower soil horizons or move them away from the point of deposition by surface runoff. Sampling pollutants that have moved into the lower soil horizons requires the use of a device that will extract a longer core than can be obtained with the short probes or punches. Three basic methods are used for sampling these deeper soils.

- Soil probes or soil augers
- Power driven cores
- Trenching

The soil probe collects 30 or 45 cm of soil in intact, relatively undisturbed soil cores whereas the auger collects a "disturbed" sample in approximately the same increments as the probe. Power augers can use split spool samplers to extract cores up to 50 cm long. With special attachments longer cores can be obtained with the power auger if this is necessary.

The requirement for detail often desired in research studies or in cases where the movement of the pollutants is suspected to be through very narrow layers cannot be met effectively with the augers. In these cases some form of core sampling or trenching should be used.

7.2.1 Soil Probes and Hand Augers

Two standard tools used in soil sampling are the soil probe (often called a King-tube) and the soil auger. These tools are designed to acquire samples from the upper two meters of the soil profiles. The soil probe is nothing more than a stainless steel or brass tube that is sharpened on one end and fitted with a long, T

shaped handle. These tubes are usually approximately 2.5 cm inside diameter although larger tubes can be obtained. The cores collected by the tube sampler or soil probe are considered to be "undisturbed" samples although in reality this is probably not the case. The tube is pushed into the soil in approximately 20 to 30 cm increments. The soil core is then removed from the probe and placed in either the sample container or in a mixing bowl for compositing.

The auger is approximately 3 cm in diameter and is used to take samples when the soil probe will not work. The samples are "disturbed"; therefore, this method should not be used when it is necessary to have a core to examine or when very fine detail is of interest to the scientist. The auger is twisted or screwed into the soil then extracted. Because of the length of the auger and the force required to pull the soil free, only about 20 to 30 cm maximum length can be extracted at one time. In very tight clays it may be necessary to limit the length of each pull to about 10 cm. Consecutive samples are taken from the same hole thus cross contamination is a real possibility. The soil is compacted into the threads of the auger and must be extracted with a stainless steel spatula.

Larger diameter augers such as the bucket auger, the Fenn auger and the blade augers can also be used if larger samples are needed. These range in size from 8 to 20 cm in diameter.

If distribution of pollutant with depth is of interest, the augers and the probes are not recommended because they tend to contaminate the lower samples with material from the surface. The probe is difficult to decontaminate without long bore brushes and some kind of washing facility. One alternative is to take several waste cores at each site prior to collecting the actual samples. This allows the probe tube to be cleaned by the scouring action of soil at similar concentrations to those found in the sample taken. This should remove any contamination leftover from previous locations. Where there is a potential for litigation, decontamination is essential to avoid any question about cross contamination. The augers have some of the same decontamination problems but the open thread surfaces allow easier access to the collection surfaces; therefore, they are easier to clean. See Section 7.8 for more detail on decontamination procedures.

One final warning about the use of the hand augers and soil probes. There are many soil scientists with back problems that have resulted from trying to extract a tool that has been inserted too far into the soil. A foot jack is a necessary accessory if these tools are to be used. The foot jack allows the tube to be removed from the soil without use of the back muscles.

7.2.2 Power Augers and Core Samplers

These truck or tripod mounted tools are used for collecting samples to depths greater than approximately 30 cm. Standard ASTM methods for use of these tools are available from the American Society for Testing and Materials or can be found at any college or university library. The methods outlined in Section 7.3 are applicable in this case an will not be discussed further.

7.2.3 Trenching

This method of soil sampling is used to carefully remove sections of soil during studies where a detailed examination of pollutant migration patterns and detailed soil structure are required. It is perhaps the lease cost effective sampling method because of the relatively high cost of excavating the trench from which the samples are collected. It should therefore be used only in those cases where detailed information is desired.

A trench approximately 1 meter wide is dug to a depth approximately one foot below the desired sampling depth. The maximum effective depth for this method is about 2 meters unless done in some stepwise fashion. Where a number of trenches are to be dug, a backhoe can greatly facilitate sampling. The samples are taken from the sides of the pit using the soil punch or a trowel.

The sampler takes the surface 15cm sample using the soil punch or by carefully excavating a 10 cm slice of soil that is 10 cm square on the surface. The soil can be treated as an individual sample or composited with other samples collected from each face of the pit. After this initial sample is taken the first layer is completely cut back exposing clean soil at the top of the second layer to be sampled. Care must be exercised to insure that the sampling area is clear of all material from the layers above. The punch or trowel is then used to take samples from the shelf created by the excavation from the side of the trench. This process is repeated until all samples are taken. The resulting hole appears as a set of steps cut into the side of the trench as is shown in Figure 7.1.

An alternate procedure that is also effective results from using the punch to remove soil cores from the side of the trench at each depth to be sampled (Figure 7.1). Care must be taken to guard against soil soughing down the side of the hole. A shovel should be used to carefully clean the soil sampling area prior to driving the punch into the trench side.

7.4 Compositing

Many sample plans call for compositing of the soils collected at a sampling location. This creates a problem from the point of view of the soil scientist. The key to any statistical sampling plan is the use of the variation within the sample set to test hypotheses about the population and to determine the precision or reliability of the data set. As was mentioned earlier, the composite sample provides an excellent estimate of the mean but does not give any information about the variation within the sampling area. Section 7.4.1 discusses one alternative that is a combination of the compositing methods and random sampling with duplication. Three methods that have been used to composite soil are presented below.

7.4.1 Estimating Sample Variance

The problem with the statistical analysis is found in the lack of duplication within the sampling location. Each subsample is combined into the composite therefore the data that is contained in the subsample is averaged with all other subsamples. The lack of a measure of the sampling error is the cause of the problem confronting the statistician. Multiple samples taken at each location would avoid this problem but costs usually preclude this. A compromise is possible by only analyzing duplicates or triplicates at a percentage of the locations. The exact location is chosen by use of a random number table and should be identified before the study begins. The duplicates should not be made up of a second set of subsamples.

Large cores such as those collected by split spoon can be split lengthwise in half. Each half is thus used as part of two separate composite samples. This avoids the time required to take the second set of cores but provides the duplication necessary for calculating the sampling error.

7.4.2 Compositing with a Mixing Cloth

Soil scientists often use a large plastic or canvas sheet for compositing samples in the field. This method works reasonably well for dry soils but has the potential for cross contamination problems. Organic chemicals can create further problems by reacting with the plastic sheet. Plastic sheeting, however, is inexpensive and can therefore be discarded after each sampling site.

This method is difficult to describe. It can be visualized if the reader will think of this page as a plastic sheet. Powder placed in the center of the sheet can be made to roll over on itself if only one corner is carefully pulled up and toward the diagonally opposite corner. This process is done from each corner. The plastic sheet acts the same way on the soil as the paper would

on the powder. The soil can be mixed quite well if it is loose. The method does not work on wet or heavy plastic soils. Clods must be broken up before attempting to mix the soil.

After the soil is mixed, it is again spread out on the cloth into a relatively flat pile. The pile is quartered. A small scoop, spoon or spatula is used to collect small samples from each quarter until the desired amount of soil is acquired (this is usually about 250 to 500 grams of soil but can be less if the laboratory desires a smaller sample). This is mixed and placed in the sample container for shipment to the laboratory. The waste material not used in the sample should be disposed of in a safe manner. This is especially important where the presence of highly toxic chemicals is suspected.

7.4.3 Compositing with a Mixing Bowl

An effective field compositing method has been to use large stainless steel mixing bowls. These can be obtained from scientific, restaurant, or hotel supply houses. They can be decontaminated and are able to stand rough handling in the field. Subsamples are placed in the bowls, broken up, then mixed using a large stainless steel scoop. The rounded bottom of the mixing bowl was designed to create a mixing action when the material in it is turned with the scoop. Careful observance of the soil will indicate the completeness of the mixing.

The soil is spread evenly in the bottom of the bowl after the mixing is complete. The soil is quartered and a small sample taken from each quarter. The subsamples are mixed together to become the sample sent to the laboratory. The excess soil is disposed of as waste.

7.4.4 Laboratory Compositing

Small sets of samples can often be composited better in the laboratory than in the field. A number of the small surface cores discussed in Section 7.1.1 can be placed in the sample bottle for shipment to the laboratory mixer and mixed to the degree needed by the analytical methods. This technique is the only method that may be useful for obtaining composite samples for some types of soils and may be the best method to use if compositing of sampler is necessary in a particular situation.

7.5 Replicate Samples

The quality control program will require duplicate or triplicate samples from a percentage of the sampling sites. These may be collected from the composite or they may be comprised of duplicate sets of samples. The latter is the preferred method.

A question often arises about how to handle the analytical data for these multiple results. All analytical results for the field replicates should be reported. Proper statistical designs can use this data to increase the precision of the estimates made. There is a tendency on the part of many scientists to discard unusual results (outliers) and to average the remainder of the samples. The discussion on soil variability given earlier should point up the problem with this approach. The outliers are probably part of the normal, wide variation seen in soils data. Averaging the numbers in effect throws away data on the sampling error that is needed to determine the reliability of the data collected.

7.6 Miscellaneous Tools

Hand tools such as shovels, trowels, spatulas, scoops and pry bars are helpful for handling a number of the sampling situations. Many of these can be obtained in a stainless steel for use in sampling hazardous pollutants. A set of tools should be available for each sampling site where cross contamination is a potential problem. These tool sets can be decontaminated on some type of schedule in order to avoid having to purchase an excessive number of thee items.

A hammer, screwdriver and wire brushes are helpful when working the split spoon samplers. The threads on the connectors often get jammed because of soil in them. This soil can be removed with the wire brush. Pipe wrenches are also a necessity as is a pipe vise or a plumbers vise.

7.7 Record Keeping

One of the vital components of the protocol is to adequately define the records required during the study. Good records become extra important if litigation results from the data collected. Every sample will be questioned in an attempt to either discredit or verify the data depending upon the side of the issue the attorney represents. Some of the records are discussed below.

7.7.1 Log Books

The sample teams should maintain an official log book of the investigation. Observations of the field conditions, equipment used, procedures followed and crew members involved are recorded for each day's sampling. These log books should be bound and all data must be recorded in ink (preferably black ink). Each log book should be maintained by the crew leader and signed by him. No erasures are allowed. When mistakes are made the data is lined out with one line only and the corrected data entered above the incorrect entry or on the next line of the log.

7.7.2 Site Description Forms

These serialized forms record the conditions at each site at the time the samples are collected. A sketch map and photographs of the site should be a part of the description. A polaroid-type camera should be used so that the pictures of the sites can be checked before leaving the area of the sample collection. These forms and the back of the photographs should be signed and dated by the crew leader responsible for taking the samples. The KNACK site description form should be used in most cases where the USEPA is involved.

7.7.3 Sample Tags

Tags made up according to the specifications provided by NEIC should be printed for use in the soils study. A tag must be prepared for each sample. All data must be included on the tag at the time the sample is collected. Wet samples should be double bagged with the tag in the outer bag. The person collecting the sample should sign the tag.

7.7.4 Chain-of-Custody Forms

This form is perhaps one of the most important as far as the legality of the samples is concerned. Chain-of-custody traces the possession of the sample from its origin through to data analysis. Most field researchers are not accustomed to observing the care needed to insure the safe custody of their samples. The samples must be in the physical custody of the scientist collecting the sample or else be secured in a facility with controlled, limited access until the samples are signed for and transferred to another responsible party. Samples must not be left unattended in an unlocked vehicle for any reason. There is nothing more disconcerting to technical representatives of the regulatory agencies than to spend hours working with data collected by field teams and then find the data is open to question because the chain-of-custody has been violated. Samples are a valuable resource and should be treated accordingly.

7.8 Decontamination

One of the major difficulties with soil sampling arises in the area of cross contamination of samples. The most reliable methods are those that completely isolate one sample from the next. Freshly cleaned or disposable sampling tools, mixing bowls, sample containers etc. are the only way to insure the integrity of the data.

Field decontamination is quite difficult to carry out, but it can be done. Hazardous chemical sampling adds another layer of aggravation to the decontamination procedures. The washing solutions must be collected for disposal at a waste disposal site. The technique outlined below has been used under field conditions.

7.8.1 Laboratory Cleanup of Sample Containers

One of the best containers for soil is in the glass canning jar fitted with Teflon or aluminum foil liners placed between the lid and the top of the jar. These items are cleaned in the laboratory prior to taking them into the field. All containers, liners and small tools should be washed with an appropriate laboratory detergent, rinsed in tap water, rinsed in distilled water and dried in an oven. They are then rinsed in spectrographic grade solvents if the containers are to be used for organic chemical analysis. Those containers used for volatile organics analysis must be baked in a convection oven at 105° C in order to drive off the rinse solvents.

The Teflon or aluminum foil used for the lid liners is treated in the same fashion as the jars. These liners must not be backed with paper or adhesive.

7.8.2 Field Decontamination

Sample collection tools are cleaned according to the following procedure.

- Washed and scrubbed with tap water using a pressure hose or pressurized stainless steel, fruit tree sprayer.
- Check for adhered organics with a clean laboratory tissue.
- If organics are present, rinse with the waste solvents from below. Discard contaminated solvent by pouring into a waste container for later disposal.
- Air dry the equipment.
- Double rinse with deionized, distilled water.
- Where organic pollutants are of concern, rinse with spectrographic grade acetone saving the solvent for use in step 3 above.
- Rinse twice in a spectrographic grade methylene chloride or hexane, saving the solvent for use in step 3.

- Air dry the equipment.
- Package in plastic bags and/or precleaned aluminum foil.

The distilled water and solvents are flowed over the surfaces of all the tools, bowls etc. The solvent should be collected in some container for disposal. One technique that has proven to be quite effective is to use a large glass or stainless steel funnel as the collector below the tools during flushing. The waste then flows into liter bottles for later disposal (use the empty solvent bottles for this). A mixing bowl can be used as a collection vessel. It is then the last item cleaned in the sequence of operations.

The solvents used are not readily available. Planning is necessary to insure an adequate supply. The waste rinse solvent can be used to remove organics stuck to the tools. The acetone is used as a drying agent prior to use of the methylene chloride or hexane.

Steam cleaning might prove to be useful in some cases but extreme care must be taken to insure public and worker safety by collecting the wastes. Steam alone will not provide assurance of decontamination. The solvents will still have to be used.

7.9 Quality Assurance

Quality assurance in EPA is usually handled by someone other than the sampling team. The field team is responsible for insuring that the quality assurance program is carried out correctly, however. The team will be required to take duplicate samples at prescribed intervals and will be required to submit field blanks of all materials used. It would be desirable to prepare a bulk soil for use as a field blank for the soil samples. This will have to be handled very carefully because of the difficulty in finding "clean" soil for use as the blank. Distilled water can be used in lieu of a soil blank. Additional samples such as equipment swipes, rinse water and solvents should be taken on a regular basis to verify the quality of the data obtained from the samples. Procedures for handling quality assurance have been outlined in an interim guideline prepared by the EPA Office of Monitoring Systems and Quality Assurance of the Office of Research and Development (OMSQA, 1980).

7.10 Safety

Toxic chemicals create a hazard for the soil sampling team. The team often is operating above plumes containing mixtures of highly toxic chemical. The drillers and excavators are in an especially hazardous position. An industrial safety specialist should be consulted prior to undertaking a study of these highly contaminated areas. Physical examination should be given to the

crew on a regular basis unless the sampling team operates only on rare occasions in which case they should have physicals before and after the sampling effort.

Many of the field team members will not want to follow the procedures outlined by the safety office. This should not be tolerated. This problem seems to be especially acute with the drilling crews. Every effort should be made to provide the teams with adequate training on the use of all safety equipment and recovery procedures prior to going into the field.

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

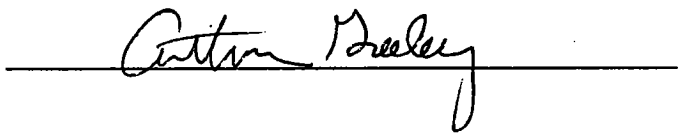
ANALYTICAL SERVICES DIVISION

QUALITY ASSURANCE PROGRAM PLAN FOR ENVIRONMENTAL CHEMICAL MONITORING

Revision No. 5

May 19, 1993

Reviewed and Approved by:



Arthur C. Greeley, Ph.D.
Manager of Analytical Services Division

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Environmental Technologies of Nevada, Inc., Analytical Services Division (ET-ASD), is a "state-of-the-art" environmental testing laboratory located in North Las Vegas, Nevada. ET-ASD provides public and private clients in Nevada and surrounding states with commercial analytical services designed to monitor environmental pollutants. To ensure data generated is scientifically sound and can be legally defensible, an extensive Quality Assurance (QA) Plan has been developed and implemented within ET-ASD. ET-ASD's QA Plan describes procedures for the handling of samples, evaluation of instrument conditions, regulation of testing methodology, performance evaluation, generation and reporting of analytical data. The effectiveness of the QA Plan is dependent upon ET-ASD's commitment to the clearly defined goals and objectives, adherence to the well documented procedures, implementation of the extensive audit system, and management's full support and cooperation.

PURPOSE

The purpose for implementing a Quality Assurance Plan at ET-ASD is to provide a framework for analytical consistency. ET-ASD's QA Plan was designed in accordance with the guidelines established in the following United States Environmental Protection Agency (U.S. EPA) documents:

* "EPA Test Methods for Evaluating Solid Waste," SW 846; 3rd Ed, November 1, 1986.

* "Interim Guidelines and Specifications for Preparing Quality Assurance Program Plans," QAMS-004/80, September 20, 1980;

* "Interim Guidelines and Specifications for Preparing Quality Assurance Program Plans," QAMS-005/80, December 29, 1980.

SCOPE

The quality of analytical data generated at the ET-ASD is controlled and monitored by the QA Plan. Listed below, are four vital areas by which ET-ASD regulates data quality:

1) Demonstrating the laboratory's capability by providing information which documents the overall qualifications of the laboratory to perform environmental analyses;

2) Controlling laboratory operations by establishing procedures which measure the laboratory's performance on a daily basis;

3) Measuring matrix effects to determine the effect of a specific matrix on method performance; and

4) Reporting appropriate QC information with the analytical results to enable the end-user to assess the quality of the data.

The existence of a "perfect" QA Plan which can eliminate errors during data generation, doesn't exist, but ET-ASD's QA Plan is designed to minimize, identify, and correct those errors which periodically arise. The QA Plan is regularly reviewed and revised to increase its effectiveness in providing ET-ASD with quality control guidance.

The framework of ET-ASD's QA Plan is designed to produce consistent quality data, but in order for this Plan to be effective, the professional judgement of the technical staff in interpreting data is essential.

DEFINITION OF TERMS

Analytical Batch -- Is a group of samples which are analyzed together with the same method sequence and the same lots of reagents and with common manipulation to each sample within the same time period or in continuous sequential time periods.

Calibration Check Standard -- Is used to determine the state of calibration of an instrument between periodic recalibrations.

CHP -- Is the Chemical Hygiene Plan for the laboratory.

CLP -- Is an acronym for Contract Laboratory Protocols.

Detection Limits -- Are graphically represented and defined in Appendix II.

Holding Time -- Is the period of time during which a collected sample is stored after preservation. Stated maximum holding times are designed to allow transfer and storage time without significantly affecting the accuracy of the analysis.

IDL -- Is the Instrument Detection Limit, (see Appendix II).

Initiate Analysis -- Is the point in time at which the sample, extract or digestate is introduced into an instrument or process which complies with the SOP for analysis of the parameter of interest.

Initiate Preparation -- Is the point in time at which the separation of organic extractable compounds or metals from the sample matrix by solvent extraction or acid digestion is begun.

Internal Standard -- Is a pure compound added to a sample extract just before instrumental analysis to permit quantitation.

PQL -- Is a method's Practical Quantitation Limit.

QA Plan -- Is an assemblage of management policies, objectives, principles, and general procedures outlining the techniques by which the laboratory produces data of known and accepted quality.

Quality Assurance (QA) -- Is a definitive approach for laboratory operation that specifies the measures used to produce data of known precision and bias.

Quality Control (QC) -- Is a set of measures within a sample analysis methodology to assure quality control throughout the analytical process.

Standard Operation Procedure (SOP) -- Is a detailed, written description to systematize and standardize the performance of laboratory activities and protocols.

Surrogate Standard -- Is a pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

SW-846 -- Is the EPA manual for Test Methods for Evaluating Solid Waste.

RESPONSIBILITIES AND AUTHORITY

Implementing ET-ASD's QA Plan is the responsibility of both staff and management. Laboratory staff's responsibility is to ensure their work is of the highest professional quality while management must provide leadership and direction. Laboratory staff report directly to the Lab Manager while the Lab Manager reports directly to ET's Corporate Management.

Responsibilities of the Lab Manager

The Lab Manager is responsible for guiding the laboratory staff toward a common goal. The responsibilities of the Lab Manager are listed below:

* Client interface re: cost estimates, capabilities, tours, resolution of problems, etc.
* Ensure full compliance with all health and safety procedures ie. Chemical Hygiene Plan/OSHA regulations.
* Conduct audits and inspections on a regular basis, reporting the results of those audits to staff and to the ET Management, and applying corrective actions as needed to ensure compliance with ET-ASD's QA Plan objectives;
* Coordinate certification programs within ET-ASD;
* Conduct meetings on QA/QC issues for laboratory staff;
* Promoting sound QA practices within the environmental regulatory and analytical communities;
* Staffing the laboratory with qualified personnel to perform environmental analysis; and
* Monitoring laboratory performance in the areas of holding times, turn-around times, and meeting contractual obligations.

Authority of the Lab Manager

The Lab Manager may recommend that procedures be amended or discontinued, or analyses suspended or repeated. In an event that unusual circumstances arise, the Laboratory Manager and Quality Assurance Officer confer on acceptance or rejection of data (provided there are technically sound reasons for doing so). All actions must be well documented with final approval being the signature of the Lab Manager. Finally, the Lab Manager can suspend or terminate employees on the grounds of dishonesty, incompetence, or repeated non-compliance with ET-ASD's QA Plan.

Responsibilities of Staff

All laboratory personnel involved in the generation and reporting of data have a responsibility to understand and follow the QA Plan implemented at ET-ASD. Laboratory staff are responsible for:

* Having a working knowledge of ET-ASD's QA Plan;
* Ensuring that all work is conducted in compliance with ET-ASD's QA Plan;
* The performance of environmental analysis in compliance with written SOPs;
* Ensuring all analyses are well documented, complete and accurate;
* Immediate notification of quality problems; and
* Having a working knowledge of health and safety procedures (MSDSs, SOPs, CHP, etc.).

Authority of Staff

Laboratory personnel have the authority to accept or reject data based on compliance with well-defined Quality Assurance criteria. The acceptance or rejection of data that fall outside of established QC guidelines must be approved by the Lab Manager or Quality Assurance Officer. All actions must be well documented.

The Responsibilities of the Q.A. Officer

The Q.A. Officer is responsible for maintaining sound quality control principles. Listed below are the responsibilities of the Q.A. Officer:

* Developing and implementing a QA Plan which generates scientifically sound, legally defensible, and of known precision and accurate data;

* Monitoring the QA Plan to ensure compliance with QA/QC objectives;

* Improve data quality by developing and implementing new QA procedures;

* Reviewing updated Standard Operating Procedures (SOPs) to ensure compliance with current SW-846 protocol.

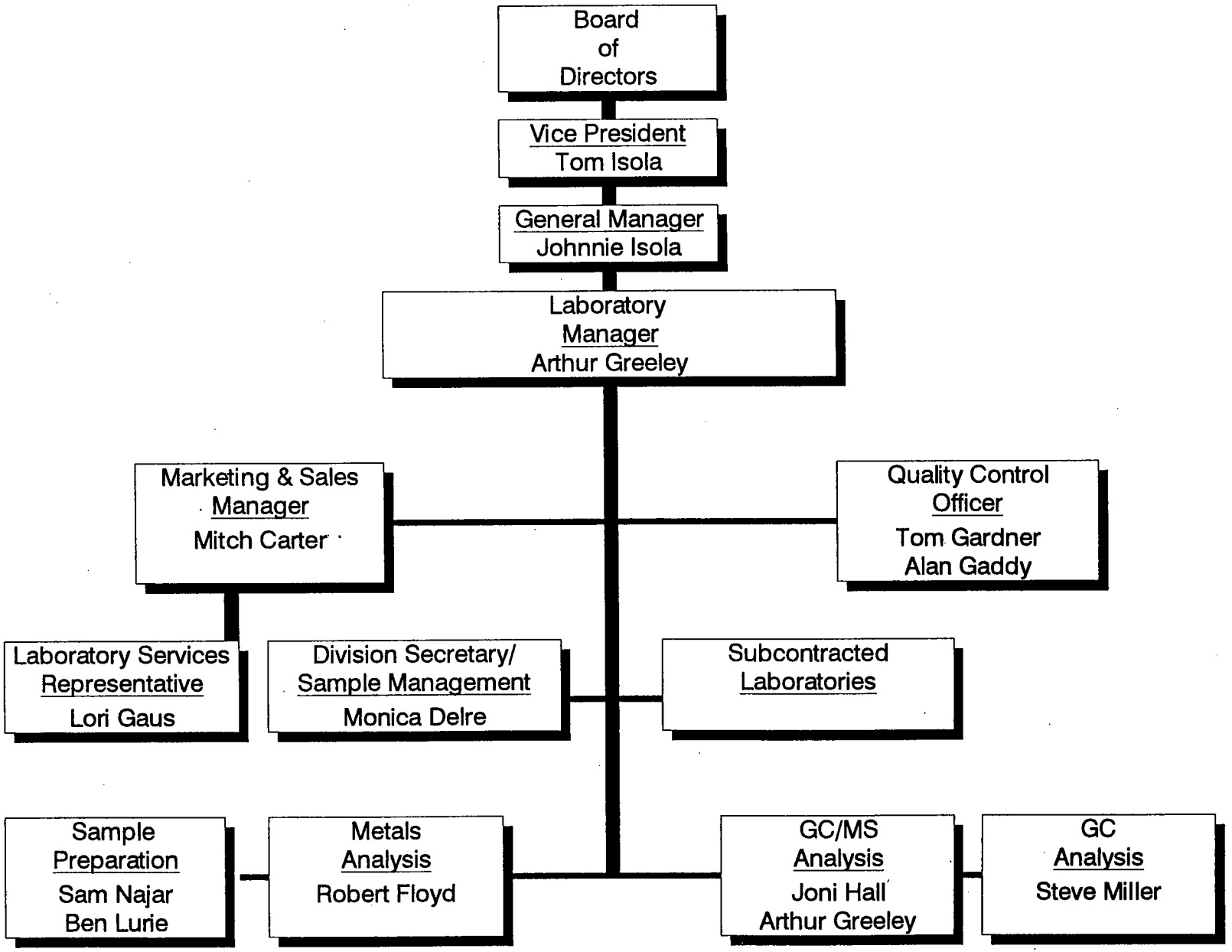
Authority of the Quality Assurance Officer

The Quality Assurance Officer has final authority on all issues dealing with data quality. Also, the Q.A. officer has the authority to require that procedures be amended or discontinued, or analysis suspended or repeated.

Laboratory Organization Chart

Refer to Figure 1-1 to review the current organizational chart of ET's Analytical Services Division.

Laboratory Organizational Chart



ANALYTICAL PROCEDURES

ET-ASD operates under guidelines of regulatory agencies, and the testing methods used to determine the concentration of environmental pollutants predominantly originate from these agencies. The methods used at ET-ASD, whether they originate from the U.S. EPA, other federal agencies, state agencies or professional organizations, are listed in the following references:

* "Test Methods for Evaluating Solid Waste", 3rd Edition (1986), Office of Solid Waste and Emergency Response, U.S. EPA;
* "Standard Methods for the Examination of Water and Waste water", 17th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, D.C. (1989);
* "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", 40 CFR, Part 136;
* Current EPA protocols for the analysis of organic and inorganic hazardous substances;
* "Annual Book of ASTM Standards", Volumes 11.01 and 11.02, American Society of Testing and Materials (ASTM), Philadelphia, PA (1987).

The selection of the appropriate analytical method is dependent upon the following criteria, which is documented in the form of a SOP:

* Regulatory or agency enforcement parameters;
* Qualitative certainty;
* Quantitative sensitivity;
* Precision and accuracy;
* Type of sample matrix to be analyzed;
* Linear range; and
* Data objectives.

DESCRIPTION OF ANALYTICAL EQUIPMENT

ET-ASD is equipped with state-of-the-art analytical instruments, which one can use to detect the presence of inorganic and organic pollutants, at low level concentrations.

Volatile Organics

Volatile Organics are performed on a Hewlett-Packard HP 5970 Mass Selective Detector (MSD), which is attached to a 5890 Series II HP Gas Chromatograph. Samples are introduced into the system using an O.I. Analytical 4460 Sample Concentrator attached to an O.I. MPM-16 Auto Sampler. Compounds are separated using a 105-meter megabore capillary column.

Semi-Volatile Organics

Semi-Volatile Organics are performed on a Hewlett-Packard 5970 Mass Selective Detector (MSD), which is attached to a 5890 Series II HP Gas Chromatograph (GC). Samples are introduced using an HP 7673 Auto Sampler. A 30-meter capillary column assists in compound separation.

Note: Each of ET-ASD's Gas Chromatograph\Mass Spectrometers (GC/MS) are equipped with a quadrapole mass analyzer and molecular turbo pumps. Data is acquired by an HP-1000 RTE-A computer system with the Aquarius software package. Each mass spectrometer has the capability of down loading the data onto CS-80 tapes.

Chlorinated Organics

Chlorinated Organics are performed on a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a linearized ^{63}Nickel Electron Capture Detector (ECD). Connected to the ECD GC is a Hewlett-Packard 3396A Integrator. Capillary columns are used to help separate the various constituents.

Non-Selective Organics

Non-Selective Organics are performed on a Hewlett-Packard 5890 Series II Gas Chromatograph configured with two Flame Ionization Detectors (FID). Each detector is connected to a separate Hewlett-Packard 3396A Integrator.

Samples are introduced into the system using manual injection. A capillary or packed column is used to assist the analyst in identifying environmental constituents.

Metals

The analysis of inorganic metals is performed on a Thermo Jarrel Ash Atom Scan 25 sequential inductively coupled plasma spectrometer (ICP). The Atom Scan 25 contains a built-in hydride generator, high solids nebulizer, and a water recirculating system. The Thermo Spec software aids in the acquisition of data. Also, ET-ASD has purchased the new Multi-Quant software package which can detect, within an accuracy of +/-25%, 72 elements using a four element standard.

The analysis of inorganic metals is also performed on a Thermo Jarrel Ash Smith Hieftje 4000 Atomic Absorption/Atomic emission (AA/AE) spectrophotometer. The TJA 4000 is capable of analyzing samples by either graphite furnace or flame. The system is software driven using an NEC PC and is automated with a 150 place auto sampler. The system is capable of the following techniques: hydride generation and mercury cold vapor generation.

General Equipment List

Mettler AE200 Analytical Balance
(Precision 200 grams ± 0.10 mg)

Mettler 300 Balance
(Precision 300 grams ± 0.01 grams)

Mettler 6000 Top Loading Balance
(Precision 6000 grams ± 0.1 grams)

Thermolyne 1400 Muffle Furnace

Organomation N-EVAP 24 Sample Evaporator

Heat Systems EPA approved W-385 Sonicator
(with a soundproof sonabox)

Corning 240 pH Meter

Branson 1200 Ultrasonic Cleaner

Precision "E" Drying Oven

Barnstead Water Purification System (18.3 megohm water)

Thermolyne Type 2200 Hot Plate

2 - 10 Vessel Rotary Extractor

8 - Hole Steam Bath

10 - Electromantles

YSI Model 35 Conductivity Meter

Electric Autoclave

Pensky-Martens Flash Point Tester

Monitek Model 21 Nephelometer

5 - Zero Headspace Extractors

Spectronic 20 Spectrometer

Mistral 2000 Centrifuge

2 - Cyanide Distillation units (with sulfur clean-up)

1 - 576 c.f Walk-in Refrigerator

5 - 4.2 c.f Refrigerators

2 - Thermolyne Roto Mix Type 48200

Chapter 2

LABORATORY OPERATIONS

SAMPLING PROCEDURES

An important concern of ET-ASD's Analytical Services Division is the integrity of the samples received for analysis. Samples must be collected in such a way that contamination by foreign material and the unacceptable loss of compounds are minimized and monitored. In order for ET-ASD to generate quality data using it's extensive QA Plan, the following must be considered in maintaining sample integrity:

* Each container must be properly cleaned to ensure sample contamination does not occur during the sampling process;

* Samples must be collected in appropriate containers established by the EPA. Generally, organic analyses samples are collected in glass containers while inorganic determination samples are collected in polyethylene containers;

* Sufficient sample is taken during the collection process which ensures detection limits can be achieved and quality control samples be analyzed;

* Samples must be preserved according to EPA methodology to ensure the loss of interested materials, due to adsorption, volatilization, chemical and biological degradation, is minimized; and

* Samples must be properly shipped to the laboratory in the appropriate time frame in order to meet the required holding time for analyses.

* Sampling procedures should be in compliance with SW-846.

It is the policy of ET-ASD to inform the client, immediately, of any deficiencies in the integrity of the sample received, such as wrong preservative or sample container used. This policy allows the client to re-sample, if necessary, or take other preventive measures. All actions must be well documented.

SAMPLE CONTAINER AND PRESERVATION

During the sample collection process, ET-ASD can provide the following client services:

* Assist in sample preservation programs;
* Preservation of samples; and
* Provide a set of sample containers, which are cleaned and appropriate preservative added, according to EPA SW-846 methodology, for the various analyses a client may request.

SAMPLE HOLDING TIMES

For some analyses, the EPA has established maximum holding time requirements. Appendix I lists the requirements for the holding and preservation of samples for the various analyses a client may request. Sample holding times differ depending on the regulatory program, but ET-ASD follows the holding times given in the SW-846, unless otherwise instructed by the client. ET-ASD will honor other holding times for the various regulatory agencies if special arrangements are made in advance.

ET-ASD is obligated to initiate preparation and/or analysis of the sample within holding times if sample delivery acceptance occurs within 72 hours of sampling or before one-half of the holding time period has expired, whichever is less. When analyses cannot be provided within maximum holding times, ET-ASD reserves the right to refuse samples for analysis.

Occasionally, a client may request a sample to be reanalyzed. If a sample is reanalyzed and is conducted outside of the established SW-846 holding time, ET-ASD will be considered to have fulfilled its obligation in meeting holding times requirements, if the first preparation and/or analysis was initiated within the prescribed holding time.

SAMPLE CUSTODY

Upon receipt at ET-ASD, samples proceed through an orderly processing sequence specifically designed to ensure integrity of both the sample and its documentation.

All samples received at ET-ASD are carefully checked for label identification, the specific analyses requested, and chain-of-custody documentation. An example of ET-ASD's chain-of-custody record (Sample Management Record) used to transmit samples from the client to the laboratory is shown in Figure 2-1.

Upon arrival at ET-ASD, each sample is crossed-checked with the chain-of-custody documentation. Each sample is logged into the ET-ASD sample management computer. The computer assigns each sample a unique laboratory identification number based on the Julian calendar date. The samples are then transferred to the walk-in refrigerator pending sample preparation/analysis. To ensure samples are analyzed within the appropriate holding times, an in-house computer software program is used to generate a work list to identify the status of all in-house samples (extraction, clean-up, analyses, etc.), plus aid the Quality Assurance Officer in auditing internal quality control programs.

A flowchart outlining the laboratory's sample receiving/log-in procedure is shown on Figure 2-2.

ENVIRONMENTAL TECHNOLOGIES of Nevada, Inc.

3060 North Commerce Avenue
North Las Vegas, Nevada 89030
(702) 734-5444 Fax (702) 399-0071

Chain of Custody Record

001278

COC #

CLIENT INFO

Name:
Address:
Phone #
Contact:
Account #
PO #
COC/Job #

PROJECT INFO

Date Sampled:
Date Recd:
Date Due:
Report Via: USM FDX UPS UPS/2 UPS/N Pickup FAX
Estimate:
Comments:

Analysis Requested

Client Sample No.	ET Lab Sample No.	SAMPLE MATRIX	SAMPLE PRESERVATIVE	SAMPLE CONTAINER DISC	NUMBER OF CONTAINERS	SAMPLE TURNAROUND	[ ] TPH (MOD 8015) [ ] TPH (OIL & GREASE)	[ ] 8240 [ ] 8270	TCLP [ ] RCRA8 [ ] VOA [ ] SVOA [ ] PEST	OIL & GREASE [ ] A/V [ ] PET [ ] TOTAL	[ ] PCB [ ] PESTICIDES	[ ] PH [ ] FLASHPOINT	[ ] TOXICITY [ ] PLATE COUNT	[ ] METALS:	Sample Condition

Special Handling | Special Reporting Requirements | Lab Use Only

Relinquished By (Name/Company)	Date / Time	Received By (Name/Company)

Sample Matrix
(S)oil (L)iquid (M)ultiphase (A)ir (S)ludge (P)roduct

Preservatives
(1) Cold (2) HNO_3 (3) HCl (4) NaOH (5) NaS_2O_3 (6) H_2SO_4 (7) None

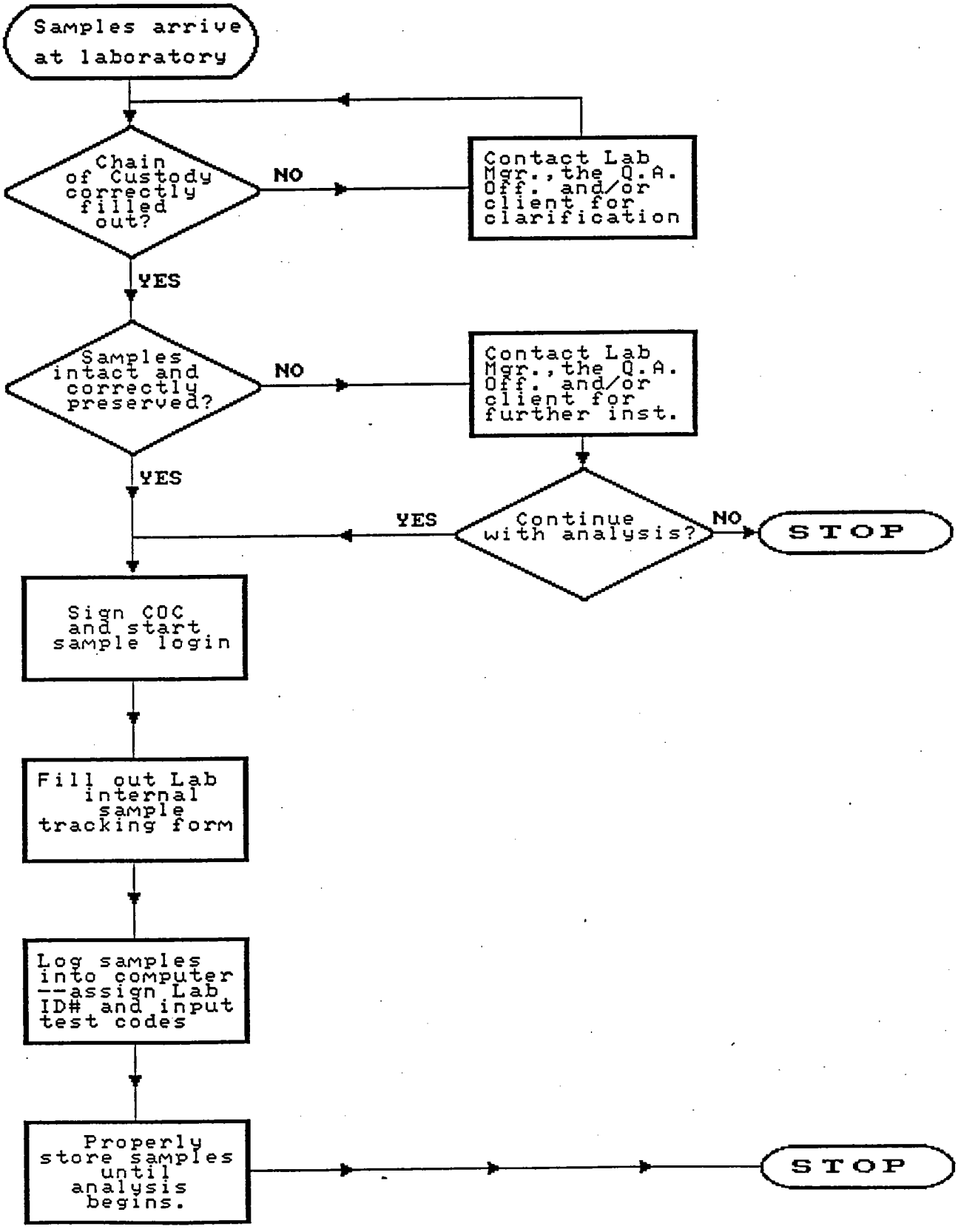
Sample Container
(1) Quart (2) 4oz (3) VOA (4) Poly 1L (5) Boston Round (6) Gas Bag (7) Other

Sample Turnaround
(1) Priority (24hr) (2) Expedited (48hr) (3) Rush (72hr) (4) Normal (10 days) (5) Other (Call in advance)

COC Rev 12.92

FIGURE 2-2

FLOWCHART OF LABORATORY SAMPLE RECEIVING/LOGIN PROCEDURES



CALIBRATION PROCEDURES AND FREQUENCY

Standard Reagent/Preparation

The purity and traceability of chemicals and/or standards used at ET-ASD play an important role. In order for ET-ASD to generate quality data, the purity and traceability of reagents and standards are monitored through a series of well-documented procedures. Stock standards used at ET-ASD are obtained from the National Institute of Standards and Technology, the EPA Repository or other reliable commercial sources.

Working standards are made from stock standards. Every time a working or reagent standard is manufactured, the analyst must complete a reagent record. The reagent record serves to identify supplier, lot number, receipt, preparation date, preparer's name and all other pertinent information.

After a working standard is prepared, each standard must be validated prior to the generation of data. Validation of a working standard can range from a check for chromatographic purity to verification of the concentration of the standard using an already existing standard prepared at a different time or obtained from a different source. To ensure the standards have not been contaminated, stock and working standards are checked on a regular basis for signs of deterioration, discoloration, formation of precipitates, or changes in concentration.

The handling and storage of working standards are carefully documented. Each container is labeled as to compound, concentration, solvent, expiration date, reagent record identification number, and preparation data (signature of preparer and date of preparation).

ET-ASD's system is designed to serve the following functions:

* Issue warnings on the expiration of a stock or working standard;
* Allows the analyst to obtain a list of all working standard solutions prepared from the same stock solution;
* Assists the Quality Assurance Officer in the auditing of reagents and standards; and
* Assists federal and state regulatory agencies in auditing data.

INSTRUMENT CALIBRATION AND FREQUENCY

The calibration of lab instrumentation is required because it informs the analyst that: 1) the system is operating correctly; and 2) the system is functioning at proper sensitivity levels thus ensuring that established reporting limits can be reached.

Each instrument is calibrated with working solutions to establish a linear range. No sample values will be reported if the sample concentration is greater than the highest working standard used without dilution. The frequency of calibration and the concentration of the calibration standard is determined by manufacturer's guidelines, the analytical method, or the requirements of special contracts.

INORGANICS

Inductive Coupled Argon Plasma Spectrometer (ICAP)

ET-ASD will analyze samples, which contain various metals, using an inductive coupled argon plasma emission spectroscopy (ICAP). The ICAP will be calibrated using prescribed SW-846 protocol prior to any analyses. Reestablishing the linear range of the instrument is performed once every quarter using a linear range verification check standard.

A calibration curve is established daily by analyzing a minimum of two standards, of which one is a calibration blank. To ensure the calibration curve is consistent throughout the day, ET-ASD will monitor the ICAP using a Continuing Calibration Blank (CCB) and a Continuing Calibration Verification (CCV) standard. In an event the system does not meet established QC criteria, the system is recalibrated and all samples, since the last acceptable calibration, are reanalyzed.

To ensure that the interelement and background correction factors have remained constant throughout each analytical run, an interelement check standard is analyzed at the beginning and end of the analytical run. Reanalyzing of samples, since the last acceptable interelement standard, will occur if the results are outside of established QC criteria.

Conventional

The field of wet chemistry (conventional) involves the use of a variety of wet chemical techniques and instrumentation.

In order for the various testing methods to be "in-control", the basic principles of calibration must exist. Prior to analyses, each system is calibrated. This is accomplish by establishing a linear range using a

series of working standard solutions, establishing limits of detection and identifying potential interferences. Similar to metal analysis, if the calibration check fails to meet any of the established quality control criteria, all samples since the last acceptable calibration check are reanalyzed.

ORGANICS

Gas Chromatography/Mass Selective Detector (GC/MSD)

ET-ASD will use the GC/MS system to detect the presence of volatile and semi-volatile pollutants. ET-ASD will use the protocol described in the U.S. EPA SW-846, 3rd Edition. The SW-846 establishes that each mass spectrometer must meet the tuning criteria every twelve hours. The tuning compound for volatile analysis is 4-bromofluorobenzene (BFB), while the tuning compound for semi-volatiles is decaflurotriphenylphosphine (DFTPP), according to the tuning criteria specified in the EPA's SW-846.

The instrument is then calibrated for all target compounds once all requirements for tuning are achieved. An initial calibration curve is produced from working standards. A mid-standard is run daily to monitor how consistent the calibration curve is. If the daily mid-standard does not meet the established criteria, as stated in the SW-846, the system is recalibrated.

Gas Chromatography (GC)

The field of chromatography involves a variety of instrumentation and detection systems. To ensure laboratory methods are "in-control", the general principles of calibration apply, similar to conventional inorganic analyses. Each system is calibrated using a series of working standards. The working standards help identify retention windows, establish limits of detection, and define the linear range. In general, all analysis must comply with current protocol as stated in SW-846. If SW-846 for a particular method differs from that of the SOP, the SOP must be followed. Before any analytical procedure is performed, a SOP must be written and approved by the Q.A. Officer.

METHOD VALIDATION CRITERIA

To test for a particular compound, many methods may apply. Before any method is used to generate analytical data, the method must meet ET-ASD's validation requirements listed below:

* Selection of new methods will be addressed by the Q.A. Officer;

* The method must be documented in the form of an SOP. This includes a summary of the method, detailed description of the analytical procedure, calculations, reporting formats, safety concerns, quality, and special remarks;

* Each method undergoes a battery of scientific tests in order to establish detection limits, linear range, reporting limits, precision, and accuracy; and

* The Quality Assurance Officer must approve the data acceptance criteria before methods are used to generate analytical results.

DATA REDUCTION AND VALIDATION

ET-ASD maintains written SOPs to govern all aspects of the data acquisition and reporting process. The data generated is extensively checked by the analyst for accuracy, precision, and completeness. A data package will be assembled for every method which generates data. The analyst (Level I reviewer), will examine the data package for:

* The information from sample extraction is complete and accurate;
* Analytical results (method, detection limit, calculations, dilution factors, etc.) are correct and precise;
* Correct SOPs were followed;
* Results from the quality control samples are complete and accurate, and are within established control limits;
* Results from the method blank are correct and complete and are within established control limits;
* Unusual sample requirements have been achieved; and
* Documentation is complete throughout the package.

This record keeping makes it possible to reanalyze data at a future date and can be used to support any scientific conclusions.

After Level I review, the data package proceeds to the next step of the review process. Level II reviewer is the Quality Assurance Officer. The function of the Level II reviewer is to provide an independent review of the data package and to ensure established guidelines were followed. Listed below are the responsibilities of the Level II reviewer:

* Information on sample preparation is correct and accurate;
* Calibration data generated is scientifically sound and legally defensible;
* Appropriate method was used in analyzing the requested constituents;
* The data generated from QC samples are within established guidelines;
* Qualitative identification and quantitative results from sample components are correct and accurate;
* The documentation within the package is accurate and complete;
* The data is ready to be incorporated into the final report; and
* The data package is complete and ready for data archive.

If mistakes are found in reviewing the data package during the Level II process, all errors will be well documented. The cause of the errors is then addressed with additional training or clarification of procedures to ensure that quality data will be generated at the bench.

Finally, the last reviewer (Level III) is the Lab Manager. The Lab Manager reviews the data to ensure all objectives were achieved and the laboratory is "in-control".

However, no data reduction program, regardless of how elaborate, can effectively eliminate all errors which may arise. ET-ASD has formed a framework, which minimizes those errors which periodically occur.

Note: Each step of this review process involves evaluation of data quality based on both the results of the QC data and the professional judgement of those conducting the review. This application of technical knowledge and experience in evaluating data is essential. This ensures ET-ASD that high quality data is consistently generated.

DATA REPORTING

Every laboratory has an unique way of reporting data to the client. Many laboratories use computerize data tables, while others put together elaborate CLP-deliverable packages. ET-ASD analytical data summary will contain:

Cover Letter The cover letter accompanies the analytical results. This letter describes the sample types that were submitted, which tests were requested, and any problems that occur.

Analytical Data will be reported by sample or by test. Pertinent sample information including the dates sampled, received, prepared, and extracted are included on each report page. The reporting limit for each analyte is also given.

QC Data QC Data is the results of the Laboratory Control Samples. The analytical results will be reported as Percent Recovery (accuracy) and Relative Percent Difference (precision). Results from the Method Blank will be located on the form which contains the analytical data. The analytical results from any matrix spikes, matrix spike duplicates, and matrix duplicates will also be reported.

Customer Services These services may include data interpretation, special consultation, holding and disposal of samples, and raw data packages (when requested).

Examples of Data Examples of ET Analytical Services Division analytical data reports may be found in Appendix IV.

CHAPTER 3

LABORATORY QUALITY CONTROL PROGRAM

Internal Quality Control checks, during data generation, serve two purposes:

1) Allows the laboratory to monitor itself, to ensure operationally, the system is within established criteria; and

2) Notifies the laboratory of matrix interferences.

The Laboratory Performance Quality Control Program is a program designed to monitor daily laboratory operations, while the Matrix-Specific Quality Control Program is designed to monitor the effect the sample has on the system. Before data is deemed accurate and precise, the internal QC checks must comply with established SOP guidelines. Internal QC checks will be required for up to 20 samples or an elapse time of 48 hours since the last acceptable QC check, whichever comes first. Its the responsibility of every analyst to ensure all methods used to generate data at ET-ASD are in compliance with established SOPs or SW-846 guidelines. The Quality Assurance Officer has the responsibility for implementing, monitoring, and updating QC guidelines.

LABORATORY PERFORMANCE QUALITY CONTROL

Laboratory Control Samples

Laboratory Control Samples (LCS) are samples which are laboratory generated and are used to monitor daily operations of the laboratory. The purpose of the LCS is to identify any background interference or contamination of the analytical system. These interferences may lead to the reporting of elevated concentration levels or false positive data. Unlike the Matrix-Specific QC Program, the LCS are independent of matrix effects. This allows the laboratory to differentiate low recoveries due to procedural errors from those of matrix effects. Laboratory Control Samples exist in two forms, a single control sample and a method blank.

Single Control Samples

Single Control Samples (SCS) are used to monitor the accuracy and precision of each analytical system on a daily basis. SCS consist of a working standard and a control matrix sample (Ottawa sand for soils and deionized water for liquids). An analytical batch using SCS consists of 20 environmental samples. SCS are analyzed with environmental samples to provide evidence that the laboratory is performing the method within acceptable QC guidelines. SCS program is designed to ensure that Laboratory Performance QC is available with each batch of samples processed.

Note: The reporting results for Single Control Samples will be accuracy (Percent Recovery) for each analyte of interest. To ensure the laboratory is "in-control", control limits for each method of interest will either be taken from the Contract Laboratory Program (CLP) or from other sources, such as the SW-846.

In cases where CLP control limits are not available, ET-ASD will establish control limits for accuracy. Based on historical data, the mean for accuracy (% recovery) will be plotted on a control chart. The control limits for each method of interest will be plus or minus three standard deviations of the mean.

Analytical data will be deemed accurate if the internal QC checks fall either within CLP requirements or within three standard deviations of the historical mean. The SOP will direct the analyst to which requirement (CLP or from other sources) to be used.

If a situation arises in which the calculated limits for internal methods are broader than CLP limits, CLP limits will be used to "control" the laboratory, unless otherwise noted in the SOP. All actions must be well documented. As stated before, data generated

outside established QC criteria will be considered "out-of-control" and unreliable.

Method Blank

Method blanks are generated laboratory samples that are processed exactly (extraction, clean-up, and analysis) as if it were an environmental sample. This helps the laboratory identify interferences or contamination which might lead to the reporting of elevated concentration levels or false positive data. The results of the method blank analysis are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for an analytical batch of samples.

Contamination from laboratory glassware and chemicals are a constant problem when measuring in the parts-per-billion range. Ideally, all compounds identified in the method blank should be below the Reporting Limit for that analyte. ET-ASD's QA Plan will allow the method blank to contain up to 5 times the Reporting Limit for the following compounds:

* Methylene Chloride (a.k.a Dichloromethane)

* Acetone (a.k.a. 2-Propanone)

* Methyl Ethyl Ketone (a.k.a. 2-Butanone)

* Phthalate Esters

This procedure is consistent with the CLP policy and has been established in recognition of the fact that these compounds are frequently found at low levels in method blanks due to the materials used in the collection, preparation, and analysis of samples for organic constituents.

In the analysis of metals, the Reporting Limit is almost equivalent to the Instrument Detection Limit (IDL). Quantifying certain metals is very difficult because of interference from other metals. ET-ASD's policy is that the concentration of the target analytes in the method blank must be two times below the Reporting Limit. If the blank value for the target analyte lies below the Reporting Limit, the Reporting Limit for that analyte in the associated samples is unaffected. If the blank value lies between the Reporting Limit and two times the Reporting Limit, the Reporting Limit for that analyte in the associated samples is raised to the level found in the blank. A blank containing an analyte(s) at concentrations two times the Reporting Limit, is considered unacceptable unless the lowest concentration of the analyte in the associated samples is at least ten times the blank concentration (as per Contract Laboratory Program protocol).

For conventional inorganic analysis, each method SOP directs how the blank is to be treated. For example, one method may state the method blank is to be used as one of the standards, while another uses the method blank to fine tune the instrument. In all cases in which organic constituents are used, the concentration found in the method blank will be reported with the concentration found in associated samples. It is the policy of ET-ASD not

to blank subtract from associated samples unless SOP methodology directs the analyst to do so.

Note: In an event the method blank fails to meet criteria established by ET-ASD, the source of the contamination must be investigated and appropriate corrective action taken. The results of the investigation must be well documented and brought to the attention of the Quality Assurance Officer.

MATRIX-SPECIFIC QUALITY CONTROL

Matrix-Specific QC is used to assess the effects of a sample matrix or field conditions on the analytical data. Matrix-Specific QC is composed of:

* The analysis of matrix spikes, matrix duplicates (upon client request), and matrix spike duplicates;
* The determination of method detection limits in a specific matrix;
* Monitoring the accuracy (% recovery) of surrogate compounds which are spiked into the sample;
* Monitoring the results of standard additions in environmental samples; and
* The analysis of field blanks.

Matrix Spike (MS)

A matrix spike is the addition of a known amount of analytes to the matrix of an environmental sample. Similar to the method blank, the matrix spike is taken through the whole process (extraction, clean-up, analysis, etc.) to determine what effect the matrix has on the analytical data generated. Results are expressed as percent recovery (accuracy).

Matrix Duplicate (MD)

The matrix duplicate is an environmental sample which is divided into two aliquots. Each aliquot is taken through the process separately. The results are used to calculate the Relative Percent Difference (RPD).

Matrix Spike Duplicate (MSD)

The matrix spike duplicate is an environmental sample which has been divided into two separate aliquots. To each aliquot, a known amount of analytes are added. Each sample is processed through the system separately. The results from the two aliquots are used to determine accuracy (% Recovery) and precision (Relative Percent Difference).

Surrogate Recoveries and Standard Additions

Surrogates are compounds of known concentration which are added to samples to monitor the effect the matrix has on the accuracy of the analysis. These compounds exhibit similar chemical characteristics of the analytes of interest, but are not normally found in environmental samples. The results are expressed in percent recovery (accuracy).

In the analysis of volatiles, semi-volatiles, etc., using GC/MS, surrogates are routinely added to environmental samples. The surrogate recoveries are primarily used to determine the effect the matrix and analytical procedure has on the environmental sample. ET-ASD's QC program is based on surrogate recovery, as "noted" below.

Note: Surrogate recoveries, due to sample preparation and analysis, must be ruled out prior to attributing low surrogate recoveries to matrix effects.

Standard Additions (AD)

The Standard Additions (AD) is the process by which a series of known concentrations of an analyte are added to an environmental sample. This method is used to calculate percent recoveries and is primarily used in analyzing metals and other inorganic tests.

Field Blanks

Field Blanks are laboratory generated blanks which help monitor contamination originating from the collection, transportation or storage of environmental samples. Two types of field blanks are: equipment and trip. The equipment blank is deionized water that is poured through the sample collection device to check the adequacy of the cleaning procedures on the sampling collection device. A trip blank is a laboratory generated sample, usually deionized water, which is sent to the field, remains unopened, and is sent back to the laboratory for analysis. The purpose of the trip blank is to monitor contamination in the field and during transportation.

PERFORMANCE and SYSTEM AUDITS

A system audit is a review of laboratory operations conducted to verify that the laboratory has the necessary:

1) Personnel;

2) Reagents and Instrumentation;

3) Methods of Analysis; and

4) Quality Assurance Program.

Performance samples verify the ability of the laboratory to correctly identify and quantitate compounds in blind check samples submitted by the auditing agency.

The laboratory participates in both the water pollution (WP) and water supply (WS) performance sample programs administered by the U.S. EPA.

PREVENTIVE MAINTENANCE

Preventive maintenance is routinely performed on each piece of analytical equipment. This helps minimize the downtime of equipment or delays in production schedules. All major equipment, such as GC, GC/MS, ICP, etc., are repaired by trained lab personnel or by service engineers employed by the instrument manufacturer.

The recommended schedules for preventative maintenance on each piece of equipment is contained within the Standard Operating Procedures. The laboratory also maintains detailed logbooks documenting the preventive maintenance and repairs performed on each analytical instrument. ET-ASD stocks many of the critical spare parts associated with the analytical equipment.

SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA QUALITY AND DETERMINE REPORTING LIMITS

This section describes procedures used to assess precision, accuracy, representativeness, completeness and comparability of the measurement systems at ET-ASD. The measurement systems follow the requirements for EPA methods or internal established quality control procedures.

Precision

Precision measures the degree of agreement among replicate analytical results of a sample, usually expressed as the standard deviation. Precision will be determined using data from the analysis of spiked environmental samples or reference materials. The equation used to measure precision, between two samples, is:

$$RPD = \frac{(D1 - D2)}{(D1 + D2)/2} \times 100$$

where: RPD = relative percent difference

D1 = first sample value

D2 = second sample value (duplicate)

The relative standard deviation (a.k.a sample coefficient of variation, CV) which expresses standard deviation as a percentage of the mean is useful in the comparison of three or more replicates.

$$RSD = 100\ (s/\bar{X})$$

where: RSD = relative standard deviation

s = standard deviation

$\bar{X}$ = mean

Accuracy

Accuracy can be defined as the combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value. Accuracy can be assessed using internal laboratory QC standard reference materials, or spiked environmental samples. Unless special contracts are arranged in advance, ET-ASD will monitor the accuracy by comparing (SCS) Single Control Sample results with control limits established at plus or minus three standard deviations units from the mean of historical SCS results. Accuracy is calculated in terms of percent recovery from the following equation.

$$\text{Percent Recovery} = \frac{X}{T} \times 100$$

where: X = the observed value of measurement

T = "true" value

Representativeness is the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Completeness is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under normal conditions.

Comparability expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is ensured through the use of established and approved analytical methods, consistency in the basis of analysis (wet weight, volume, etc.), consistency in reporting units (ppm, ppb, etc.), and analysis of standard reference material.

Reporting Limits are a number of terms (detection limits) used by the U.S. EPA or other technical groups to express the lowest concentration of an analyte which can be measured. With regulatory action levels being pushed lower and lower, the validity of any given measurement becomes even more important. The consequences of false data, can have a significant impact. Appendix II shows the various reporting limits with graphical representation.

ET-ASD will follow the EPA recommended procedure for calculating minimum or method detection limits (MDL) by analyzing replicate spiked samples at a level close to the estimated MDL, calculating the standard deviation and multiplying this value by the appropriate student t value. Depending on

the precision of the method, the practical quantitation limit (PQL) will be 2 to 10 times the MDL.

CORRECTIVE ACTION

ET-ASD's QA Plan is designed to minimize errors, deficiencies, or "out of control" situations. In an event that errors occur, laboratory personnel must initiate corrective actions immediately. Laboratory personnel are alerted that corrective actions may be necessary, if:

* QC data are outside the acceptable windows for precision and accuracy;
* Blanks and SCS contain contaminants above acceptable levels;
* Undesirable trends are detected in spike recoveries or RPD;
* There are unusual changes in detection limits;
* Deficiencies are detected by internal or external audits or from the results of performance evaluation samples; and
* Inquiries concerning data quality are received from clients.

"Out-of-control" data will result in a series of actions that laboratory personnel will initiate. All actions must be well documented and presented to the QA Officer for final approval. These actions are listed in Figure 3-1.

FIGURE 3-1

OUT OF CONTROL PROCEDURES

Suspected Cause	Test	Remedial Action
Mathematical Error (bookkeeping-right values for parameters)	Check calculations	Correct error and continue analysis
Quality Control Check (or instrument check) Sample deviates from expected concentration	Prepare fresh quality Control check sample and analyze	Proceed with analysis
Instrument Calibration	Make new calibration standards, recalibrate, re-analyze quality control check sample	Re-evaluate all environmental samples just preceding bad Q.C. result. If new result deviated by more than 25% and client specifications require tight precision, then re-analyze all samples since last valid Q.C. result
Instrument Maintenance Required	Perform instrument maintenance as required in SOP manual. Perform sensitivity checks and re-calibrate	Re-analyze all samples since last valid Q.C. result

QUALITY ASSURANCE REPORTS TO MANAGEMENT

Once a month, a QA report will be prepared and presented to ET-ASD laboratory staff and to ET management. This report will include an assessment of data accuracy, precision, and completeness derived from monthly summaries of QA/QC bench sheets. This report serves as an instrument for evaluating program design, identifying problems and trends, and future planning needs. Each report will contain:

* Results of internal audits;
* Performance evaluation scores and commentaries;
* Holding time violations; and
* Corrective actions for all violations.

APPENDIX I

MAXIMUM HOLDING TIMES

and

SAMPLE COLLECTION/PRESERVATIVE INFORMATION

Table A - Volatile Organics

Table B - Semi-Volatile Organics

Table C - Miscellaneous Organics

Table D - Metals

Table E - Conventional Inorganics

Table F - CLP Holding Times

Sources: Table A-E
Federal Register, October 26, 1984
SW-846, 3rd Edition, Update I
State of California Leaking Underground Fuel Tank Field Manual, May 1988

Table F
Contract Laboratory Program Statement of Work for Organic Analysis, dated 10/86
Contract Laboratory Program Statement of Work for Inorganic Analysis, dated 12/87

TABLE A - VOLATILE ORGANICS

Matrix	Container	Minimum Sample Size	Preservative	Holding Time (from date sampled)
Residual C1-not present	3 vials with Teflon lined septum	40 ml/vial	4 drops conc. HC1, 4°C	14 days
Residual C1-present	3 vials with Teflon lined	40 ml/vial	4 drops of 10% $Na_2O_3S_2$, 4 drops conc. HC1, 4°C	14 days
Acrolein & Acrylonitrile.	3 vials with Teflon lined	40 ml/vial	adjust pH 4-5, 4°C	14 days
Soil/Sediments & Sludges	Glass jar with Teflon liner or core tube	50 g	4°C	14 days
Concentrated waste samples	Glass jar with Teflon liner or core tube	50 g	none	14 days

The above information applies to the following parameters and methods:

Parameter	Method
Volatile Halocarbons	601/8010 (GC)
Volatile Aromatics	602/8020 (GC)
Volatile Organics	624/8240/8260 (GC/MS)
Acrolein/Acrylonitrile	603/8030 (GC)

TABLE B - SEMI-VOLATILE ORGANICS

Matrix	Container	Minimum Sample Size	Preservative	Holding Time (from date sampled)
Residual Cl-not present	1 liter glass with Teflon liner	2 liter	4°C	Samples must be extracted w/in 7 days and analyzed w/in 40 days of extraction.
Residual Cl-present	1 liter glass jar with lined septum caps	2 liter	3 ml of 10% $Na_2O_3S_2$ 4°C	Samples must be extracted w/in 7 days and analyzed w/in 40 days of extraction.
Soil/Sediments & sludges	Glass jar with Teflon liner or core tube	100 g	4°C	Samples must be extracted w/in 14 days and analyzed w/in 40 days of extraction.
Concentrated waste samples	Glass jar with Teflon liner or core tube	100 g	none	Samples must be extracted w/in 14 days and analyzed w/in 40 days of extraction.

The above information applies to the following parameters and methods:

Parameter	Method
Phenols	604/8040 (GC)
Phthalate Esters	606/8060 (GC)
Organochlorine Pesticides/PCB's	608/8080 (GC)
Polynuclear aromatic hydrocarbons	610/8310 (HPLC)
Organophosphorus Pesticides	614/8140 (GC)
Phenoxy acid Herbicides	615/8150 (GC)
Semi-Volatile Organics	625/8270 (GC/MS)
Carbamate & urea Pesticides	632 (HPLC)

TABLE C - MISCELLANEOUS ORGANICS

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative	Min Sample Size
Dioxins/ Furans	8280	Water	30 days extn. 45 days anal. (b)	1 liter glass jar	4°C	1000 ml
		Soil/Waste	30 days extn 45 days anal. (b)	Core tube or glass jar		50 g
Petroleum Hydrocarbons as gas	TPH-Gas Purge/trap (LUFT manual)	Water	14 days	3 vials w/teflon liners	4°c,HCL to pH<2	40 ml/vial
		Soil/Waste	14 days	Core tube/glass jar	4°C	100 g
Petroleum Hydrocarbons as gas	TPH-Gas Extractable (LUFT manual)	Water	14 days extn. 40 days anal.	2 liter glass	4°C,HCL	500 ml to pH<2
		Soil/waste	14 days extn. 40 days anal.	Core tube or glass jar	4°C	50 g
Petroleum Hydrocarbons as Diesel	TPH-Diesel Extractable (LUFT)	Water	14 days extn. 40 days anal.	2 liter glass	4°C jar	500 ml
		Soil/waste	14 days extn. 40 days anal.	Core tube or glass jar	4°C	100 g
Petroleum Hydrocarbons (TPH)	TPH-IR (418.1)	Water	28 days	1 liter glass	4°C, H_2SO_4 to pH<2	1000 ml

(a) extn: extraction anal: analysis
(b) from date of collection

TABLE D — METALS

Parameter	Method#	Matrix	Holding Time (from date sampled)	Container	Preservative (a)	Min Sample Size
Metals (ICP)	200.7/6010	Water	6 months	Poly	HNO_3 to pH <2.0	100 ml
		Soil/Waste	6 months	Core tube	4°C	10 g
Arsenic (GF-AA)	206.2/7060	Water	6 months	Poly	HNO_3 to pH <2,	100 ml
		Soil/Waste	6 months	Core tube glass jar	4°C	10 g
Mercury (CV-AA)	245.1/7470	Water	28 days	Poly	HNO_3 to pH <2.0,	100 ml
		Soil/Waste	28 days	Core tube	4°C	10 g
Selenium (GF-AA)	270.2/7740	Water	6 months	Poly	HNO_3 to pH <2.0,	100 ml
		Soil/Waste	6 months	Core tube glass jar	4°C	10 g
Silica	200.7/6010	Water	28 days	Poly	4°C	100 ml
		Soil/Waste	28 days	Core tube glass jar	4°C	10 g

TABLE D METALS
(continued)

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Thallium (GF-AA)	279.2/7841	Water	6 months	Poly	HNO_3 to pH <2.0, 4°C	100 ml
		Soil/Waste	6 months	Core tube glass jar		10 g
Lead (GF-AA)	239.2/7421	Water	6 months	Poly	HNO_3 to pH <2.0, 4°C	100 ml
		Soil/Waste	6 months	Core tube glass jar		10 g
Chromium (III, VI)	220.7, 218.4 312B,7197	Water	24 hours	Poly	4°C	100 ml
		Soil/Waste	24 hours extn.	Core tube glass jar	4°C	10 g

(a) Listed preservative is for total metals. Dissolved or suspended metals require filtration prior to pH.

(b) extn: extraction

TABLE E - CONVE..IONAL ANALYSIS

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Color	110.2	Water	48 hours	Poly	4°C	100 ml
Oil & Grease	413.1/413.2	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	1 liter
Specific	120.1	Water	28 days	Poly	4°C	50 ml
Acidity	305.1	Water	14 days	Poly	4°C	50 ml
pH	150.1	Water	ASAP	Poly	4°C	50 ml
Alkalinity	310.1	Water	14 days	Poly	4°C	50 ml
Hardness	200.7	Water	6 months	Poly	HNO_3 to pH<2	50 ml
Surfactants	425.1	Water	48 hours	Poly	4°C	100 ml
Gross Alpha, Beta & Radium	9310/9315	Water	6 months	Poly	HNO_3 to pH<2	2 liters
Odor	140.1	Water	ASAP	Glass	4°C	1 liter

TABLE E - CONVENTIONAL ANALYSIS (continued)

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Sulfite	377.1	Water	ASAP	Poly	4°C	100 ml
Sulfide	376.2	Water	7 days	Poly	4°C, NaOH to pH<9, $Zn(C_2H_3O_3)_2$	100 ml
Cyanide	335.1/335.2 335.3	Water	14 days	Poly	4°C, NaOH to pH<12	250 ml
Coliform Total & Fecal	909A, 909C	Water	6 hours	Sterile Poly	4°C, $Na_2S_2O_3$	100 ml
Bromide	Dionex	Water	28 days	Poly	4°C	50 ml
Chloride	300.0	Water	28 days	Poly	4°C	50 ml
Chlorine, Residual	330.1	Water	ASAP	Poly	4°C	100 ml
Fluoride	340.2	Water	28 days	Poly	4°C	50 ml
Iodine	Dionex	Water	28 days	Poly	4°C	50 ml
Total Organic Halogen (TOX)	9020	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	200 ml
Phenolics	420.1/420.2	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml

TABLE E - CONVENTIONAL ANALYSIS
(continued)

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Biochemical Oxygen Demand	405.1	Water	48 hours	Poly	4°C	100 ml
Chemical Oxygen Demand	410.4	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml
Total Organic Carbon (TOC)	415.1	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	100 ml
Ortho-phosphate	365.3	Water	48hours	Poly	4°C	100 ml
Phosphorous (Total)	365.3	Water	28 days	Glass	H_2SO_4 to pH<2	100 ml
Total Kjeldahl Nitrogen	351.2	Water	28 days	Glass	4°C, H_2SO_4 pH<2	100 ml
Ammonia	350.1	Water	28 days	Glass	4°C, H_2SO_4 to pH<2	50 ml
Nitrite	354.1	Water	48 hours	Poly	4°C	50 ml
Nitrate	353.2/0 300.0	Water	48 hours	Poly	4°C	50 ml
Sulfate	300.0	Water	28 days	Poly	4°C	50 ml

TABLE F - CLP HOLDING TIMES

Parameter	Method#	Matrix	Holding Time (a) (from date sampled)	Container	Preservative (a)	Min Sample Size
Volatile Organics		Water	10 days	2 vials with Teflon lined Caps	4°C	40 ml/vial
		Soil	10 days	Glass jar with Teflon Liner/core Tube	4°C	10 g
Extractable Organics		Water	5 days extn. 40 days anal.	1 liter glass w/ teflon liner	4°C	1 liter
		Soil	10 days extn. 40 days anal.	Glass jar w/ teflon liner/core tube	4°C	50 g
Metals (other than Mercury)		Water	180 days	P,G (b)	HNO_3 to pH<2	100 ml
		Soil	180 days		4°C	10 g
Mercury		Water	26 days	P,G	HNO_3 to pH<2	100 ml
		Soil	26 days	P,G	4°C	10 g
Cyanide		Water	14 days	P,G	0.6g Ascorbic acid, (c), NaOH to pH<12, 4°C	100 ml
		Soil	14 days	P,G	4°C	10 g

(a) Holding times calculated from date of receipt in laboratory.
(b) Polyethylene (P) or glass (G).
(c) Only used in the presence of residual chlorine.

APPENDIX II

DEFINITION OF DETECTION LIMIT TERMS

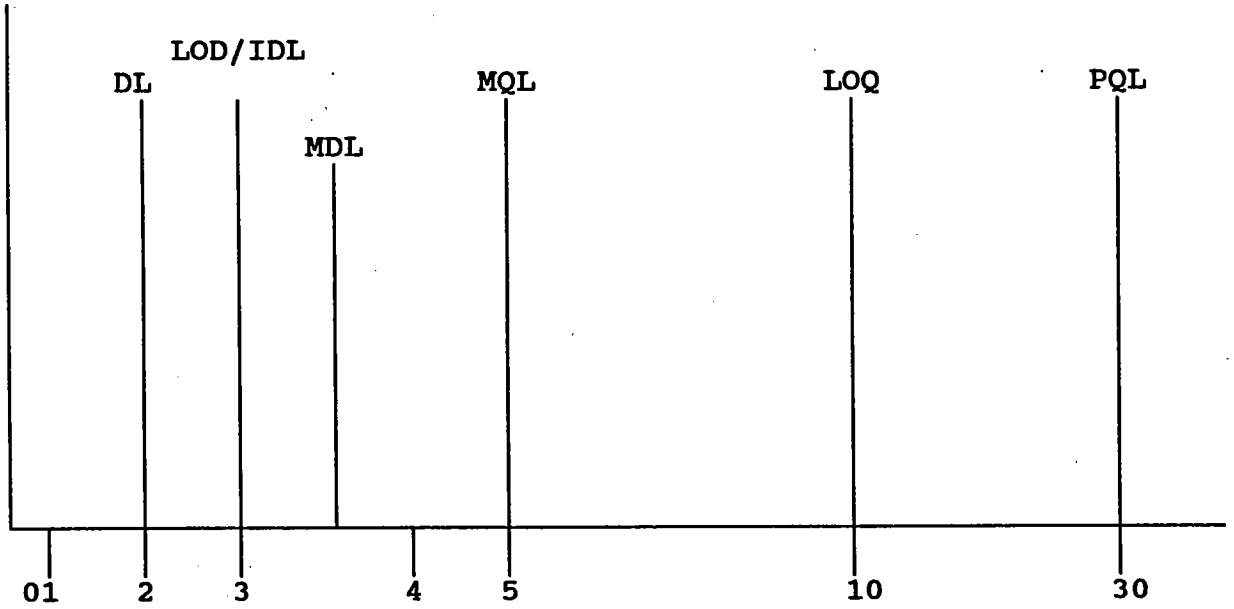
AND

GRAPHICAL PRESENTATION OF DETECTION LIMIT TERMS

DEFINITION OF DETECTION LIMIT TERMS

	DEFINITION	DETERMINATION	CALCULATION	SOURCE
Detection Limit (DL)	The concentration which is distinctly detectable above, but close to blank.	Analysis of replicate standards.	Two times the standard deviation.	Methods for chemical analysis of water and wastes.
Limit of Detection (LOD)	The lowest concentration that can be determined to be statistically different from blank.	Analysis of replicate samples.	Three times the standard deviation.	ACS Definition.
Method Detection Limit (MDL)	The minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.	Analysis of a minimum of seven replicates spiked at 1 to 5 times the expected detection limit.	The standard deviation times the student value at the desired confidence level. (For seven replicates, the value is 3.14).	40 CFR 136 Definition of EPA Water Program.
Instrument Detection Limit (IDL)	The smallest signal above background noise that an instrument can detect reliably.	Analysis of three replicate standards at concentrations of 3-5 times the detection limit.	Three times the standard deviation.	Contract Laboratory Program.
Method Quantitation Limit (MQL)	The minimum concentration of a substance that can be measured and reported.	Analysis of replicate samples.	Five times the standard deviation.	SW-846.
Limit of Quantitation	The level above which quantitative results may be obtained with a specified degree of confidence.	Analysis of replicate samples.	Ten times the standard deviation.	ACS Definition.
Practical Quantitation Limit (PQL)	The lowest level that can be reliably determined within specified limits of precision and accuracy during routine laboratory operating conditions.	Inter-laboratory analysis of check samples.	1) Ten times the MDL 2) Value where 80% of laboratories are within 20% of the true value.	RCRA SDWA Programs.
Contract Required Detection Limit (CRDL)	Reporting limit specified for laboratories under contract to the EPA for analysis.	Unknown.	Unknown.	Contract Laboratory Program.

GRAPHICAL REPRESENTATION OF DETECTION LIMIT TERMS



MULTIPLIER OF STANDARD DEVIATION OF REPLICATES

NOTE: The values along the horizontal "Standard Deviation (SD)" axis are approximate values and are meant to show the relative, not absolute, relationship between the terms.

APPENDIX III

ET-ASD PERSONNEL CLASSIFICATION

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

THOMAS A. ISOLA
Vice President

RESPONSIBILITIES

Chief Executive Officer - Responsible for the development and implementation of all ET operations and facilities.

EDUCATION

Bachelor of Business Administration, College of Santa Fe, New Mexico (1971)
Bishop Gorman High School, Las Vegas, NV (1967)

PROFESSIONAL HISTORY

1971 - Present	Corporate Vice-president and Major Stockholder: Environmental Technologies of Nevada, Inc. Silver State Disposal Service, Inc. Disposal Urban Maintenance Processing Company, Inc. Las Vegas, Nevada

BACKGROUND INFORMATION

Family is from the San Francisco area with four generations servicing the solid waste industry dating back to the 1800s. I moved to Las Vegas, Nevada in 1954 when Alfred Isola purchased an interest in the above companies that service all of the solid waste collection and disposal needs for Las Vegas, North Las Vegas, Henderson, Clark County, Laughlin, Blue Diamond, Indian Springs, and Nellis Air Force Base. I managed the implementation of a 2000 ton per day solid waste transfer station (1982) in North Las Vegas and the fully-lined solid waste landfill (1987) in Laughlin, Nevada. I am personally involved with, and have directed many community action programs including:

- Founder of Big Brothers and Big Sisters of Southern Nevada
- Las Vegas Metropolitan Beautification Committee
- Saint Viator's Parent Involvement Program
- Bishop Gorman High School Building Fund
- Young Presidents Organization
- Southern Nevada Clean Communities
- Catholic Community Services
- Y.M.C.A
- Southern Nevada Youth Fair
- Dountown Progress Association
- National Conference of Christians and Jews
- March of Dimes
- Las Vegas Rotary Club
- Boys Clubs of Clark County

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

JOHN R. ISOLA
General Manager

RESPONSIBILITIES

Management of all operations associated with the Soil Treatment Facility; ET Administrative an Office Manager; and general operations/facility planning, development and implementation.

EDUCATION

Bachelor of Business Administration, St. Marys College, Moraga, CA (1986)
Chapparal High School, Las Vegas, Nevada (1982)

PROFESSIONAL HISTORY

1988 - Present	General Manager Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1986 - 1988	Sales Manager Silver State Disposal Services, Inc. Las Vegas, Nevada
1979 - 1985	Heavy Equipment Operator Silver State Disposal Services, Inc. Las Vegas, Nevada

SELECTED TRAINING COURSES

RCRA Update Conference
Government Institutes Inc., Washington D.C. 1987

OSHA 40-Hour Health & Safety Training Program
American Environmental Management Corporation, Sacramento, CA 1987

Incineration of Hazardous and Non-Hazardous Waste
Center for Professional Advancement, Chicago, Illinois 1987

Containment of Hazardous Materials
Clyde B. Strong & Associates, Long Beach, CA 1987

Hazardous/Toxic Waste Management

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

MITCH CARTER
Director of Sales and Marketing

RESPONSIBILITIES

Sales, market development, customer service, public relations, bid/proposal development, and contract management.

EDUCATION

Havre High School, Havre, Montana (1979)

PROFESSIONAL HISTORY

1990 - Present	Director Sales and Marketing Environmental Technologies of Nevada, Inc.
1989 - 1990	Regional Sales Manager U S Ecology, Inc. Las Vegas, Nevada
1988 - 1989	Technical Services Representative U S Ecology, Inc. Las Vegas, Nevada
1987 - 1988	Field Services Representative U S Ecology, Inc. Las Vegas, Nevada
1985 - 1987	Field Operations Supervisor Special Services Division U S Ecology, Inc. Las Vegas, Nevada
1984 - 1985	Disposal Facility Equipment Operator Chemical and Radioactive Shipments U S Ecology, Inc. Beatty, Nevada

SELECTED TRAINING COURSES

Certified Emergency Medical Technician (EMT), 1983
Certified Emergency Medical Technician Instructor, 1984
OSHA 40 - Hour Health and Safety Training Program, U S Ecology, Inc. 1987
Hazardous Material Worker Qualification, Texas Ecologists, Robstown, TX, 1984

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

TOM GARDNER
Regulatory Compliance Manager

RESPONSIBILITIES

Assuring company compliance with applicable federal, state and local regulations. Client compliance consultation in areas of waste management, pollution prevention, health and safety and transportation.

EDUCATION

University of California, Los Angeles, CA (1988) - Bachelors of Science Degree in Chemistry
University of California, San Diego, CA (1990) - Hazardous Material Management

PROFESSIONAL HISTORY

1993 - Present	Regulatory Compliance Manager Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1990 - 1993	Area Environmental Coordinator Van Waters & Rogers, Inc. Phoenix, Arizona
1989 - 1990	Environmental Coordinator Hughes Aircraft Carlsbad, California
1988 - 1989	Field Chemist IT Corporation San Diego, California

SELECTED TRAINING COURSES

Environmental Auditing
Emergency Response
DOT Hazardous Materials

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

ALAN GADDY
Regulatory Compliance Manager

RESPONSIBILITIES

Assuring company compliance with applicable federal, state and local regulations. Client compliance consultation in areas of waste management, pollution prevention, health and safety and transportation.

EDUCATION

Washington State University (1982) - Master of Science/Environmental Engineering
University of Nevada, Las Vegas, NV (1980) - Bachelor of Science/Engineering and Environmental Science.

PROFESSIONAL HISTORY

1993 - Present	Regulatory Compliance Manager Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1987 - 1993	Senior Environmental Specialist - Senior Process Engineer Kerr-McGee Chemical Corporation Henderson, Nevada
1984 - 1987	Environmental/Production Chemist Unocal- Molycorp Division Mt. Pass, California
1981 - 1984	Environmental Scientist Washington State University Pullman, Washington

SELECTED TRAINING COURSES

Nevada Certified Environmental Manager #1102
California Registered Environmental Assessor #04117
Certified Safety Supervisor by the National Safety Council
HAZWOPR Trained and Certified as Hazardous Materials Specialist

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.

LORI GAUS
Laboratory Services Representative

RESPONSIBILITIES

Customer service, market development, bid/proposal development, contract management.

EDUCATION

Buena Park High School, Buena Park, California (1986)

PROFESSIONAL HISTORY

1993 - Present	Laboratory Services Representative Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1988 - 1992	Executive Assistant Applied Environmental Solutions, Inc. San Jose, California
1987 - 1988	Sales and Marketing Classic Wines Norwalk, California

SELECTED TRAINING COURSES

Wordperfect Computer Course 1990
Management Skills For Women 1990
Management Skills 1989

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

ARTHUR C. GREELEY
Laboratory Manager

RESPONSIBILITIES

Overseeing the following managerial functions: analysis of soil and water; sample tracking; data review; state certifications, scheduling projects and personnel; and client representation.

EDUCATION

University of Nevada, Las Vegas, NV (1992) - Chem 201 Environmental Regulations, Chem 202 Environmental Toxicology
Ph.D., Chemistry, University of California, Irvine (1985)
B.A., Chemistry, Point Loma College, San Diego, CA (1980)
Certificate in Computer Science, San Diege, CA (1980)

PROFESSIONAL HISTORY

1990 - Present	Laboratory Manager Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1987 - 1990	Laboratory Supervisor Aerojet Solid Propulsion Sacramento, California
1986 - 1987	Group Leader Aerojet Solid Propulsion Sacramento, California
1985 - 1986	Senior Chemist Aerojet Solid Propulsion Sacramento, California

SELECTED TRAINING COURSES

Hewlett Packard RTE-A Operator (1991)
Total Quality Management Training Program (1990)
Frontline Supervisor Training (1988)
Perkin-Elmer Lims Training Program (1987)

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

MONICA DELRE
Sample Management Control/Secretary

RESPONSIBILITIES

Manage samples in and out of the laboratory, plus provide secretarial support.

EDUCATION

H.S. Diploma, Eldorado High School, Las Vegas, Nevada (1982)

PROFESSIONAL HISTORY

1990 - Present	Sample Management Control/Secretary Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1987 - 1990	Billing Clerk Greyhound Exposition Services Las Vegas, Nevada
1985 - 1987	PBX Operator/Sales Broadway Southwest Las Vegas, Nevada
1982 - 1985	PBX Operator Montgomery Ward Las Vegas, Nevada

SELECTED TRAINING COURSES

Word Perfect Intermediate Computer Course (1990)
Word Perfect Basic Computer Course (1990)

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

SAM NAJAR
Technician

RESPONSIBILITIES

Sample preparation/extraction, wet chemistry, and equipment monitoring.

EDUCATION

H.S. Diploma, Flagstaff High School, Flagstaff, AZ (1953)

PROFESSIONAL HISTORY

1992 - Present	Technician Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1989 - 1991	Inventory Supervisor Black Diamond Auto Body Las Vegas, Nevada
1986 - 1989	Inventory Supervisor Gary Hanna Nissan Las Vegas, Nevada

SELECTED TRAINING COURSES

Auto Body Training Course

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

BENJAMIN LURIE
Technician

RESPONSIBILITIES

Sample preparation/extraction, wet chemistry and bacteriological testing

EDUCATION

Southern Utah University, Cedar City, UT (1993) - B.S. Zoology, Minor in Chemistry

PROFESSIONAL HISTORY

1993 - Present	Technician Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1991 - 1992	Paramedic Mercy Ambulance Las Vegas, Nevada
1981 - 1991	Driver Silver State Disposal Las Vegas, Nevada

SELECTED TRAINING COURSES

Bacteriological Training - Solmar (1993)
Culture Preparation - Dr. Palmer (1992)

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

STEVE MILLER
GC Chemist

RESPONSIBILITIES

GC Analytical Analysis

EDUCATION

University of Southern California, Los Angeles, CA (1984) - M.S., Engineering
California State University, Long Beach, CA (1981) - B.S. Chemistry

PROFESSIONAL HISTORY

1993 - Present	GC Chemist Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1988 - 1993	Group Leader West Coast Analytical Service, Inc. Santa Fe Springs, California
1986 - 1988	Laboratory Manager Radian Corporation El Segundo, California
1984 - 1986	Environmental Scientist GeoResearch Company Long Beach, California

SELECTED TRAINING COURSES

Restek Capillary Chromatography Training Program (1993)
National Well Water Association - Safety Protocol in Hazardous Waste Investigation (1987)

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

ROBERT FLOYD
AA/ICP Operator

RESPONSIBILITIES

Analyze samples for the presence of environmental pollutants.

EDUCATION

H.S. Diploma, Santa Fe High School, Alachua, Florida (1981)

PROFESSIONAL HISTORY

1992 - Present	AA/ICP Operator Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1989 - 1992	Trace Metals Group Leader McCoy and McCoy Labs Inc. Madisonville, KY
1986 - 1989	AA/ICP Analyst Environmental Science and Engineering Gainsville, FL
1981 - 1986	Technical Training Instructor/Base Fuels Lab Technician US Air Force

SELECTED TRAINING COURSES

Plasma Emission Spectroscopy
Petroleum and Cryogenics Quality Assurance/USAF
Petroleum Testing/CCUSAF

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

JONI HALL
GC/MS Chemist

RESPONSIBILITIES

Analyze environmental samples using EPA approved methodology.

EDUCATION

B.S. in Biological Science, Minor in Chemistry, Illinois State University, Normal, IL (1989)

PROFESSIONAL HISTORY

1992 - Present	Environmental Chemist Environmental Technologies of Nevada, Inc. Las Vegas, Nevada
1990 - 1992	Staff Scientist PDC Laboratories Peoria, IL
1989 - 1990	Assistant Toxicologist Illinois Institute of Technical Research Institute Chicago, IL

SELECTED TRAINING COURSES

Mass Spectral Interpretation
Hewlett Packard Capillary Chromatography

APPENDIX IV

EXAMPLE DATA REPORTS

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Solid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT
Total Petroleum Hydrocarbons
Extractables
Modified 8015, GC-FID

Reporting Units:

PETROLEUM HYDROCARBONS	SAMPLE	METHOD BLANK	*PQL
Gasoline Range:			10
Diesel Range:			10
Motor Oil Range:			50
Total Petroleum Hydrocarbons:			

CARBON NUMBER RANGE	
Gasoline Range:	
Diesel Range:	
Motor Oil Range:	

PEAK CARBON RANGE	
Gasoline Range:	
Diesel Range:	
Motor Oil Range:	

NA: Not Applicable
ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

GC Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

TCLP Constituents
and Regulatory Levels

Reporting Units:

ANALYTE		WASTE CODE	SAMPLE	*MDL	REGULATORY LEVEL	METHOD USED
Arsenic	(As)	D004		0.1	5.0	6010
Barium	(Ba)	D005		0.1	100.0	6010
Cadmium	(Cd)	D006		0.1	1.0	6010
Chromium	(Cr)	D007		0.1	5.0	6010
Lead	(Pb)	D008		0.1	5.0	6010
Mercury	(Hg)	D009		0.1	0.2	6010
Selenium	(Se)	D010		0.1	1.0	6010
Silver	(Ag)	D011		0.1	5.0	6010
Chlordane		D020		0.002	0.03	8080
Endrin		D012		0.0006	0.02	8080
Heptachlor (and epoxide)		D031		0.0006	0.008	8080
Lindane (gamma-BHC)		D013		0.0006	0.4	8080
Methoxychlor		D014		0.002	10.0	8080
Toxaphene		D015		0.01	0.5	8080
2,4,5-TP (Silvex)		D017			1.0	8150
2,4-D		D016			10.0	8150
1,1-Dichloroethylene		D029		0.05	0.7	8240
1,2-Dichloroethane		D028		0.05	0.05	8240
Benzene		D018		0.05	0.5	8240
Carbon Tetrachloride		D019		0.05	0.5	8240
Chlorobenzene		D021		0.05	100.0	8240
Chloroform		D022		0.05	6.0	8240
Methyl ethyl ketone		D035		0.5	200.0	8240
Tetrachloroethylene		D039		0.05	0.7	8240
Trichloroethylene		D040		0.05	0.5	8240
Vinyl chloride		D043		0.1	0.2	8240
1,4-Dichlorobenzene		D027		0.011	7.5	8270
2,4,5-Trichlorophenol		D041		0.01	400.0	8270
2,4,6-Trichlorophenol		D042		0.01	2.0	8270

NOTE: Sample extracted in accordance with SW-846 Method 1311 prior to analysis.
ND: Analyte Not Detected at or above MDL
--: Analyte Not Requested
*MDL: Method Detection Limit

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

TCLP Constituents
and Regulatory Levels

Reporting Units:

ANALYTE	WASTE CODE	SAMPLE	*MDL	REGULATORY LEVEL	METHOD USED
2,4-Dinitrophenol	D030		0.01	0.13	8270
Total Cresol	D026		0.01	200.0	8270
Hexachlorobenzene	D032		0.01	0.13	8270
Hexachloroethane	D034		0.015	3.0	8270
Hexachloro-1,3-butadiene	D033		0.015	0.5	8270
Nitrobenzene	D036		0.01	2.0	8270
Pentachlorophenol	D037		0.05	100.0	8270
Pyridine	D038		0.01	5.0	8270

NOTE: Sample extracted in accordance with SW-846 Method 1311 prior to analysis.
ND: Analyte Not Detected at or above MDL
--: Analyte Not Requested
*MDL: Method Detection Limit

Laboratory Manager

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Solid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Semi-Volatile Organics
EPA Method 8270, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
N-Nitrosodimethylamine			660
Phenol			660
Aniline			660
Bis(2-chloroethyl)ether			660
2-Chlorophenol			660
1,3-Dichlorobenzene			660
1,4-Dichlorobenzene			660
Benzyl Alcohol			1,300
1,2-Dichlorobenzene			660
2-Methylphenol			660
Bis(2-chloroisopropyl)ether			660
4-Methylphenol			660
-Nitroso-di-n-propylamine			660
Hexachloroethane			660
Nitrobenzene			660
Isophorone			660
2-Nitrophenol			660
2,4-Dimethylphenol			660
Bis(2-chloroethoxy)methane			660
Benzoic acid			3,300
2,4-Dichlorophenol			660
1,2,4-Trichlorobenzene			660
Naphthalene			660
4-Chloroaniline			1,300
Hexachlorobutadiene			660
4-Chloro-3-methylphenol			1,300
2-Methylnaphthalene			660
Hexachlorocyclopentadiene			660
2,4,6-Trichlorophenol			660

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Solid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Semi-Volatile Organics
EPA Method 8270, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
2,4,5-Trichlorophenol			660
2-Chloronaphthalene			660
2-Nitroaniline			3,300
Dimethyl phthalate			660
Acenaphthylene			660
2,6-Dinitrotoluene			660
3-Nitroaniline			3,300
Acenaphthene			660
2,4-Dinitrophenol			3,300
4-Nitrophenol			3,300
Debenzofuran			660
,4-Dinitrotoluene			660
iethyl phthalate			660
Fluorene			660
4-Chlorophenylphenylether			660
4-Nitroaniline			660
2-Methyl-4,6-dinitrophenol			3,300
N-Nitrosodiphenylamine			660
Azobenzene			660
4-Bromophenylphenylether			660
alpha-BHC			2,000
Hexachlorobenzene			660
gamma-BHC			2,000
Pentachlorophenol			3,300
beta-BHC			2,000
Phenanthrene			660
Anthracene			660
delta-BHC			2,000
Heptachlor			2,000

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Solid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Semi-Volatile Organics
EPA Method 8270, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
Di-n-butyl phthalate			2,000
Aldrin			2,000
Heptachlor epoxide			2,000
Fluoranthene			660
Endosulfan I			2,000
Benzidine			3,300
Pyrene			660
4,4'-DDE			2,000
Dieldrin			2,000
Endrin			2,000
Endosulfan II			2,000
',4'-DDD			2,000
utyl benzyl phthalate			660
4,4'-DDT			2,000
Benzo(a)anthracene			660
3,3'-Dichlorobenzidine			2,000
Chrysene			660
Endosulfan sulfate			2,000
Bis(2-ethylhexyl)phthalate			2,000
Di-n-octyl phthalate			660
Benzo(b)fluoranthene			660
Benzo(k)fluoranthene			660
Benzo(a)pyrene			660
Indeno(1,2,3-c,d)pyrene			660
Dibenzo(a,h)anthracene			660
Benzo(g,h,i)perylene			660

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

GC/MS Supervisor

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Volatile Organics
EPA Method 8240, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
Chloromethane			10
Vinyl chloride			10
Dichlorodifluoromethane			10
Bromomethane			10
Chloroethane			10
Acetone			50
1,1-Dichloroethene			5
Methylene Chloride			5
Trichlorofluoromethane			5
Carbon Disulfide			5
trans-1,2-Dichloroethene			5
1,1-Dichloroethane			5
Chloroform			5
1,2-Dichloroethane			5
Vinyl Acetate			30
2-Butanone (MEK)			50
1,1,1-Trichloroethane			5
Benzene			5
Carbon Tetrachloride			5
1,2-Dichloropropane			5
Bromodichloromethane			5
Trichloroethene			5
2-Chloroethyl vinyl ether			10
cis-1,3-Dichloropropene			5
trans-1,3-Dichloropropene			5
1,1,2-Trichloroethane			5
Dibromochloromethane			5
Bromoform			5
4-Methyl-2-pentanone (MIBK)			30

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Volatile Organics
EPA Method 8240, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
Toluene			5
2-Hexanone			30
Tetrachloroethene			5
Chlorobenzene			5
Ethylbenzene			5
Styrene			5
1,1,2,2-Tetrachloroethane			5
P & M-Xylene			5
O-Xylene			5
1,3-Dichlorobenzene			5
1,4-Dichlorobenzene			5
,2-Dichlorobenzene			5

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

GC/MS Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Liquid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT
Polychlorinated Biphenyls
PCB's
EPA Method 8080, GC-ECD

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*PQL
Aroclor-1016			5
Aroclor-1221			5
Aroclor-1232			5
Aroclor-1242			5
Aroclor-1248			5
Aroclor-1254			5
Aroclor-1260			5

ND: Analyte Not Detected at or above PQL
--: Analyte Not Requested
*PQL: Practical Quantitation Limit

GC Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

ANALYTICAL REPORT
Sulfate
EPA Method 375.3
Gravimetric

ET Lab Project ID:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

Reporting Units:

CLIENT SAMPLE ID	ET LAB SAMPLE ID	SAMPLE	METHOD BLANK

Inorganic Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

ANALYTICAL REPORT

ET Lab Project ID:
Sample Matrix:
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

pH Electrometric Measurement
EPA SW 846 Method 9040

CLIENT SAMPLE ID	ET LAB SAMPLE ID	SAMPLE	SAMPLE TEMP.

Inorganic Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Liquid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Volatile Organics
EPA Method 624, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*MDL
Chloromethane			8.3
Vinyl chloride			9.6
Bromomethane			6.5
Chloroethane			8.7
1,1-Dichloroethene			3.4
Methylene Chloride			4.4
Trichlorofluoromethane			3.6
trans-1,2-Dichloroethene			3.5
1,1-Dichloroethane			3.5
Chloroform			2.9
1,2-Dichloroethane			3.4
1,1,1-Trichloroethane			2.6
Benzene			2.2
Carbon Tetrachloride			2.8
1,2-Dichloropropane			3.6
Bromodichloromethane			3.6
Trichloroethene			3.2
2-Chloroethyl vinyl ether			5.6
cis-1,3-Dichloropropene			3.4
trans-1,3-Dichloropropene			3.7
1,1,2-Trichloroethane			4
Dibromochloromethane			4.1
Bromoform			4.5
Toluene			3.4
Tetrachloroethene			3.1
Chlorobenzene			2.7
Ethylbenzene			3.5
1,1,2,2-Tetrachloroethane			5
1,3-Dichlorobenzene			3.7

Note: Method modified by incorporating capillary column technology.
ND: Analyte Not Detected at or above MDL
--: Analyte Not Requested
*MDL: Method Detection Limit

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

ENVIRONMENTAL TECHNOLOGIES OF NEVADA, INC.
Analytical Services Division

Client:
Account #:
Customer ID:

Client Sample ID #:
ET Lab Sample ID #:
Sample Matrix: Liquid
Date Sampled:
Date Extracted:
Date Analyzed:
Date Reported:
Dilution Factor:
Analyst:

ANALYTICAL REPORT

Volatile Organics
EPA Method 624, GC/MS

Reporting Units:

ANALYTE	SAMPLE	METHOD BLANK	*MDL
1,4-Dichlorobenzene			2.8
1,2-Dichlorobenzene			3.3

Note: Method modified by incorporating capillary column technology.
ND: Analyte Not Detected at or above MDL
--: Analyte Not Requested
*MDL: Method Detection Limit

GC/MS Supervisor

3060 N. Commerce, North Las Vegas, NV 89030 (702) 734-5444 Fax (702) 399-0071

METHOD STANDARD OPERATING PROCEDURES (SOP's)

1000 - 5000 SERIES

BOOK #0044

TABLE OF CONTENTS

ENVIRONMENTAL TECHNOLOGIES ANALYTICAL SERVICES DIVISION STANDARD OPERATING PROCEDURES

2004 - Extraction of Septic/Sewer samples for TPH Analysis by Modified 8015

II. 3000 Series - Gas Chromatography/Mass Spectroscopy

3001 - GC/MS Analysis of Volatile Organics SW-846 Method 8240

3002 - GC/MS Analysis of Semi-Volatile Organics SW-846 Method 8270

III. 4000 Series - Inorganic and Metals

4001 - ICP Analysis of Metals using SW-846 Method 6010

4002 - Total Cyanide

4003 - Total Suspended Solids (TSS)

4004 - Total Dissolved Solids (TDS)

4005 - Alkalinity

4006 - Hardness

4007 - pH

4008 - Oil and Grease Partition - Gravimetric Method

4009 - Chlorine Demand

4010 - Mercury Analysis in Water by Manual Cold Vapor Technique

4011 - Mercury Analysis in Soil/Sediment by Manual Cold Vapor Technique

4012 - Sulfate - Turbidimetric

4013 - Conductivity

4014 - Turbidity

4015 - Surfactants (MBAS)

4016 - Sulfide

4017 - Flashpoint/Ignitability

4018 - WAD Cyanide

4019 - Fluoride by Ion Selective Electrode

4020 - Iridite 14-2, Isoprep 33,44, and 185 for EG&G

4021 - Nitrate by HACH Test Kit

4022 - Nitrite by HACH Test Kit

4023 - Color, True and Apparent by HACH Test Kit

4024 - Phosphorus, Reactive by HACH Test Kit

4025 - Total Phenolics by 4-AAP

4026 - Metals by Graphite Furnace Atomic Absorption

4027 - Nitrogen, Ammonia by HACH Test Kit

4028 - Chloride - Argentometric Method

IV. 5000 Series - Other Extraction/Analytical Procedures

5000 - Toxicity Characteristic Leaching Procedure (TCLP)

5002 - Glassware Preparation

5003 - Standardization of pH Meter

5004 - Preventive Maintenance on Lab Equipment

5005 - Daily Hood Velocity Log

5006 - Daily Temperature Log

5007 - Daily Balance Calibration

Form: SOPTITL
Rev: 8/20/92

Subject or Title:

Extraction of PCBs

SOP No.:	Revision No.:	Effective Date:
ETASD-2002	Original	November 6, 1991

Supercedes: None

1 FILING INSTRUCTIONS

1.1 This procedure shall be filed at ETASD as document number ETASD-2002 in the 2000 series section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 This method is suitable for the extraction of PCBs from environmental matrices and oils.

2.2 Reporting Limits

2.2.1 The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

2.3 Applicable Matrices

2.3.1 The extraction of PCBs is applicable to water, soil, oil (transformer), and wipes.

2.4 Dynamic Range; Not Applicable

2.5 Analysis Time; Depends on Matrix

Prepared by: Date:

Management Approval: Date:

Arthur J. Greeley 12/3/91

QA Officer Approval: Date:

Kenneth A. Hoar 12/5/91

3 METHOD SUMMARY

3.1 ETASD extracts soil, oil, water, and wipe samples for PCB analysis. Soils and wipes are sonicated, oils are processed by solvent dilution, and water are prepared by both continuous liquid/liquid and separatory funnel shakeout techniques. Extracts are dried, concentrated, hexane exchanged, and cleaned with florisil and sulfuric acid.

4 COMMENTS

4.1 No surrogate is used in this method.

4.2 Interferences by phthalate esters can pose a major problem in analysis when using the electron capture detector. These compounds are present in many flexible plastics, and can be leached off of plastic gloves during the handling of solvent wetted glassware. Avoid use of any plastics in sample prep and make sure all glassware is adquetely cleaned.

5 SAFETY ISSUES

5.1 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 data handling sheets should also be made available to all personnel involved in the chemical analysis.

5.2 The following parameters covered by this SOP have been tentatively classified as known or suspected, human or mammalian carcinogens: Polychlorinated biphenyls (Aroclors).

5.3 Proper protective gear (i.e. safety glasses, lab coat, viton gloves, etc.) should be worn at all times.

5.4 All samples should be opened and handled in a properly vented fume hood.

5.5 Consult laboratory management, Material Safety Data Sheets, or other related sources for detailed cautions and instructions.

5.6 Sulfuric acid is extraordinarily caustic and should only be handled while one is wearing appropriate protective gear.

6 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Samples should be collected in glass or brass (steel) containers.

6.2 Samples should be stored at 4°C.

6.3 Samples must be extracted with 7 days of sampling and analyzed within 40 days from extraction.

7 APPARATUS

7.1 40 ml VOA vial

7.2 Pasteur pipets

7.3 Pipet bulbs

7.4 Analytical balance (+/- 0.1 grams)

7.5 Silica gel cartridges

7.6 5 ml syringe

7.7 100 ml beakers

7.8 Sonicator/Extractor

7.9 K-D concentration apparatus

7.10 Clean glass wool

7.11 Filter funnels

7.12 10 ml volumetric flasks

7.13 Drying column

8 REAGENTS AND STANDARDS

8.1 Hexane: Pesticide grade or equivalent.

8.2 Methylene Chloride: Pesticide grade or equivalent.

8.3 Sulfuric acid (concentrated): Hexane rinsed before use to remove hexane extractable impurities.

8.4 Nitrogen gas cylinder

8.5 Florisil

8.6 Sodium Sulfate (anhydrous): Pesticide grade or equivalent.

8.7 Reagent water: Organic free 18 Mohm or equivalent.

9 PROCEDURE:

9.1 Soils or wipes are extracted by the following sonication technique:

9.1.1 Rinse all glassware with $MeCl_2$.

9.1.2 Open and examine, oil and water content. Extreme oil content is noted. Place about 1

g of sample into a beaker and add 10 ml of Methylene Chloride. Swirl the mixture to determine solubility and content of contamination. For highly contaminated samples, a minimum of 1 g is sufficient. For low contamination, a maximum of 30 grams may be used. Weigh out appropriate amount of sample (1-100 grams) into a clean rinsed beaker. Add 10-50 grams of sodium sulfate and unify the mixture with a spatula.

9.1.3 Choose the cleanest sample as MS and MSD. Weigh out the same amount as prepared for sample extraction, add sodium sulfate and mix.

9.1.4 Prepare the QA/QC, (Reagent blank, laboratory control spike) adding appropriate amount of sodium sulfate to a beaker.

9.1.5 There is no surrogate used for PCBs, but LCS, MS, and MSD are spiked with PCB Matrix Spike. The spike is added to the solvent just prior to sonication.

9.1.6 Clean the horn by sonicating 50 mls of solvent. Rinse the horn and wipe clean with a kim wipe.

9.1.7 Use the following order when sonicating: Reagent blank, laboratory control spike, matrix spike, matrix spike duplicate and samples.

9.1.8 Add 50 mls of methylene chloride to the beaker and spike if appropriate. Sonicate for 2 minutes at 50% duty cycle, output of 5. Turn sonicator off, remove horn and rinse.

9.1.9 Pour the liquid layer into funnel plugged with glass wool and 1/2 filled with sodium sulfate. Collect in a clean flask or KD.

9.1.10 Add 50 ml solvent to the beaker and repeat sonication for two more aliquots. After the

third sonication, pour the remaining soil with the liquid extract onto the funnel with Methylene Chloride.

9.2 Oil samples are prepared by the following solvent dilution technique.

9.2.1 Take a 10 ml volumetric flask and add 1.0 grams of sample (measured to the nearest 0.05 grams).

9.2.2 Dilute to volume with hexane. Vortex for 2 minutes. To 5 ml of this extract in a vial add 5 ml concentrated H_2SO_4. Vortex for 2 minutes.

9.2.3 If sample appears colored or analysis shows contamination, use silica gel cartridge.

9.2.4 Prepare the silica gel cartridge by placing 2 ml of methanol and then 5 ml of hexane via syringe then put a portion of the H_2SO_4 cleaned-up extract.

9.3 Liquid samples are extracted by liquid/liquid continuous technique, or separatory funnel extraction.

9.3.1 Rinse all glassware with methylene chloride before use.

9.3.2 Prepare 3 round bottom flasks for QA/QC and one for each sample.

9.3.3 Fill the 500 ml round bottom flask with methylene chloride and decant 1/2 into the continuous extractor. Add boiling chips and a washed teflon sleeves to flasks. Attach flask to the extractor.

9.3.4 For reagent blanks and laboratory control spike add 1000 ml of DI water to the extractor using a 1 liter graduated cylinder. Be careful not to get water in the flask. Spike the water layer of the LCS with PCB spike.

9.3.5 For samples, add 1000 ml of sample to the extractor. If the sample is extremely dirty,

dilute as little as 200 ml into 1000 mls of reagent water and add to the extractor.

9.3.6 Rinse the joint of the condenser with methylene chloride and place on the top of the extractor. Turn on the water and check flow. Turn on the heating mantle to 6 and let reflux for 18 hours. After 1/2 hour check extracts to verify proper working order.

9.3.7 After 18 hours turn the mantle off and let cool for 1/2 hour. Decant the remaining methylene chloride from the extractor to the flask. Avoid getting water in the flask.

9.3.8 The samples are ready for concentration.

9.3.9 Alternatively the sample may be extracted by placing a measured volume of sample (1 liter) into a 2 liter separatory funnel. Adjust the pH to 7 and extract with 3 x 50 ml portions of methylene chloride. Concentrate the combined portions as outlined below.

9.4 Concentration of Samples:

9.4.1 Rinse the KD, KD tubes and Snyder columns with methylene chloride.

9.4.2 Add a boiling chip to the tube.

9.4.3 For liquid samples, prepare a sodium sulfate funnel by plugging with glass wool, filling 1/2 with sodium sulfate and rinsing 3 times with methylene chloride. Place the funnel on the KD.

9.4.4 Pour extracts through the funnels (soil samples are poured without the funnel if already dried). Rinse the flask 3 times with 10 ml methylene chloride and pour onto funnel. Once the extract has gone through the funnel, rinse the funnel 3 times with 20 ml methylene chloride.

9.4.5 Tap the funnel to allow excess methylene chloride to flow, remove funnel and place sodium sulfate into a 2 liter beaker or bucket to dry in the hood.

9.4.6 Place the column on the KD and heat the extract in the hot water bath. The balls of the column should rattle but not overflow. Concentrate until 6 ml remain and remove from bath.

9.4.7 Before removing the tube, dry the outside surface to prevent water contamination. Remove the tube, the sample is ready for hexane exchange.

9.5 Hexane Exchange

9.5.1 Turn the heater to 2 on the nitrogen exchanger. Load the samples and blow to 1.0 ml with a steady stream of nitrogen. The liquid should not splash. Add 9 ml of hexane and blow to 1.0 ml. Repeat for 3 exchanges.

9.5.2 Alternatively, 50 mls of hexane can be added to the KD through the Snyder column after the sample has cooled. The sample is concentrated to 5 mls. Repeat this procedure 2 more times. The samples are ready for florisil and sulfuric acid clean-ups.

9.6 Florisil Clean-up

9.6.1 Florisil clean-up for PCBs may be done before or after acid cleaning.

9.6.2 Plug the stem of a drying column with glass wool and fill with prepared florisil. Tap gently to remove air spaces. Add 1 gram of sodium sulfate to the top of the column.

9.6.3 Pre-wet column with 1.0 ml of hexane. Add the 1.0 ml extract to the column with a pipet. Rinse the KD-tube with 1.0 ml hexane and add to the column. Elute 11 ml into a 12 ml vial.

9.6.4 Blow volume down to </= 5 ml on the nitrogen

exchange as before. Bring volume to 5.0 ml with hexane. The extract is ready for acid cleaning.

9.6.5 Alternatively, florisil may be added directly to 1 to 2 ml of sample extract, vortexed for 1 ml and allowed to settle. Remove upper hexane layer for analysis.

9.7 Acid Clean-up

9.7.1 Place approximately 1.5 ml of the blank into a 2.0 ml vial before cleaning.

9.7.2 To the remaining portion of the reagent blank and all dirty samples (except LCS), add 1 ml of sulfuric acid. Shake for 2 minutes and let settle. Place the hexane layer into a clean vial using a pipet. Repeat for samples until acid is clear or retains the same color for 2 shakes.

9.7.3 If cleaning before florisil do procedure 8.7 only once. After removing hexane layer rinse acid with additional hexane. Add the rinse to the sample and blow down for florisil clean-up.

9.8 Sulfur Clean-up

9.8.1 Follow directions from reference 3 for TBA-Sulfide Clean-up Procedure.

10 QA/QC REQUIREMENTS

10.1 The method blank is mandatory and must be performed for every set, and every 20 samples, when an extraction batch exceeds 20 samples. The method blank for this method is 10 ml of hexane treated in the same manner as described above.

10.2 The Laboratory control Samples are mandatory and must be performed for every 20 samples. LCS for this method is 0.5 ml of Aroclor 1254 spiking standard (concentration = 10 ug/ml) to a final volume of 10 ml with hexane to yield a final concentration of 5000 ug 1254/kg oil. LCS are then prepared in the same manner as samples.

10.3 Matrix spikes and Matrix Spike Duplicates are optional and must be requested. Matrix spikes are samples to which 0.5 ml of Aroclor 1254 spiking standard has been added before the hexane is added, then prepared in the same manner as un-spiked samples.

11 CALCULATIONS

11.1 Calculations to confirm spike levels:

C spike (ng/ul * [V spike (ul) / M sample (g)] = S spike (ng/g)

Where:
C spike = Concentration of spike solution
V spike = Volume of spike solution used
M sample = Mass of sample spiked
S spike = Actual spike level in sample

Note: ng/uL = ug/ml, and ng/g = ug/kg

11.2 Calculation to determine amount of spike standard necessary to spike at a certain level:

S spike (ng/g) * [M sample (g) / C spike (ng/ml)] = V spike (uL)

Where: See Above

Note: See Above

12 REFERENCES

12.1 40 CFR part 761.125 (PCB wipes)

12.2 The determination of Polychlorinated Biphenyls in transformer fluid and waste oils EPA -600 14-81-045 Sept. 1982.

12.3 Test Methods for Evaluation Solid Waste SW 846 3rd Edition. November 1986. Clean-up Methods, Silica Gel Method 3630 Acid - Base partition Method 3650. Sulfur Clean-up 3660. Analytical Method 8080.

12.4 Standard Methods for the Examination of Water and Wastewater. 17th Edition., 1989.

Subject or Title:

Analysis of Organochlorine Pesticides and PCBs (EPA Method 8080)

SOP No.: ETASD-2003 Revision No.: 1992-7 Effective Date: July 30, 1992

Supersedes: Original

1 FILING INSTRUCTIONS:

1.1 This procedure shall be filed at ETASD as document ETASD-2003 in the 2000 section of the SOP Manual.

2 SCOPE AND APPLICATION:

2.1 Analytes: Organochlorine pesticides and polychlorinated biphenyls (PCBs) (see accompanying analyte list).

2.2 Detection Limits: See analyte lists.

2.3 Applicable matrices: water, soils, and multiphase.

2.4 Linear Range of Instrument

2.4.1 Calibration standards are run at 5 levels and a calibration curve is generated for each compound.

2.5 Analysis Time

2.5.1 Sample prep requires at least 1.5 hours for completion unless clean up is required.

Prepared by: Date:

Management Approval: Date: 8-19-92

QA Officer Approval: Date: 8-19-92

2.5.2 Analysis time is approximately 40 min. per sample or standard.

3 SUMMARY OF METHOD:

3.1 Samples are extracted with methylene chloride (CH_2Cl_2). Extracts are exchanged to hexane, and concentrated to a final volume of 1.0 mL. Analysis is performed on a gas chromatograph equipped with an electron capture detector. Samples are analyzed using capillary columns.

3.2 Reporting limits for the target parameters are presented in the following tables:

ANALYTE	WATER ug/L	SOIL ug/kg	OIL mg/kg
Aldrin	0.2	3	--
alpha-BHC	0.1	3	--
beta-BHC	0.1	3	--
delta-BHC	0.3	3	--
gamma BHC (Lindane)	0.1	3	--
4,4'-DDD	0.2	3	--
4,4'-DDE	0.2	3	--
4,4'-DDT	0.3	3	--
Dieldrin	0.1	3	--
Endosulfan I	0.1	3	--
Endosulfan II	0.1	3	--
Endosulfan sulfate	0.1	3	--
Endrin	0.1	3	--
Endrin aldehyde	0.1	3	--
Heptachlor	0.1	33	--
Heptachlor epoxide	0.1	3	--
Methoxychlor	2	100	--
Chlordane	2	100	--
Toxaphene	10	100	--
Aroclor-1016	5	10	1.0
Aroclor-1221	5	10	1.0

ANALYTE	WATER ug/L	SOIL ug/kg	OIL mg/kg
Aroclor-1232	5	10	1.0
Aroclor-1242	5	10	1.0
Aroclor-1248	5	10	1.0
Aroclor-1254	5	10	1.0
Aroclor-1260	5	10	1.0

4 COMMENTS:

4.1 Polar Compounds such as sulfur may interfere. A column clean-up is often required for soil samples. If samples contain sulfur they must be cleaned before being analyzed on a capillary column.

4.2 Helpful Hints

If a dirty looking sample must be analyzed, inject a hexane blank in the next auto-sampler position following the sample.

5 SAFETY:

5.1 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 data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst.

5.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or

mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHC's, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6 SAMPLE COLLECTION, PRESERVATION AND HANDLING:

6.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

6.2 All samples must be iced or refrigerated at 4°C from the time of collection until extraction.

6.3 All aqueous samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction. Soil/waste samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

7 APPARATUS:

7.1 Separatory funnel - 2 L, with Teflon stop-cock

7.2 Filtering funnel - 75 mm top diameter

7.3 Chromatographic column - Rt_x5 (Restek) 30 meter, 0.25 mm ID or equivalent.

7.4 Concentrator tube, Kuderna-Danish - 10 mL graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

7.5 Evaporative flask, Kuderna-Danish - 500 mL.

7.6 Snyder column, Kuderna/Danish - Three ball macro.

7.7 Vials - 1 to 4 mL with Teflon-lined screw cap.

7.8 Boiling chips - Approximately 10/40 mesh.

7.9 Water bath - Heated, with concentric ring over cover, capable of temperature control (± 2°C). The bath should be used in a hood.

7.10 Balance - Analytical capable of accurately weighing 0.0001g.

7.11 Sonicator - A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model is recommended:

Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc. Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1.2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

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

7.13 Gas Chromatography - An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-cart recorder. A

data system is recommended for measuring peak areas. Data from both columns must be evaluated.

7.14 Detector - Electron capture detector

8 REAGENTS AND STANDARDS:

8.1 *Reagent water* - Reagent water is defined as a water in which an interference is not observed at the method detection limit of each parameter of interest.

8.2 Sodium Hydroxide solution (6N)

8.3 Sulfuric Acid (1:1) ACS sp. gr. 1.84

8.4 Acetone, hexane, methylene chloride - Pesticide Quality or equivalent.

8.5 *Sodium Sulfate* - (ACS) granular, anhydrous. Dry in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. Alternatively, heat 16 hours at 450-500°C in a shallow tray or Soxhlet extract with CH_2Cl_2 for 48 hours.

8.6 *Florisil* - PR grade (60/100 mesh.) Purchase activated at 1250°F and store in dark in glass container with ground glass stopper or foil-lined screw cap. Before use, activate each batch at least 16 hours at 130°C in a foil covered glass container.

8.7 *TBA-Sulfite (Tetrabutylammonium sulfite)* - for sulfur clean-up of pesticide samples - 3.39 g of tetrabutylammonium hydrogen sulfate into 100 mL reagent water with 25 g sodium sulfite. Store in amber bottle.

8.8 *Isopropyl Alcohol*

8.9 Primary standards solutions may be prepared from pure

standard materials or purchased as certified solutions.

8.10 *Pesticide Surrogate Stock Solution* - 10 mL of 2000 ug/L dibutyl chlorendate (Ultra Scientific or equivalent) into a 10 mL volumetric and fill to the mark with hexane. This gives a 2.0 ug/mL concentration.

8.11 *Pesticide Surrogate Working Solution* - 1.0 mL of above stock diluted to 10 mL in a volumetric with hexane to give 0.2 ug/uL. Use 100 mL per 1 liter sample. Final concentration in a 1.0 mL extract is 20 ug/L.

9 PROCEDURE:

9.1 Method Summary

This method is applicable to the determination of organochlorine and PCBs in aqueous samples. A 1 liter water sample is extracted with (CH_2Cl_2). The extract is dried, exchanged to hexane and concentrated to a volume of 1.0 mL. Analysis is performed on a gas chromatograph equipped with an electron capture detector.

9.2 Extraction of Liquid Samples

9.2.1 In general, pesticide recoveries may be poor if there is an extreme amount of sediment or an extreme emulsion forms during emulsion test.

Note: All glass-ware must be solvent rinsed before use.

9.2.2 For samples in a 1 liter or smaller bottle, mark the meniscus on the side of the sample bottle. After emptying the sample into a separatory funnel, fill the bottle with tap water and measure that amount in a graduated cylinder. For samples in larger bottles, measure 1.0 L into a

graduated cylinder. Pour sample into a 2 L separatory funnel. For blanks and quality control samples, pour 1.0 L of Reagent water into the separatory funnel. Record the volume of sample extracted in the sample prep log book.

9.2.3 For pesticides, add 100 uL of the 0.2 ug/mL dibutylchlorendate surrogate standard to the sample using a syringe. Make sure the syringe needle is below the surface of the sample while the standard is being added. Mix the sample immediately by swirling. Record the name of the surrogate solution reference number in the Sample Prep Log Book.

9.2.4 Add the spiking standard, if appropriate, using the procedure described in step 9.2.3.

9.2.5 Check the pH and note the initial pH on the prep sheet. Adjust the pH to 5-8, if necessary, with 6N NaOH or 1:1 H_2SO_4. Note the adjusted pH in the prep log book.

9.2.6 For samples that were mixed before pouring, add 50-60 mL CH_2Cl_2 to the sample bottle to rinse the inner walls. DO NOT cap and shake the bottle, rinse the glass only; transfer the solvent to the separatory funnel. For samples that were decanted, add the first aliquot of CH_2Cl_2 directly to the separatory funnel. Extract the sample by shaking it for two minutes with frequent ventilation.

9.2.7 Allow the layers to separate. If there is an emulsion, break it mechanically or by centrifuging. Note any emulsions and corrective actions on the prep log book.

9.2.8 Put a plug of glass wool in a funnel and fill about 2/3 full with Na_2SO_4. Rinse the funnel and Na_2SO_4 with 30-40 mL of CH_2Cl_2, and drain into an appropriate waste container. Place the funnel onto the 500 mL Kuderna-Danish (K-D) evaporative concentrator.

9.2.9 Drain the bottom organic layer (CH_2Cl_2) into the funnel.

9.2.10 Repeat the extraction twice more using a 50-60 mL aliquot of CH_2Cl_2 each time. Collect the solvent in the same K-D

9.2.11 Add a boiling chip to the K-D and attach a 3 ball Snyder column to the top. Pre-wet the column by adding about 1 mL of CH_2Cl_2 to the top.

Note: The concentration step is critical; losses of target compounds can occur if the bath temperature is too high or too low or if extract are allowed to boil too long.

9.2.12 Place the K-D in a hot water bath so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 5-10 mL, add 50 mL of hexane. Repeat the process 2 more times.

9.2.13 Carefully concentrate the extract to 1 mL under a gentle stream of nitrogen using the N-evap apparatus. Transfer the extract to a 2.0 mL vial with a teflon lined cap and mark the meniscus. Write your initials, date of final concentration, parameter, and sample number on the vial. Record

final volume, initials, and date in sample prep log book.

9.2.14 A florisil column can be used to clean-up all organochlorine pesticide fractions.

9.2.15 Complete the prep sheet for the extraction and concentration steps.

9.3 Continuous Extractor Techniques

9.3.1 Put 250 mL CH_2Cl_2 in a round bottom flask and add a few boiling chips. Add 250 mL of CH_2Cl_2 to the extractor flask.

9.3.2 For blanks and quality control samples, carefully pour 1.0 liter of deionized water into the extractor. Minimize the disturbance of the solvent layer and avoid getting water into either side arm by pouring the water down the back of the extractor.

9.3.3 Open the sample container and remove a small aliquot of the sample with a pasteur pipet. Place enough of the sample on a pH paper to thoroughly soak the paper. Compare the pH paper with the chart on the container.

9.3.4 a: For water samples:

Decant ground water samples into the extractor. Mix all other water samples by shaking the sample bottle. After emptying the sample into the extractor, fill the bottle with tap water and measure that amount in a graduated cylinder. For samples in larger bottles, measure 1.0 L into a graduated cylinder. Pour the sample into the extractor. For blanks and quality control

samples, pour 1.0 L of deionized water into the extractor. Record the volume of sample extracted in the sample prep log book.

b: For sludge samples:

Weigh the bottle containing the sample and carefully transfer the sample to the extractor flask. Re-weigh the bottle, calculate the difference, and record it as the amount extracted on the prep sheet.

9.3.5 Add enough deionized water to allow proper operation.

9.3.6 Add the appropriate surrogate standard to the extractor using a syringe. Make sure that the tip of the syringe is below the surface of the liquid in the extractor as the surrogate or spiking standard is being added. Mix the sample immediately using a glass stirring rod. Record information as described above.

9.3.7 Add the spike mix, if appropriate, using the procedure described in the preceding step.

9.3.8 Adjust the pH to 5-8 with 10 N NaOH or 1:1 H_2SO_4 as appropriate.

9.3.9 Add enough reagent water to the extractor flask to allow the solvent in the removable side arm to just begin to drip into the round bottom flask

9.3.10 Remove the condenser from the rack and rinse the lower joint and lip with a squirt bottle (CH_2Cl_2.) Place the condenser on top of the extractor. Turn on the cooling water to the condensers.

9.3.11 Turn on the heating mantle to setting 6. Check after 15 min. to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip of the condenser, and that the volume of the solvent in the round bottom flask is still approximately 250 mL. Adjust the rheostat so that the light is just bright after re-fluxing has started. Check all extractor joints for leaks with the corner of a Kimwipe.

9.3.12 Allow the extraction to proceed for a minimum of 18-24 hours.

9.3.13 Turn off the heating mantle and allow the apparatus to cool (30-60 min.) with water flowing through the condenser.

9.3.14 The solvent (CH_2Cl_2) contained in the round bottom flask is the extract. Carefully decant remaining CH_2Cl_2 from extractor into the round bottom. Remove the flask from the extractor and transfer the extract to a cleaned K-D apparatus with a funnel and sodium sulfate. Rinse the funnel with a small aliquot of CH_2Cl_2.

9.3.15 Continue as before with the concentration step.

9.4 Extraction of Soil Samples by Sonication

Note: All glass-ware must be solvent rinsed with CH_2Cl_2 before use.

9.4.1 Weigh 30 g of the sample into a 250 mL beaker. Add 10 g of dried Na_2SO_4 and stir the mixture well with a steel spatula. The sample should have a grainy texture. If it forms a large clump, add more Na_2SO_4 and note it on the prep sheet.

9.4.2 Add 50-60 mL of CH_2Cl_2 to all samples.

9.4.3 Add the appropriate surrogate standard using a syringe.

9.4.4 Add the spike, if appropriate, using the procedure described in the previous step.

9.4.5 Sonicate the samples for 3 min. at an output setting of 5-7 with the 3/4 inch sonicator horn 1/2 inch below the surface of the solvent.

9.4.6 Repeat the extraction twice more using 50-60 mL aliquots of CH_2Cl_2.

9.4.7 Put a plug of glass wool in a funnel and fill 2/3 full with Na_2SO_4 into a 500 mL Kuderna-Danish (K-D) evaporative concentrator. Rinse the beaker then the Na_2SO_4 with small amounts of CH_2Cl_2 into the K-D flask.

9.4.8 Add boiling chip to the K-D and attach a 3 ball Snyder to the top. Pre-wet the column by adding about 1 mL of CH_2Cl_2 through the top.

Note: The concentration step is critical; losses target compounds can occur if the temperature of the bath is too high or too low or the extract is exposed to heat too long.

9.4.9 Place the K-D in a heated water bath so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 5-10 ml, add 50 ml of hexane and concentrate back down.

Repeat the process 2 more times.

9.4.10 When the K-D has reached an apparent volume of 5-10 mL through the top of the Snyder column, shake the snyder column to make sure that the balls have not stuck. Note: losses of target compounds can occur at this step. Make sure solvent loss is rapid (10-15). Do not allow the extract to cook.

9.4.11 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of hexane. Transfer the extract to a calibrated 15 mL centrifuge tube, rinsing all of the ground glass joints well, as compounds collect on the ground glass.

9.4.12 Carefully concentrate the extract to 10.0 mL under a gentle stream of nitrogen using the N-evap apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, consult the Lab Manager. Transfer the extract to a labeled 2 mL screw-top vial with a Teflon lined cap, and place on a rack with other samples with the same project number, if any. Include the following information on the label: sample number, parameter, your initials, and date of final concentration. Record final volume, initial and date in sample prep log book.

9.4.13 If the extract is colored or a precipitate forms, organochlorine pesticide extracts will need a florisil column clean-up. If the extract is to be analyzed for PCBs only, the appropriate clean-up procedure is found in SOP ETASD-2002. If there is any question, consult the Lab Manager.

9.5 Florisil Clean-up for Pesticide Samples

Method Summary: A sample extract in hexane is subjected to a florisil absorption by taking a small amount of extract and adding a small amount of silica gel. Polar impurities will be absorbed. This should also be done to the method blank and matrix spike to check for losses.

9.6 Sulfur Clean-up of Pesticide Extracts

9.6.1 Transfer 0.5 mL of the pesticide extract into a 12 mL screw top vial with a Teflon lined cap.

9.6.2 Add 1.0 mL of Tetrabutylammonium (TBA) sulfite reagent and 2.0 mL of 2-propanol to the vial. Cap the vial and shake for at least 1 minute.

9.6.3 If the sample is colorless or the initial color is un-changed and if clear crystals are present, proceed to step 4. However, if there are no crystals present, add sodium sulfite in small portions and shake. Repeat until clear crystals are observed.

9.6.4 Add 5 mL of reagent water and shake for at least 1 minute. Allow the sample to settle for 5-10 minutes, then transfer the hexane (top) layer into a clean 2 mL vial.

9.6.5 Add a small amount (less than 1 cm) of dried Na_2SO_4 and shake for 1 minute. Enough Na_2SO_4 has been added if it remains grainy after shaking.

9.6.6 Transfer the hexane to a 2 mL vial labeled as "Sulfur Cleaned" and store with other samples in the same project.

9.6.7 Preparation of the TBA-sulfite Reagent:

9.6.7.1 Dissolve 3.39 g of tetrabutylammonium

hydrogen sulfate in 1009 mL of distilled water.

9.6.7.2 To remove impurities, extract this solution 3 times with 20 mL portions of hexane in 500 mL separatory funnel. Discard the hexane extracts.

9.6.7.3 Add 25 g of Na_2SO_4 to the water solution.

9.6.7.4 Store the resulting solution, which is saturated with Na_2SO_4, in an amber bottle with a Teflon lined screw cap.

9.6.7.5 This solution can be stored for approximately one month at room temperature.

9.7 Analysis

9.7.1 Calibration of Instrument

9.7.1.1 Calibration standards are run at 5 levels and a calibration curve is generated for each compound. Most compounds are linear in the 0.005-0.05 range ug/mL. Pesticide standards are run at 5,10,50,100,150 ug/L levels. PCBs are run typically at 0.25,0.5,0.75,1.0,1.5 ug/mL, depending on the PCB's actual response. External standard technique is used to quantify samples. Acceptance limits for the curve are 20% Relative Standard Deviation.

9.7.1.2 Run a mid-level check standard after every 10th injection and at the end of the sequence. Calibration factors should not exceed + or - 15% of the calibration

curve.

9.7.1.3 A column evaluation standard run is performed at the beginning of the day when running pesticides contain endrin and p,p'-DDT.

9.7.1.4 The analyst should examine the shape of all peaks to ascertain that they are generally symmetrical. Tailing peaks are an indication that the system requires routine maintenance.

9.7.1.5 De-gradation of endrin and p,p'-DDT on the column are limited by the EPA to 20% of either compound and this criteria is applied to all work. By the time column de-gradation is approaching these values, maintenance as described above is mandatory.

9.7.1.6 De-gradation in the column evaluation standard will be determined as follows:

Using area counts calculate endrin de-gradation as a percentage of the total endrin:

$$\frac{\text{endrin aldehyde + endrin ketone}}{\text{endrin + endrin aldehyde + endrin ketone}} \times 100 =$$

Similarly, calculate the de-gradation of p,p'-DDT;

$$\frac{\text{p,p'-DDE + p,p'-DDD}}{\text{p,p'-DDT + p,p'-DDE + p,p'-DDD}} 100\% =$$

% RSD is calculated by:

$$\% \text{ RSD} = \frac{SD}{C_f}$$

Where

SD = Standard deviation of curve calibration factors

C_f = Average calibration factor

% Difference is calculated by:

$$\% \text{ Difference} = \frac{\overline{C_f} - C_f}{\overline{C_f}} \times 100$$

Where

$\overline{C_f}$ = Average calibration factor

C_f = Calibration factor for mid-point continuing calibration check standard.

9.8 GC Conditions

9.8.1 Load appropriate GC method into the system.

9.8.2 Inject 2 ul of the sample or standard extract using the solvent-flush technique or auto sampler.

9.8.3 Analyze samples in groups of no more than 10 samples. After the analysis of the first group of up to 10 samples, analyze a continuing

calibration check standard (ccv). Subsequent groups of up to 10 samples may be analyzed by repeating this sequence. The pesticide/PCB analytical sequence must end with CCV regardless of the number of samples analyzed. If multi-response pesticide/PCB is detected in either of the preceding groups of 10 samples, the appropriate multi-response pesticide/PCB may be substituted.

9.8.4 If it is determined during the course of a 24 hour sequence that one or more of the criteria have been violated, stop the run and take corrective action. After the corrective action has been taken, the 24 hour sequence may be re-started as follows. If a standard violated the criterion, re-start the sequence with that standard, determine that the criteria have been met, and continue with sample analysis. If a sample violated the criterion re-start the sequence with the standard that would have <u>followed</u> that group of samples.

If it is determined <u>after</u> the completion of a 24 hour sequence that one or more of the criteria have been violated, proceed as follows. If a standard violated the criterion, all samples analyzed after that standard must be re-analyzed as part of a new 24 hour sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that <u>did not</u> meet the criterion must be re-analyzed as part of the new 24 hour sequence.

9.8.5 Inject the method blank (extracted with each set of samples) on every instrument and GC column on which the samples are analyzed.

9.9 Evaluation of Chromatograms

9.9.1 Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample analysis is complete at this point.
Confirmation is not required.

9.9.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was analyzed on the same instrument within a 72 hour period.

9.9.3 Determine if any pesticides PCBs are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

9.9.3.1 If the response is on scale, the extract is ready for confirmation and quantification. If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50 an 100% full scale and re-analyze. Use this dilution quantification.

9.9.4 If identification of compounds of interest are prevented by the presence of interferences, further clean-up is required. If sulfur is evident, go to sulfur clean-up.

9.10 GC/ECD Confirmation Analysis

9.10.1 Positive results are confirmed by GC/MS if the concentration is sufficiently high or the extract can be concentrated further to within detectable

ranges for the GC/MS. Alternatively the samples may be confirmed by using a second capillary column of different polarity on the GC/ECD. PCBs, chlordane, and toxaphene need not be confirmed due to pattern matching and recognition to standards.

9.11 Calculations

9.11.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

9.11.1.1 Water
Concentration ug/L =

$$\overline{C_f} \times (A_x) \times \frac{(V_e)}{V_s} \times (D)$$

Where

$\overline{C_f}$ = Average calibration factor from initial curve for analyte

A_x = Area counts for analyte from sample extract

V_e = Extract volume

V_s = Original sample volume extracted

D = Dilution factor

9.11.1.2 Sediment/Soil

Concentration ug/kg = (Dry Weight Basis)

$$\frac{\overline{C_f} \times (A_x) \times (V_e)}{W_s} \times (D)$$

$\overline{C_f}$, A_x, V_e, D same as above

W_s = Weight of sample extracted (30 grams)

9.11.2 For multi-component mixtures (chlordane, toxaphene and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak (<50% of the total area must be used) unless interference with individual peaks persist after clean-up. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

9.11.3 Calculation for surrogate and matrix spike recoveries.

$$\text{Percent Recovery} = \frac{\text{Concentration found}}{\text{Concentration actual}} \times 100$$

9.11.4 Report results in micrograms per liter or micrograms per kilograms without correction for recovery data.

10 QA/QC REQUIREMENTS:

10.1 A minimum of one method blank, one LCS (laboratory control standard), one matrix spike and one matrix spike duplicate should be run per batch of samples or every 70

samples which ever is smaller. Calibration acceptance criteria must be met before sample analysis proceeds.

11 CALCULATION:

11.1 See each individual section for necessary calculations.

12 REFERENCES:

12.1 USEPA SW846 3rd Edition, Method 8080

13 CORRECTIVE ACTIONS

13.1 See individual sections.

13.2 If problems occur, contact the supervisor.

Subject or Title: Page 1 of 38

GC/MS Analysis of Volatile Organics SW-846 Method 8240

SOP NO.:	Revision No.:	Effective Date:
ETASD-3001	original	January 1, 1991

Supercedes: None

1 FILING INSTRUCTIONS

1.1 This procedure shall be filed at ETASD as document number ETASD-3001 in the 3000 series section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 Analytes: Quantitative analysis is performed for the compounds listed in Appendix A. Qualitative analysis by mass spectral identification can be performed on other purgeable, chromatographable compounds, provided they meet acceptable Quality Control as outlined in Section 9.

2.2 Reporting Limits: See Appendix A.

2.3 Applicable matrices: Water, soil, solids, sludge, and waste.

2.4 Dynamic range: Analytes can typically be quantitated between 5 ppb and 200 ppb for water samples and soils analyzed by the low level direct purge method. Analytes in soils analyzed by the methanol extraction method can be quantitated between 500 and 20000 ppb. Samples which exceed this concentration range for any analyte in Appendix A should be diluted to be within the dynamic range of the method. Samples should also

Prepared By: Date:

Management Approval: Date:

6-7-93

QA Officer Approval: Date:

6-21-93

be diluted when any other volatile component of the sample exceeds this range. Reporting limits will be adjusted to reflect the dilution performed.

2.5 Analysis time: Approximate analytical time is 45 minutes per GC/MS run. The time required for data reduction will be dependent upon the complexity of the sample.

3 METHOD SUMMARY

3.1 Aqueous samples are analyzed by quantitative and/or qualitative purge and trap-GC/MS using an internal standard method.

2.2 Low level solid samples are analyzed by quantitative and/or qualitative purge and trap - GC/MS using an internal standard method.

2.3 Medium to high level solid samples are extracted with methanol and the extract is analyzed by purge and trap-GC/MS for quantitative and/or qualitative identification using the same internal standard method.

2.4 Alternatively, lower detection limits can be achieved for analytes in soil samples by using the direct purge method.

4 COMMENTS

4.1 All deviations made from this SOP MUST be approved by the supervisor and well documented.

4.2 All re-useable glassware should be rinsed with methanol and oven dried prior to use.

4.3 Care should be taken not to introduce contamination into the samples. Particular attention should be paid to contamination by common laboratory solvents.

4.4 Care should be taken when handling samples for volatiles analysis to avoid loss of analytes.

4.5 Do not over stock traps. Tenax has a life time of only a few months. Traps will also de-grade with use due to the break down of tenax from rapid temperature changes.

5 SAFETY ISSUES

5.1 The toxicity or carcinogenicity of each chemical used in this procedure has not been precisely defined, however, each chemical compound should be treated as a potential health hazard. From this view point, exposure to these chemicals should be reduced to the lowest possible by using chemicals in an approved hood and wearing appropriate personal protective equipment (ie lab coat or apron, safety glasses, and gloves).

5.2 A Material Safety Data Sheet (MSDS) is available for all laboratory standard and reagent chemicals. The appropriate MSDS must be read before handling the chemicals.

5.3 All laboratory personnel should be thoroughly familiar with the laboratory Safety Manual and Hazard Communication Standard before undertaking any laboratory work.

6 SAMPLE COLLECTION, PRESERVATION, CONTAINERS, AND HOLDING TIMES

6.1 Standard 40 mL glass screw-cap VOA vials with Teflon-faced silicone septa may be used for both liquid and solid matrices. Solid samples may also be collected in wide-mouth glass jars with Teflon-lined caps. Samples should be introduced into the containers with minimum agitation to avoid loss of volatile components. For liquid samples, each VOA vial should be filled without introduction of bubbles. Fill until there is a meniscus over the lip of the vial. The lid with septum

(Teflon side toward the sample) should be tightened onto the vial. After tightening the lid, the vial should be inverted and tapped to check for air bubbles. If there are any air bubbles present the sample must be re-taken. Sample containers for solid samples should be filled as completely as possible with minimum air space.

6.2 Water samples may be preserved with HCl to extend the holding time of samples to be analyzed for aromatic compounds. Aromatic compounds are particularly susceptible to bio-degradation at normal pH. The pH of the sample should be adjusted to less than 2 with HCl in the field at the time of sampling, or prior to sampling the 40 ml VOA vials may have 4-5 drops of concentrated HCl added as preservative.

6.3 All samples must be iced or refrigerated at 4°C from the time of collection until analysis or extraction.

6.4 All aqueous preserved samples must be analyzed within 14 days of collection. Soil/waste samples must be analyzed within 14 days of collection. Soil samples which are analyzed by the low level method must be analyzed within 14 days from the sampling date.

7 APPARATUS

7.1 Gas-tight syringes: 10 uL, 25 uL, 50 uL, 100 uL, 250 uL, 500 uL, and 1 mL.

7.2 Syringe valve: Two-way with Luer ends.

7.3 5 mL gas tight syringe, luer-lock type.

7.4 Analytical balance capable of weighing 0.0001 g.

7.5 Top-loading balance capable of weighing 0.1 g.

7.6 Disposable glass test tubes for autosampler.

(15 mm x 180 mm)

7.7 Glass vials with screw cap and teflon liner.

7.8 Volumetric flasks: 10 mL-100 mL

7.9 GC auto-sampler vials for storage of methanol extracts

7.10 Disposable pasteur pipits

7.11 Stainless steel spatula

7.12 Purge-and-trap device including the sample purger, the trap and the de-sorber. (Tekmar LSC-2 or equivalent) Device may include automatic sampler (Tekmar ALS or equivalent.

7.13 Purging chamber

7.13.1 Disposable test tubes or fritted glass to hold 5 mL sample allowing gaseous headspace between the water column and the trap to be less than 15 mL. This type of sparger may be used for purging aqueous samples and low to medium level soil samples.

7.14 Traps

7.14.1 Four phase: Silica Gel/Tenax/3%OV-1/carbosieve (charcoal) for the analysis of all volatile compounds or equivalent.

7.14.2 Three phase: Silica gel/Tenax for the analysis 3% OV-1 of volatile compounds excluding fluorocarbons.

7.14.3 Two phase: Tenax/3% OV-1 for the analysis of volatile compounds excluding fluorocarbons and purgeable aromatics.

7.15 Chromatographic Columns

7.15.1 Analytical Column: 6' x 2 mm id glass column packed with 1% SP-1000 on Carbopack B (60/80 mesh) or 105 m long x 0.53 mm ID Rtx - 1 Megabore (Restek Corporation) Column with 3.0 um film thickness, or their equivalents.

7.16 Gas Chromatograph/Mass Spectrometer

7.16.1 Gas chromatograph: An analytical system that includes a temperature-programmable gas chromatograph including all required accessories such as syringes, columns, and gases.

7.16.2 Mass spectrometer: Capable of scanning from 35 to 260 amu every 3 seconds or less, using 70 electron volts.

7.16.3 GC/MS interface: An interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria. An all glass interface is recommended.

7.16.4 Data system: A computer system must be interfaced to the mass spectrometer which will allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the analytical run. The software should be capable of producing extracted ion profiles and integrating these abundances. The EPA/NIH Mass Spectral Library should also be available on the system.

8 REAGENTS AND STANDARDS

8.1 Reagent water - Carbon filtered house distilled water, sparged with an inert gas prior to use for volatiles

analysis, or equivalent prep that results in no analytes of interest at or above the reporting limit.

8.2 GC/MS tune check solution: 50 ng/uL BFB in methanol.

8.3 Combined internal standard and surrogate spiking solution. (See Appendix B)

8.4 Surrogate standard spiking solution. (See Appendix B)

8.5 Internal standard solution. (See Appendix B)

8.6 Laboratory Control Sample/Matrix Spike standard solution. (See Appendix B.)

8.7 Calibration standard solutions. (See Appendix B)

8.8 Methanol: purge-and-trap grade or equivalent. Store apart from other solvents.

8.9 Standard solutions of analytes: Prepared from manufacturers mixes or from pure compounds. Prepare in methanol secondary solutions from stocks.

9 PROCEDURE

9.1 Scheduling Samples for Analysis

9.1.1 Samples will be scheduled for analysis by the section supervisor according to the following priorities:

a. Meet holding times
b. Requested turnaround

9.2 Methanol extraction of soil samples for analysis by the medium-level method.

9.2.1 Carefully mix the contents of the sample container. Do not discard any supernatant

liquids. Weigh 5 g of sample to the nearest 0.1 g into a VOA vial. Note and record the actual weight. Add 5 mls purge and trap grade methanol. Shake the vial by hand for 2 minutes, let solid material settle to the bottom and transfer methanol extract to autosampler vial with zero headspace. Store extract in volatile extraction refrigerator until analysis as described in section 8.6.4.

9.3 Instrument Set-up for the GC/MS

9.3.1 Chromatographic Conditions

9.3.1.1 Column: See section 6.15

9.3.1.2 Column Temperature Program Packed:

	Packed Column:	Capillary Column:
Initial Temperature:	45 c	34° C
Initial hold time:	1 min.	8 min.
Temperature ramp:	10 C/min.	7 c/min.
Final temperature:	220 C	220 c
*Final hold time:	5-10 min.	1.4 min.

* The final hold time should be adjusted according to the retention time of the final compound in the standard.

9.3.1.3 Mass spectrometer parameters:

9.3.1.4 Mass range: 34-260 amu.

9.3.1.5 Scanning rate: 1 second/scan

9.3.1.6 Zone Temperatures:

Injection port: 200 c
Transfer line: 280 c

9.3.2 Purge and Trap Parameters

9.3.2.1 Trap: As described in section 6.14.

9.3.2.2 Purge Flow: 15-40 mL/min (measured at vent in purge mode.)

9.3.2.3 Purge pressure: 20 lb/in^2 (measured on the gauge.)

9.3.2.4 Bake Time: 13 minutes or more.

9.3.2.5 Temperature settings:

SP1 Purge Ready Temp: 30 c
SP3 Desorb Preheat Temp: 100 c
SP4 Desorb Temp: 180 c
SP5 Trap Bake Out Temp: 180 c

9.3.2.6 The above parameters outline the recommended chromatographic conditions. Different conditions or techniques may be used as long as they meet QA/QC as outlined in SW846 method 8240 section 8.5.

9.4 Installation and conditioning of trap in the purge and-trap device.

9.4.1 All traps should be installed in accordance with manufacturers precribed instructions.

9.4.2 Adjust purge flow by measuring the flow at the vent in purge mode.

The faster the purge flow the more efficient the purging process. The limit to increasing the flow is governed by the ability of the

trap to absorb and contain the purged analytes.

If the total purge volume is too large (flow rate too high) then the lightest compounds such as the gases will break through the end of the trap and their respective RF's will drop correspondingly. If the purge flow is slow the heavier and more polar compounds will not purge efficiently. Thus to improve the gases, the purge flow should be decreased and to improve bromoform the purge flow should be increased.

If optimization of overall RF's by changing the purge flow cannot be attained, a new trap may need to be installed.

9.4.3 To condition the trap, place the purge and trap unit into BAKE mode, and then hold the bake program. This will heat the trap under reverse flow indefinitely. The trap should be baked out for a minimum of 1 hour. It can be left in BAKE mode indefinitely. Tenax breakdown occurs largely during the heating and cooling phases, not at constant elevated temperatures.

9.5 GC/MS Tuning Criteria

9.5.1 BFB

9.5.1.1 Each GC/MS MUST be hardware tuned to meet the EPA ion abundance criteria for BFB. The instrument tune MUST be verified at the start of every 12 hours of operation. Ion abundance criteria are listed in Appendix C, Table C-1.

9.5.1.2 Inject 50 ng of BFB under appropriate chromatographic conditions. Acquire 200-300 scans.

9.5.1.3 Evaluate the spectrum of BFB. Ion abundance criteria given in Table C-1 must be met. Averaging scans across the peak and reasonable background subtraction is acceptable. Manipulations which will distort the spectrum, such as excessive back ground subtraction, are not acceptable.

9.5.1.4 If the ion abundance criteria are met, generate a hard copy of the spectrum, mass abundance table, and ion abundance summary, and proceed with analysis. Otherwise re-tune and evaluate additional injections of BFB until criteria is met.

9.5.2 Initial Calibration: An initial calibration must be performed before analysis of samples can begin. This consists of a five point calibration curve for all of the analytes of interest. Standards are analyzed at concentrations of 10 ppb, 50 ppb, 100 ppb, 150 ppb, and 200 ppb, except purgeable gases and 2-chlorethylvinylether which are at 2 times the above levels and ketone analytes which are at 3 times the above levels.

Certain compounds have been selected to monitor instrument performance. These compounds are identified as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC.)

The average response factor for each System Performance Check Compounds (SPCC) MUST be 0.300 or greater except bromoform which must be 0.250 or greater.

The percent relative standard deviation

(%RSD) for each Calibration Check Compound (CCC) MUST be less than 30%. The %RSD for all compounds should also be reviewed. Any values greater than 30% should be evaluated before analysis are continued.

If samples are NOT being analyzed for these specific compounds, the criteria for these compounds need not be met. The fact that these compounds are not in the analyte set should be documented.
See Table C-2 for a summary of CCC and SPCC criteria.

9.5.2.1 Standard solutions should be allowed to warm to room temperature before using. Remove the plunger from a 5 mL gas-tight syringe and attach a closed syringe valve. Rinse the syringe with purged reagent water. Fill the syringe barrel with purged reagent water. Replace the syringe plunger and compress the water. Open the syringe valve and vent any residual air while adjusting the volume to 5.0 mL.

Add internal standards, surrogates, and analytes for each calibration level.

9.5.2.2 Standards can be analyzed using the automatic purge and trap system. Load each standard level into a purge chamber on the automatic purge and trap system, and begin data acquisition.

9.5.2.3 Immediately check the area of the bromochloromethane in the 10 ppb standard for saturation.

9.5.2.4 The analyst should complete the data

reduction of the 10 ppb standard while the 50 ppb standard is running.

9.5.2.5 The SPCC limits MUST be verified. If a SPCC RF is <0.300 consult your supervisor to determine if corrective action will be taken or analysis will proceed. Corrective action may include replacement of the trap or the analytical column. Document corrective action taken or decision to proceed. This documentation will be kept with the output for the initial calibration. If necessary, re-inject the 10 ppb standard.

9.5.2.6 Review the quantitation list to ensure that the following compounds have proper integration and peak assignment.

Chloromethane
Vinyl Chloride
Acetone
Cis-1,3-dichloropropene
Trans-1,3-dichloropropene
2-chloroethylvinyl ether
2-hexanone
4-methyl-2-pentanone

9.5.2.7 Each of the other standards analyzed should be evaluated in the same manner as the 10 ppb standard, with particular attention focused on the "troublesome" compounds.

9.5.2.8 The table of response factors will be printed. Verify that the CCC and SPCC criteria have been met. Review average response factors of all the other analytes. Investigate each individual

standard level for a compound having a %RSD that is greater than 30%.

9.5.2.9 If the calibration criteria are not met and the decision is make to continue analysis, the rationale must be documented by the individual making that decision. This documentation must be kept on file with the initial calibration record.

9.5.2.10 If the standard evaluation criteria have been met, run the necessary programs to update the library with the average response factor. The analyst should then run the necessary programs to update the library with the current retention times using the middle calibration standard analyzed in the five point calibration.

9.5.3 Continuing Calibration: The 100 ppb standard is used as the continuing calibration standard. It MUST be analyzed for each twelve hour period immediately following a successful BFB analysis.

The percent difference for each CCC compound should be less than 25%. If this parameter is found to be out in any of the samples analyzed within this twelve hour period, re-analysis may be required. Report this to your supervisor. Response factors for all analytes should be reviewed. Any significant deviations from the initial calibration should be evaluated before analysis are continued. (e.g. deviations of greater than 50%.) All SPCC criteria should be met.

9.5.3.1 Purge the 100 ppb standard . The

concentration of each of the surrogate compounds and the internal standard compounds is 50 ppb.

9.5.3.2 Review the quantitation list to ensure that the internal standards are correctly identified and that the analytes are properly quantitated. ALWAYS check the following compounds for proper integration and peak assignment:

Chloromethane
Vinyl Chloride
Acetone
Cis-1,3-dichloropropene
Trans-1,3-dichloropropene
2-Chloroethylvinyl ether
2-Hexanone
4-Methyl-2-pentanone

9.5.3.3 Compare the CCC and SPCC compounds of the continuing calibration to the initial calibration.

9.5.3.4 If the standard evaluation criteria are NOT met, corrective action must be taken. Corrective action may include replacement of the trap or the analytical column. Document corrective action taken.

9.5.3.5 If these criteria are not met and the decision is made to continue analysis, the rationale must be documented by the individual making that decision. This documentation must be kept on file with the continuing calibration record.

9.5.3.6 If the standard evaluation criteria have been met or the decision has been made

to continue, update the library with the retention times of the continuing calibration standard just analyzed.

9.6 Sample Analysis

9.6.1 Scheduling

9.6.1.1 Analysis are scheduled by the supervisor or a senior operator.

9.6.1.2 The type of analysis required will be assigned during sample log-in. Modifications to the normal analytical protocol such as low detection limits, special compounds or special criteria should be indicated at the time of sample log-in.

9.6.2 Analysis Sequence

9.6.2.1 Method blanks and laboratory control samples will be analyzed first following successful calibration. Method blank and LCS sample results must be verified before samples can be analyzed. See section 8.6.5 for data processing. See section 9.0 for QC criteria for method blank and LCS samples.

9.6.2.2 If the QC criteria are met, the samples will be analyzed according to the scheduling sheet. Matrix spike and matrix spike duplicates will be performed one each per batch of samples.

9.6.3 Analysis of Water Samples

9.6.3.1 All samples and spiking solutions must

be allowed to warm to ambient temperature before analysis.

9.6.3.2 Rinse the chamber(s) of the purging device. ALWAYS clean each sparger with 10 mL aliquots of purge water, or use disposable glass test tube sparging cells.

9.6.3.3 Review the screen data to determine if any samples require dilution before analysis. Dilutions of up to 1:500 can be made in the syringe. Always be sure that the final total volume in the purge chamber is 5.0 mL. Dilutions of greater than 1:500 should be made using intermediate dilutions. The intermediate dilution can be made in a volumetric flask. Always use purged reagent water for making these dilutions.

9.6.3.4 Remove the plunger from a 5 mL gas-tight syringe. Rinse the syringe with purged reagent water. Open the sample bottle and carefully pour the sample into the syringe barrel nearly filling the barrel. Replace the syringe plunger, invert the syringe and compress the sample to vent any residual air, while adjusting the sample volume to 5.0 mL.

9.6.3.5 Add 10 uL of the internal standard + surrogate mix (25 ng/uL solution) to the sample in the syringe by inserting the needle of the micro-syringe through the Luer end of the sample syringe.

9.6.3.6 Attach the syringe to the valve on the purging chamber. Open the valve on the

syringe and the valve on the chamber and inject the sample into the purging chamber.

9.6.3.7 Close the valve on the purging chamber and remove the syringe assembly.

9.6.3.8 Record sample number and sample size in the instrument log book.

9.6.3.9 If the sample is to be analyzed using manual operation of the purge and trap. Prepare aquisition and start sample sparging.

9.6.3.10 For automated runs, complete loading all of the samples to be analyzed. Load blanks into chambers which are suspected to be contaminated from previous samples.

9.6.3.11 LCS are prepared using 5.0 mL of purged reagent water. Add 10 uL of internal standard and surrogate solution to the water in the syringe. Add 5 uL of Matrix spike solution in addition to the surrogates and internal standards.

9.6.3.12 Matrix spikes are prepared in the same manner. The additional aliquot(s) of the sample to be spiked is (are) placed in 5 mL gas tight syringes. If the sample requires dilution, dilute the matrix spike aliquot as well. Add 5 uL of the Matrix Spike Solution to each aliquot prepared.

9.6.3.13 After analysis are completed, remove samples and clean the purging chambers.

9.6.4 Analysis of Methanol Extracts for the Medium Soil Method.

9.6.4.1 The samples are extracted as described in section 8.2.

9.6.4.2 Fill a 5 mL gas tight syringe with purged reagent water. Adjust the volume to 4.9 mL. Add 100 uL of the methanol extract to the syringe. If the sample requires dilution add the appropriate volume of the methanol extract.

9.6.4.3 Add 10 uL of internal standard mix to the syringe and place the sample in the purging chamber as described above.

9.6.4.4 Rinse the 5 mL syringe with purged water a minimum of three times.

9.6.4.5 Load samples into each clean chamber. Load blanks into chambers which are suspected to be contaminated from previous samples.

9.6.4.6 Laboratory control samples may be prepared at the time of purging. Take a 100 uL aliquot of the methanol blank with surrogates added. Add 10 uL of the internal standard solution and 5 uL of the Matrix Spike solution. Analyze 1 LCS per batch of samples.

9.6.4.7 Method blanks and laboratory control samples are prepared using reagent water only. No solid matrix is used. Add 10 uL of internal standard and surrogate solution to the water in the syringe. For LCS samples, add 5 uL of Matrix spike solution. Place each aliquot into

a purge vial and affix to the unit as described above.

9.6.4.8 Matrix spikes are prepared as the samples. Weigh the same amount of sample for each aliquot required. In addition to the 10 uL of internal standard and surrogate added to the reagent water, add 5 uL of Matrix Spike solution. Matrix spike samples should be analyzed along with the corresponding sample.

9.6.5 Data acquisition and processing using the purge and trap autosampler.

NOTE: QC DATA MUST BE VERIFIED BEFORE SAMPLES ARE ANALYZED. SEE SECTION 9.0.

NOTE: BE SURE TO NOTE THE DISTINCTION BETWEEN THE THE PURGE-AND-TRAP UNIT AND THE AUTOMATIC SAMPLER WHEN SETTING SYSTEM.

9.6.5.1 Record sample numbers and dilutions in the instrument log book and the ALS log book. Be sure to note the chamber or cell number for each sample.

9.6.5.2 Set total sample # indicator dial on automatic sampler to number of the last chamber in which a sample is loaded.

9.6.5.3 Begin purging first chamber of the series by pressing the start button on the purge and trap unit.

9.6.5.4 While the first sample is purging, set up the data acquisition using the system's autosampler software.

9.6.5.5 The program will display a name list into which you should place the file names of the samples that are being analyzed, in the order they were loaded into the automatic sampler.

9.6.5.6 The program will display sample entries into which you should enter all sample ID, concentration factors, etc, as prompted.

If all of the data is OK, save the information on the disk. Start the auto sampler. It will go through three wait cycles.

1) Waiting for auto sampler ready
2) Waiting for GC ready
3) Waiting for sample injected

The auto sampler, when ready will step the purge and trap unit into "desorb preheat" mode over riding the "HOLD" switch.

9.6.5.7 After each acquisition, the programs used for data processing will be run.

9.6.6 Review the internal standard retention times. No internal standard retention time should vary by more than 30 seconds from the daily standard. If this occurs, the chromatographic system should be checked and corrections made as necessary. Affected samples will be re-analyzed.

9.6.7 Review the internal standard areas. The areas should not vary by more than a factor

of two (-50% to +100%) If the areas do vary by more than a factor of two, the analyst should first check to see if the peak has been correctly integrated. If the area is outside the limits, the system should be checked and corrected if necessary. The sample will be re-analyzed.

9.6.8 Verify that the sample was analyzed at the proper dilution. If any sample contains target compounds that are outside the range of the calibration curve (over 200 on the QUANT report), the sample should be diluted by the appropriate factor and re-analyzed. Any sample that has been diluted should contain levels of compounds (either target or non-target compounds) that are high enough to justify the dilution. In the absence of target compounds, the peak height of non-target compounds should be approximately greater than or equal to the peak height of the nearest internal standard. If not, the sample should be re-analyzed at the correct dilution.

9.6.9 Blank data

9.6.9.1 If the blank value is above the reporting limit, the system should be investigated for contamination, and when corrected, a new method blank run.

If the blank value lies above the reporting limit, the supervisor is consulted to schedule the blank and all samples associated with the blank for re-preparation and/or re-analysis.

If the decision is make to continue with the analysis, this must be documented,

signed by the person making the decision and the record kept with the method blank data.

9.6.9.2 Record blank information on the Method Blank form.

9.6.10 When all data review has been completed the analyst should assemble the data package. The BFB output and continuing calibration output should be on top of the data package.

10 QA/QC REQUIREMENTS (SEE ET Lab QAP)

10.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8 SW846 method 8240.

10.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted to certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8 SW846 method 8240.

10.3 LCS. Duplicate laboratory control samples are analyzed for every 20 samples. LCS components and spike concentrations are given in Appendix D. For aqueous samples, LCS components are spiked into organic-free water. For solid samples, the LCS components are spiked into the extraction solvent. No solid matrix (sand or Celite) is incorporated since there is no true representative solid matrix.

10.4 Method blank. A surrogate control sample is analyzed with every analytical lot. This sample serves as the method blank. An analytical lot for volatile organics

is defined as samples analyzed within a twelve hour period. For aqueous samples, the surrogate components are spiked into organic-free water. For solid samples, the surrogate components are spiked into the extraction solvent. No solid matrix (sand or Celite) is incorporated since there is no true representative solid matrix.

10.5 Blank. If an analyte is detected in the blank equal to or greater than the reporting limit, corrective action must be taken.

10.6 Surrogates Spiked into Samples. Surrogate compounds are required to be spiked into all samples and QC samples for this method. Surrogates and spike concentrations are given in Appendix C.

10.7 Matrix specific QC. Matrix spike (MS) and matrix spike duplicates (MSD) are performed per batch of up to 20 samples. Matrix spike compounds will be the same as those used for the LCS. See Appendix D. These compounds will be spiked into aliquots of the sample specified by the client at the same concentration level as the LCS.

10.8 Data acceptability is based upon the results of the Laboratory Control Samples unless otherwise negotiated with the client. QC data must fall within established control limits in order for the laboratory to be considered "in control" when samples from that QC lot were analyzed.

10.9 Control Limits: Control limits will be determined as described in ET Labs QAP Manual. These limits are listed in Table D-2. Current historical limits generated by the laboratory will be available through analysis.

is defined as samples analyzed within a twelve hour period. For aqueous samples, the surrogate components are spiked into organic-free water. For solid samples, the surrogate components are spiked into the extraction solvent. No solid matrix (sand or Celite) is incorporated since there is no true representative solid matrix.

10.5 Blank. If an analyte is detected in the blank equal to or greater than the reporting limit, corrective action must be taken.

10.6 Surrogates Spiked into Samples. Surrogate compounds are required to be spiked into all samples and QC samples for this method. Surrogates and spike concentrations are given in Appendix C.

10.7 Matrix specific QC. Matrix spike (MS) and matrix spike duplicates (MSD) are performed per batch of up to 20 samples. Matrix spike compounds will be the same as those used for the LCS. See Appendix D. These compounds will be spiked into aliquots of the sample specified by the client at the same concentration level as the LCS.

10.8 Data acceptability is based upon the results of the Laboratory Control Samples unless otherwise negotiated with the client. QC data must fall within established control limits in order for the laboratory to be considered "in control" when samples from that QC lot were analyzed.

10.9 Control Limits: Control limits will be determined as described in ET Labs QAP Manual. These limits are listed in Table D-2. Current historical limits generated by the laboratory will be available through analysis.

11 CALCULATIONS

11.1 Calculations required to run data processing programs

11.1.1 Concentration factor for sample (CF):

CF = NOMINAL SAMPLE SIZE/ACTUAL SAMPLE AMT USED

The nominal sample size is 5 mL for water and 5 g for soil.

11.1.2 VOA SURROGATE CONCENTRATION FACTOR (SCF):

SCF = (vol. purged x 100)/amt. spiked (total ng)

11.2 Calculations required to verify automated data reduction

11.2.1 Response factors

$$RF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the internal standard (ng/uL.)

C_x = Concentration of the compound to be measured (ng/uL.)

11.2.2 Average response factor

$$RF_{ave} = (RF_{10} + RF_{50} + RF_{100} + RF_{150}\ RF_{200})/5$$

Where: RF_x = Response factor of a compound in each of the calibration solutions.

11.2.3 Percent Relative Standard Deviation

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

RSD = Relative Standard Deviation

SD = Standard Deviation of initial response factors (per compound)

Where:

$$SD = \sum_{i=1}^{N} \frac{(x_i - x)^2}{N-1}$$

RF_{ave} = mean of initial response factors (per compound)

11.2.4 Percent Deviation from average response factor

$$\% \text{ Difference} = \frac{RF_I - RF_C}{RF_I} \times 100$$

Where:

RF_I = average response factor from initial calibration.

RF_c = response factor from current

calibration check standard.

11.2.5 Percent Recovery

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added from Spiking Mix

11.2.6 Relative Percent Difference

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

11.2.7 Analyte concentration in an aqueous sample

$$\text{Concentration ug/L} = \frac{(A_x)\ (I_s)}{(A_{is})\ (RF)\ (V_o)}$$

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard injected in nanograms (ng)

RF = Response factor for the compound being measured, determined from the 50 ppb calibration solution.

V_o = Volume of water purged in milliliters (mL) (take into account any dilutions.)

11.2.8 Analyte concentration in a medium-level soil sample (dry weight.)

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{is})\ (RF)\ (V_i)\ (W_s)\ (D)}$$

Where:

A_x, I_s, A_{is}, RF = Same as given for water, above.

V_t = Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made.)

V_i = Volume of extract added for purging (uL)

$$D = \frac{100 - \%\ \text{moisture}}{100}$$

W_s = Weight of sample extracted (grams)

11.2.8.1 Analyte concentration in a medium level soil sample (wet weight.)

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{is})\ (RF)\ (V_i)\ (W_s)}$$

Where:

$A_x, I_s, A_{is}, RF, V_t, V_t$ = Same as given for soil, dry

weight, above.

11.2.9 Analyte concentration in a low-level soil sample (dry weight):

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{is})\ (RF)\ (V_i)\ (W_s)\ (D)}$$

Where:

A_x, I_s, A_{is}, RF = Same as given for water, above

$$D = \frac{100 - \%\ \text{moisture}}{100}$$

W_s = Weight of sample purged (grams)

11.2.10 Analyte concentration in a low-level soil sample (wet weight):

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)}{(A_{is})\ (RF)\ (W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as given for water, above

W_s = Grams of sample purged

12 REPORTING REQUIREMENTS

12.1 Units: Aqueous samples will be reported in ug/L Solid and sludge samples will be reported in ug/Kg on a wet weight basis, unless requested otherwise by the client.

12.2 Reporting limits will be adjusted according to sample dilution.

12.3 Significant figures: All data <10 ug/L will be reported with one significant figure. All other data will be reported with two significant figures.

12.4 Analysis data entry

13 REFERENCES

13.1 Method Source: Method 8240, SW-846 Third Edition, USEPA, Office of Solid Wave and Emergency Response, Washington, DC 20460, September 1986.

13.2 Deviations from Source Methods

13.2.1 Deviations from the specified criteria for initial and continuing calibration are allowed, provided the rationale is documented and QA/QC is met as outlined in method 8240 section 8.5.

13.2.2 An internal QA/QC program has been adopted by ET Lab. This is described in ET Lab's "Quality Assurance Program Plan. The laboratory control samples generated in this program are used to monitor method performance. Matrix spikes are performed per batch of up to 20 samples.

13.2.3 The medium level method for soil referred to in this SOP is equivalent to the High-level method described in method 8240. The only exception is that this SOP uses a 5 g sample compared to the 4 g sample recommended in method 8240.

APPENDIX A -- TABLES OF ANALYTE LISTS TO INCLUDE ANALYTE NAME, REPORTING LIMIT AND QUANTITATION IONS.

APPENDIX B -- TABLES OF SOLUTIONS USED IN THIS METHOD TO INCLUDE ANALYTE LIST, CONCENTRATION OF SOLUTION, AND AMOUNT TO USE TO SPIKE SAMPLES OR INJECT.

TABLE B-1 SURROGATE STANDARD SPIKING SOLUTION
TABLE B-2 MATRIX STANDARD SPIKING SOLUTION
TABLE B-3 INTERNAL STANDARD SOLUTION
TABLE B-4 CALIBRATION STANDARD SOLUTIONS PURCHASED BY VENDORS
TABLE B-5 CALIBRATION STANDARD SOLUTIONS PREPARED FROM NEAT COMPOUNDS
TABLE B-6 PREPARATION OF STANDARD FOR 5-POINT CALIBRATION CURVE

TABLE A-1: LIST OF COMPOUNDS ANALYZED BY THIS METHOD AND REPORTING LIMIT

Compound	Water MDL	Low Level Solid MDL	High Level Solid MDL
Chloromethane	10	10	500
Vinyl Chloride	10	10	500
Dichlorodifluoromethane	10	10	500
Bromomethane	10	10	500
Chloroethane	10	10	500
Acetone	50	50	2500
1,1-Dichloroethene	5	5	250
Methylene Chloride	5	5	250
Trichlorofluoromethane	5	5	250
Carbon Disulfide	5	5	250
trans-1,2-Dichloroethene	5	5	250
1,1-Dichloroethane	5	5	250
Chloroform	5	5	250
1,2-Dichloroethane	5	5	250
Vinyl Acetate	25	25	1250
2-Butanone (MEK)	50	50	2500

1,1,1-Trichloroethane	5	5	250
Benzene	5	5	250
Carbon Tetrachloride	5	5	250
1,2-Dichloropropene	5	5	250
Bromodichloromethane	5	5	250
Trichloroethene	5	5	250
2-Chloroethylvinylether	10	10	500
cis-1,3-Dichloropropene	5	5	250
trans-1,3-Dichloropropene	5	5	250
1,1,2-Trichloroethane	5	5	250
Dibromochloromethane	5	5	250
Bromoform	5	5	250
4-Methyl-2-pentanone	25	25	1250
Toluene	5	5	250
2-Hexanone	25	25	1250
Tetrachloroethene	5	5	250
Chlorobenzene	5	5	250
Ethylbenzene	5	5	250
Styrene	5	5	250
1,1,2,2-Tetrachloroethane	5	5	250
P & M-Xylene	5	5	250
O-Xylene	5	5	250
1,3-Dichlorobenzene	5	5	250
1,4-Dichlorobenzene	5	5	250
1,2-Dichlorobenzene	5	5	250

TABLE B-1: SURROGATE STANDARD SPIKING SOLUTION

Compound	Standard Conc.	Conc. after spiking
1,2-Dichloroethane-d4	1000 ug/ml	50 ug/L
Toluene-d8	1000 ug/ml	50 ug/L
4-Bromofluorobenzene	1000 ug/ml	50 ug/L

TABLE B-2: MATRIX SPIKE STANDARD SPIKING SOLUTION

Compound	Standard Conc.	Conc. after spiking
1,1-Dichloroethene	1000 ug/ml	50 ug/L
Benzene	1000 ug/ml	50 ug/L
Toluene	1000 ug/ml	50 ug/L
Trichloroethene	1000 ug/ml	50 ug/L
Chlorobenzene	1000 ug/ml	50 ug/L

TABLE B-3: INTERNAL STANDARD SOLUTION

Compound	Standard Conc.	Conc. after spiking
Bromochloromethane	1000 ug/ml	50 ug/L
1,4-Difluorobenzene	1000 ug/ml	50 ug/L
Chlorobenzene-d5	1000 ug/ml	50 ug/L

TABLE B-4: CALIBRATION STANDARD SOLUTIONS PURCHASED BY VENDORS

Vendor: Ultra Scientific

Standard Mix Name	Standard Concentration
PMX-110	100 ug/ml
Purgeable Gases	100 ug/ml
p-Xylene	100 ug/ml
m-Xylene	100 ug/ml
2-Chloroethylvinyl ether	100 ug/ml
HSL Volatile Mix (Chem Service)	200 ug/ml

TABLE B-5: CALIBRATION STANDARD SOLUTIONS PREPARED FROM NEAT COMPOUNDS

Standard Solution Name: Ketone Stock Solution **Final Volume: 10 m**

Compound	Density	Amount spiked for stock std.	Final conc.
Acetone	0.788	50.7 ul	4000 ug/ml
2-Butanone	0.805	49.7 ul	4000 ug/ml
4-Methyl-2-pentanone	0.801	50.0 ul	4000 ug/ml
Vinyl acetate	0.932	64.4 ul	6000 ug/ml
2-Hexanone	0.830	48.2 ul	4000 ug/ml

A 1:10 dilution of the Ketone stock solution yields the 400/600 ug/ml Ketone working solution.

TABLE B-6: PREPARATION OF STANDARD FOR 5-POINT CALIBRATION CURVE

Standard Name: Volatile Standard **Final Volume: 1 ml**

Standard Mix Name	Amount spiked for stock std.	Standard conc.
PMX-110	200 ul	20 ug/ml
Purgeable Gases	200 ul	20 ug/ml
p-Xylene	100 ul	10 ug/ml
m-Xylene	100 ul	10 ug/ml
2-Chloroethylvinyl ether	200 ul	20 ug/ml
HSL Volatile Mix	100 ul	20 ug/ml
Ketone Working Solution	100 ul	40/60 ug/ml

Standard Name: Volatile IS + SS Standard **Final volume: 1 ml**

Standard Mix Name	Amount spiked for stock std.	Standard conc.
Volatile Internal std	100 ul	25 ug/ml
Volatile surrogate std	100 ul	25 ug/ml

5-Point Calibration Line (5 ml purge)

Calibration Conc.	Amount spiked of VOA std.	Amount spiked of IS + SS std
10 ppb Cal std	2.5 ul	10.0 ul
50 ppb Cal std	12.5 ul	10.0 ul
100 ppb Cal std	25.0 ul	10.0 ul
150 ppb Cal std	37.5 ul	10.0 ul
200 ppb Cal std	50.0 ul	10.0 ul

APPENDIX C

TABLE C-1

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of the base peak
173	less than 1.00 percent of the base peak
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

TABLE C-2

CALIBRATION CHECK COMPOUNDS

Initial Calibration: The percent relative standard deviation for each compound listed below should be <30%.

Continuing Calibration: The response factor for each compound listed below should be ≥0.300, 0.250 for Bromoform.

Chloromethane
1,1-Dichloroethane
Bromoform
1,1,2,2-Tetrachloroethane
Chlorobenzene

APPENDIX D

TABLE D-1

SPIKE LEVELS FOR LABORATORY CONTROL SAMPLES

	Spike Level Aqueous or Low-level Solid (ppb)
LCS, MS/MSD	
1,1-Dichloroethene	50
Trichloroethene	50
Chlorobenzene	50
Toluene	50
Benzene	50
Surrogates	
1,2-Dichloroethane-d_4	50
4-Bromofluorobenze (BFB)	50
Toluene-d_8	50

TABLE D-2

CONTROL LIMITS

LCS, MS/MSD

	AQUEOUS		SOLID	
	LCS,MS/MSD	RPD	LCS,MS/MSD	RPD
1,1-Dichloroethene	61-145	14	59-172	22
Trichloroethene	71-120	14	62-137	24
Chlorobenzene	75-130	13	60-133	21
Toluene	76-125	13	59-139	21
Benzene	76-127	11	66-142	21

METHOD BLANK/SAMPLE SURROGATE RECOVERY

	AQUEOUS	SOLID
1,2-Dichloroethane-d_4	76-114	70-121
4-Bromofluorobenze (BFB)	86-115	74-121
Toluene-d_8	88-110	81-117

Subject or title: Page 1 of 52

GC/MS Analysis of Semi-volatile Organics SW846 Method 8270

SOP No.:	Revision No.:	Effective Date:
ETASD-3002	original	January 1, 1991

Supercedes: none

1 SCOPE AND APPLICATION

1.1 Analytes: Quantitative analysis is performed for the compounds listed in Appendix A. Qualitative analysis by mass spectral identification can be performed on other extractable, chromatographable compounds, provided they meet acceptable QA/QC.

1.2 Reporting Limits: See Appendix A.

1.3 Applicable Matrices: Water, soil, solid waste.

1.4 Dynamic Range: Analytes can typically be quantitated between 10ug/mL and 160ug/mL. Samples which exceed this concentration range for any analyte in Table 1 should be diluted to be within the dynamic range of the method. Sample extracts should also be diluted when any other semi-volatile component of the sample exceeds this range. Reporting limits will be adjusted to reflect the dilution performed.

1.5 Analysis time: Approximate analytical time is 45 minutes per GC/MS run. The time required for data reduction will be dependent upon the complexity of the sample.

Prepared by: Date:

Management Approval: Arthur Neeley Date: 5-13-91

QA Officer Approval: Date:

2 METHOD SUMMARY

2.1 Aqueous samples are extracted with dichlormethane into base/neutral and acid fractions. Sample extracts are combined for quantitative and/or qualitative GC/MS analysis using an internal standard method.

2.2 Solid samples are extracted wih an appropriate solvent and the extract is analyzed by GC/MS for quantitative and/or qualitative identification using the same internal standard method.

3 COMMENTS

3.1 All deviations made from this SOP MUST be approved by the supervisor and well documented.

3.2 All reusable glassware should be solvent rinsed prior to use.

3.3 Care should be taken not to introduce contamination into the samples. Particular attention should be paid to selecting a protective glove that does not contribute contamination during sample preparation.

3.4 pH adjustments required for the preparation of aqueous samples are critical. Analyte recoveries can be adversely affected if the pH of the sample is not sufficiently basic or acidic.

4 SAFETY ISSUES

4.1 The toxicity or carcinogenicity of each chemical used in this procedure has not been precisely defined, however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be reduced to the lowest possible by using chemicals in an approved hood and wearing appropriate personal protective equipment (i.e. lab coat or apron, safety glasses, and gloves).

4.2 A Material Safety Data Sheet (MSDS) is available for all laboratory standard and reagent chemicals. The appropriate MSDS must be read before handling the chemical(s).

4.3 All laboratory personnel should be thoroughly familiar with the laboratory Safety Manual and Hazard Communication Standard before undertaking any laboratory work.

5 SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

5.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-rinsed with sample before collection. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination. Solid samples should be collected in wide mouth glass jars.

5.2 All samples must be iced or refrigerated at 4°C from the time of collection until extraction.

5.3 All aqueous samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction. Soil/waste samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

6 APPARATUS

6.1 Separatory funnel - 2 L, with Teflon stopcock.

6.2 Filtering Funnel - 75 mm top diameter or equivalent

6.3 Pyrex glass wool (silanized)

6.4 Disposable 1 mL pipet

6.5 Concentrator tube, Kuderna-Danish - 10 mL graduated (Kontes K-570050-1025 or equivalent).

6.6 Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-

6.17 Continuous liquid-liquid extractors-equipped with Teflon or glass connecting joints and stop-cocks requiring no lubrication.

6.18 Capillary column. Use one of the following or an approved substitute.

6.18.1 J&W 30 m DB-5, 0.25 mm id, 0.25 um film thickness Restek Rtx-5, 0.25 mm id, 0.25 um film thickness.

6.19 Syringes - 10 uL, 25 uL, 50 uL, 100 uL, 500 uL and 1 mL, as appropriate for making injections, adding internal standard and preparing sample dilutions.

6.20 Soxhlet extractor 40 mm I.D., with 500 mL round bottom flask or equivalent.

6.21 Glass or paper thimbles Whatman 33 mm x 94 mm or equivalent.

6.22 Heating mantle - rheostat controlled.

6.23 Gas Chromatograph/Mass Spectrometer:

6.23.1 Gas chromatograph: An analytical system that includes a temperature-programmable gas chromatograph suitable for splitless injection including all required accessories such as syringes, columns, and gases.

6.23.2 Mass spectrometer: Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

6.23.3 GC/MS interface: An interface that allows direct coupling of the capillary column and adequate analyte response.

6.23.4 Data system: A computer system is interfaced to the mass spectrometer which allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the analytical run. The software is capable of producing extracted ion profiles and integrating these abundances. The EPA/NIH Mass Spectral Library is available on the system.

7 REAGENTS AND STANDARDS

7.1 Reagent water - Carbon filtered house distilled water, or equivalent prep that results in no Interferents being observed at or above the reporting limit of the parameters of interest.

7.2 Sodium hydroxide solution (10 N) - Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

7.3 Sulfuric Acid (1+1) - Slowly add 50 mL of $H_2 SO_4$ (ACS sp. gr. 1.84) to 50 mL of reagent water.

7.4 Acetone, methanol, methylene chloride - pesticide quality or equivalent.

7.5 Sodium sulfate - (ACS), anhydrous. Granulated for drying extracts, powdered for extracting soil samples.

7.6 Surrogate standard spiking solution. (See Appendix B)

7.7 Laboratory Control Sample standard spiking solution. (See Appendix B).

7.8 GC calibration standard. (See Appendix B)

7.9 Internal standard solution. (See Appendix B)

7.10 Calibration standard solutions. (See Appendix B)

8 PROCEDURE

8.1 Scheduling Samples For Extraction -

8.1.1 Samples will be scheduled for extraction by the section supervisor. Samples should be scheduled for preparation according to the following priorities:

a) Meet holding times
b) Meet promised due date
c) Re-analyze to verify anomalies

8.2 Preparation of Water Samples:

NOTE: BEFORE USE, ALL GLASSWARE MUST BE SOLVENT RINSED WITH ACETONE AND METHYLENE CHLORIDE.

8.2.1 Emulsion test - Perform this test if a sample contains particulate matter. It is used to determine if the sample will be extracted using a separatory funnel or a continuous liquid-liquid extractor.

8.2.1.1 Transfer 3-4 mL of sample to a 12 mL screw top glass vial with a Teflon liner.

8.2.1.2 Add approximately 1 mL of CH_2-C1_2. Shake vigorously for about 30 seconds and allow the layers to separate.

8.2.1.3 If no emulsion forms, proceed with the shake-out technique in section 8.2.2.

8.2.1.4 If an emulsion forms, proceed with the continuous extractor technique in section 8.2.3.

8.2.2 Separatory Funnel Extraction (Shake-out Technique)

8.2.2.1 Samples that are clearly described as ground waters are decanted from any sediment in the bottle, all others are mixed by shaking the bottle.

8.2.2.2 If the sample is in a larger bottle or requires decanting, use a 1 L graduated cylinder to measure the sample volume. Pour the sample into a 2 L separatory funnel.

8.2.2.3 If the sample does not require decanting and is in a 1 L or smaller bottle, mark the water meniscus on the side of the sample bottle. This mark will be used to measure the sample volume. Pour the sample into a 2 L separatory funnel. After the sample bottle is rinsed with methylene chloride (section 8.2.2.11), measure the sample volume used by adding tap water to the bottle to the marked level. Measure the volume added with a graduated cylinder. (This step can be done after the initial extraction has been performed while waiting for layers to separate.)

8.2.2.4 Record the volume of each sample in the appropriate data book.

8.2.2.5 For blanks and quality control samples, pour 1 L of reagent water into the separatory funnel.

8.2.2.6 For matrix specific QC, measure 1 L of the appropriate sample required for each QC sample into a separatory funnel. If insufficient sample is available to use at least 500 mL per aliquot, consult your supervisor. Record volume of sample used for each portion.

8.2.2.7 Add 1 mL of the surrogate standard spiking solution to each sample and QC sample using a 1 mL disposable pipet, or a 1 mL syringe. Make sure the Pipet tip is below the surface of the sample while the standard is being added. Mix the sample immediately by stoppering and shaking the separatory funnel. In the appropriate data book, note the addition of the spiking solution, including who added it and the date and by whom the standard was made.

8.2.2.8 Add 1 mL of the LCS or matrix standard spiking solution, if appropriate, using the procedure described in 8.2.2.7.

8.2.2.9 Check the pH by removing a small aliquot of the sample with a pasteur pipet. Place enough of the sample on a pH paper to thoroughly soak the paper. Compare the pH paper with the chart on the container and record the initial pH on the prep sheet.

8.2.2.10 Adjust the pH to >11 with 10 N NaOH.

8.2.2.11 For samples that were mixed before pouring, add 60 mL methylene chloride (CH_2 Cl_2) to the sample bottle to rinse the inner walls. Do **NOT** cap and shake the bottle, rinse the glass only; transfer the solvent to the separatory funnel. For samples that were decanted, add the first aliquot of CH_2 Cl_2 directly to the separatory funnel.

8.2.2.12 Extract the sample by shaking it for two minutes with frequent ventilation. Allow the layers to separate. If there is an emulsion, break it. The optimum

technique will depend upon the sample, and may include: stirring, centrifugation, filtration through glass wool or other physical methods. If the emulsion cannot be broken, the sample must be transferred to a continuous extractor. See section 8.2.3.

8.2.2.13 Drain the bottom layer (CH_2 Cl_2) into an appropriate container.

8.2.2.14 Repeat the extraction twice more using a 60 mL aliquot of CH_2 Cl_2 each time. Collect the solvent in the same container described in 8.2.2.12.

8.2.2.15 Adjust the pH to <2 with 1:1 H_2 SO_4.

NOTE:THIS pH ADJUSTMENT IS CRITICAL. PHENOL RECOVERIES MAY BE LOW IF THE pH IS NOT LESS THAN 2.

8.2.2.16 Repeat the extraction another three times at the acidic pH using a 60 mL aliquot of CH_2 CL_2 each time. Collect the solvent in the same container described in 8.2.2.12. The extracts may be stored at this point at 4°C, or concentrated as outlined below.

8.2.2.17 Put a plug of glass wool in a funnel and fill about 2/3 full with granular anhydrous Na_2 SO_4. Rinse the funnel and Na_2 SO_4 with 30-40 mL of CH_2 Cl_2. Discard the CH_2 Cl_2.

8.2.2.18 Pour the extract through the Na_2 SO_4 into a 500 mL Kuderna-Danish (K-D) evaporative concentrator. Rinse the container which contained the extract and then the Na_2 SO_4 in the funnel with small amounts of

CH_2 $C1_2$. Add these rinses to the K-D.

8.2.2.19 Add a boiling chip to the K-D and attach a 3 - ball Snyder column to the top. Pre-wet the column by adding about 1 mL of CH_2 $C1_2$ to the top.

NOTE:THE CONCENTRATION STEP IS CRITICAL; LOSSES OF TARGET COMPOUNDS CAN OCCUR IF CARE IS NOT TAKEN.

8.2.2.20 Place the K-D in a 95° C hot water bath so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 2-5 mL, remove the K-D from the bath and allow it to cool completely.

8.2.2.21 When the K-D has cooled, rinse down the column and flask with a small amount of CH_2 $C1_2$. Transfer the extract to a calibrated 15 mL centrifuge tube, or equivalent rinsing with a small amount of CH_2 $C1_2$.

8.2.2.22 Carefully concentrate the extract to 1.0 mL under a gentle stream of nitrogen using the N-evap apparatus. The temperature of the water bath should be 35-40° C. If the extract is highly colored, forms a precipitate, or stops evaporating, consult a supervisor.

8.2.2.23 Transfer the extract to a labeled auto-sampler vial with Teflon lined cap, mark the meniscus, and place on a rack with any other samples with the same project number.

8.2.2.24 Complete the data book for the extraction and concentration steps.

8.2.3 Continuous Extractor:

8.2.3.1 Set-up the continuous extractor.

8.2.3.2 Put 250 mL CH_2 Cl_2 in a round bottom flask, add a few boiling chips. Add 300 mL of CH_2 Cl_2 to the extractor flask. If necessary, add sufficient reagent water into the extractor, to insure proper operation. Minimize the disturbance of the solvent layer and avoid getting water into either sidearm by pouring the water down the back of the extractor.

8.2.3.3 Open the sample container and remove a small aliquot of the sample with a pasteur pipet. Place enough of the sample on a pH paper to thoroughly soak the paper. Compare the pH paper with the chart on the container and record the initial pH in the data book.

8.2.3.4 Samples that are clearly described as ground waters in the project folder are decanted from any sediment in the bottle, all others are mixed by shaking the bottle.

8.2.3.5 If the sample is in a larger bottle or requires decanting, use a 1 L graduated cylinder to measure the sample volume. Pour the sample into the extractor.

8.2.3.6 If the sample does not require decanting and is in a 1 L or smaller bottle, mark the water meniscus on the side of the sample bottle. This mark will be used to measure the sample volume. Pour the

sample into the extractor. After the sample bottle is rinsed with methylene chloride (section 8.2.2.11), measure the sample volume used by adding tap water to the bottle to the marked level. Measure the volume added with a graduated cylinder. (This step can be done after the initial extraction has been performed while waiting for layers to separate.)

8.2.3.7 Record the volume of each sample in the data book.

8.2.3.8 For blanks and quality control samples, pour 1 L of reagent water into the separatory funnel.

8.2.3.9 For matrix specific QC, measure 1 L of the appropriate sample required for each QC sample into a separatory funnel. If insufficient sample is available to use at least 500 mL per aliquot, consult your supervisor. Record volume of sample used for each portion.

8.2.3.10 If less than 1 L of sample is used in extraction, make up the difference with reagent. Make sure that the extractor stays in a strictly vertical position.

8.2.3.11 Add 1 mL of the surrogate spiking solution to each sample and QC sample using a 1 mL disposable pipet, or syringe. Make sure that the tip of the pipet is below the surface of the liquid in the extractor as the standard is being added. Mix the sample immediately using a glass stirring rod. Note the volume of the surrogate solution added and all necessary information from the label of the standard in the data book.

8.2.3.12 Add the LCS or matrix spike mix, if appropriate, using the procedure described in the preceding step.

8.2.3.13 Adjust the pH to >11 with 10 N NaOH; stir carefully with a glass rod. If an excessive amount of NaOH is needed (more than about 15 mL), make a note on the prep sheet.

8.2.3.14 Add enough Methylene chloride to the continuous extractor flask to allow the solvent in the sidearm to just begin to drip into the round bottom flask. Check the pH to ensure that it is still >11. Add additional 10 N NaOH if necessary.

8.2.3.15 Remove the condenser from the rack and wipe the lower joint and lip with a tissue soaked with solvent. Place the condenser on the top of the extractor. Turn on the water and check the flow indicators.

8.2.3.16 Turn on the heating mantle to the appropriate setting. Record the starting time on the prep sheet. Check after 15 minutes to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip of the condenser, and that the volume of the solvent in the round bottom flask is still about 250 mL. Check all extractor joints for leaks with the corner of a Kim-wipe.

8.2.3.17 Allow the extraction to proceed for a minimum of eighteen hours.

8.2.3.18 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.

8.2.3.19 The solvent contained in the round bottom flask is the base/neutral extract. Remove this flask, cap, and refrigerate. Replace with a clean round bottom flask containing 250 mL CH_2 Cl_2 and a few boiling chips.

8.2.3.20 Remove the condenser and adjust the pH to <2 with 1:1 H_2 SO_4.

NOTE: THIS pH ADJUSTMENT IS CRITICAL. PHENOL RECOVERIES MAY BE LOW IF THE pH IS NOT LESS THAN 2.

8.2.3.21 Repeat steps 8.2.3.16-8.2.3.19 for the acid extraction.

8.2.3.22 The solvent contained in the round bottom flask is the acid fraction. Remove the round bottom flask, cap and refrigerate.

8.2.3.23 Pour the contents of the extractor into a separatory funnel to separate the water from the methylene chloride. Add the methylene chloride portion to the round bottom flask containing the acid or the base/neutral fraction. Discard the water layer into the appropriate solvent/aqueous waste container.

8.2.3.24 The drying and concentration steps are similar to those described in section 8.2.2.17 to 8.2.2.18. The concentration is then completed as described in sections 8.2.2.19 to 8.2.2.24. Repeat this procedure for both the acid and base/neutral portions of the extract.

8.2.3.25 Complete the data book for the extraction and concentration steps.

8.3 Preparation of Soil Sample

8.3.1 Percent Moisture Determination (optional) Weigh 5-10 g of sample into a tared weighing dish. Record the sample's wet weight. Allow to dry overnight at 105° C. Reweigh the sample. Record the sample's dry weight. (Correct for weight of weighing dish.) Calculate percent moisture using equation 10.2.7.

8.3.2 pH Determination (optional)

Transfer 50 g of sample to 100 mL beaker. Add 50 mL of water and a teflon-coated magnetic stirring bar. Stir for one hour on a magnetic stir plate. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets or data books.

8.3.3 Extraction by Sonication Technique

NOTE: ALL GLASSWARE MUST BE SOLVENT RINSED BEFORE USE. RINSE WITH ACETONE, AND METHYLENE CHLORIDE.

8.3.3.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, discarding any foreign objects such as sticks, leaves and rocks.

8.3.3.2 Weigh approximately 30 g of sample to the nearest 0.1 g into a 450 mL beaker. Add 60 g of anhydrous powdered sodium sulfate. Mix well. Add 100 mL of 1:1 methylene chloride-acetone to the sample, then add 1.0 mL of surrogate spiking solution.

8.3.3.3 Place the bottom surface of the tip of

the sonicator horn about 1/2 inch below the surface of the solvent but above the sediment layer.

8.3.3.4 Sonicate for 3 minutes.

8.3.3.5 Decant the solvent layer through a funnel stuffed with glass wool and filled with anhydrous sodium sulfate and into a pre-assembled K-D apparatus (less the Snyder column.)

8.3.3.6 Repeat the extraction twice more using 100 mL aliquots of 1:1 CH_2 $C1_2$ -acetone each time. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required break up large lumps with a clean spatula. Collect these extracts in the same K-D apparatus described in 8.3.3.5.

8.3.3.7 After the third extraction, pour the remainder of sample and sodium sulfate into the funnel and rinse the 450 mL funnel with methylene chloride 3 times.

8.3.3.8 Add a boiling chip to the K-D and attach a 3 - ball Snyder column to the top. Pre-wet the column by adding about 1 mL of CH_2 $C1_2$ to the top.

NOTE: THE CONCENTRATION STEP IS CRITICAL; LOSSES OF TARGET COMPOUNDS CAN OCCUR IF CARE IS NOT TAKEN.

8.3.3.9 Place the K-D in a heated water bath set at 95° C so that the receiver tube is immersed in hot water, and the entire lower rounded surface is bathed in steam. At the proper rate of distillation, the

balls of the column will actively chatter, but the chambers will not flood. When the apparent volume reaches 2-5 mL, remove the K-D from the bath and allow it to completely cool.

8.3.3.10 After the K-D has cooled, rinse the Snyder column and flask with a small amount of methylene chloride. Transfer the extract to a calibrated 10 mL centrifuge tube, rinsing with a small amount of methylene chloride. Be sure to rinse all of the ground glass joints well, as compounds collect on the ground glass.

8.3.3.11 Carefully concentrate the extract to 1.0 mL under a gentle stream of nitrogen using the N-evap apparatus. The temperature of the water bath should be 35-40° C. If the extract is highly colored, forms a precipitate, or stops evaporating, consult a supervisor.

8.3.3.12 Transfer to an auto-sampler vial with Teflon lined cap. Mark the meniscus.

8.3.3.13 Complete the data book for the extraction and concentration steps.

8.4 Preparation of Sludge Samples:

8.4.1 Weigh approximately 10 g of sample into a pre-weighed aluminum weigh boat and air-dry it overnight to determine the percent moisture.

8.4.2 Set up a continuous extractor as described in sections 8.2.3.1 to 8.2.3.4.

8.4.3 Weigh the bottle containing the sample and carefully transfer 50g of the sample to the

extractor flask. Re-weigh the bottle, calculate the difference, and record it as the amount extracted on the prep sheet.

8.4.4 Continue with the continuous extractor method as described in sections 8.2.3.9 to 8.2.3.26.

8.5 Soxhlet Extraction

8.5.1 Sample Handling:

8.5.1.1 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.

8.5.1.2 Waste samples: Samples consisting of multi-phases must be prepared by the phase separation before extraction. This procedure is for solids only.

8.5.1.3 Dry waste samples amenable to grinding: Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

8.5.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

8.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the

percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

8.5.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (See Table B-1 for details on the surrogate standard and matrix spiking solutions).

8.5.4 Place 200 mL methylene chloride and 100 mL acetone into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr.

8.5.5 Allow the extract to cool after the extraction is complete.

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

8.5.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

8.5.8 Add one or two clean boiling chips to the

flask and attach a three-ball Snyder column. Pre-wet 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 (15-20°C above the boiling point of the solvent) 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 10-20 min. 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 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

8.5.9 If a solvent exchange is required, momentarily remove the Snyder column, add 50 mL of the exchange solvent and a described in paragraph 8.5.8 raising the temperature of the water bath, if necessary, to maintain proper distillation.

8.5.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in paragraph 8.5.9 adjusted to 10.0 mL with the solvent last used.

8.5.11 If further concentration is indicated in the Table, add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the column by adding 0.5 mL of methylene chloride

or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. 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 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as with solvent.

8.5.12 The extracts obtained may now be analyzed for analyte content. If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.5.13 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.6 Instrument Set-up for the GC/MS:

8.6.1 Chromatographic Conditions

8.6.1.1 Column: See section 6.18.
8.6.1.2 Temperature Program:

Initial Temperature:	45 C
Initial Hold Time:	0 minutes
Temperature Ramp:	12 C/min

Final Temperature:	295 C
*Final Hold Time:	15 min
Oven Equilib. Time:	0.2 min
Splitless Valve Time:	0.8 min

* The final hold time should be adjusted according to the retention time of the final compound in the standard.

8.6.2 Mass Spectrometer Parameters:

8.6.2.1 Mass range: 35-450 amu
8.6.2.2 Scanning rate: 1 second/scan

8.6.2.3 Number of A/D samples: 2

8.6.2.4 Zone Temperatures:

Injection port: 250 C
Transfer line: 280 C

8.6.3 Acquisition Parameters Verify the following parameters:

Scan start time:	1-4 minutes
Run Time:	48-50 minutes
Threshold:	10-50
GC Peak Threshold:	20000 counts

8.6.4 The above parameters outline the recommended chromatographic conditions. Different conditions or techniques may be used as long as they meet QA/QC as outlined in SW846 method 8270 section 8.5.

8.7 Instrument Calibration:

8.7.1 DFTPP

8.7.2 Each GC/MS MUST be hardware tuned to meet the EPA ion abundance criteria for DFTPP. The instrument tune MUST be verified at the start

of every 12 hours of operation. Ion abundance criteria are listed in Appendix C, Table C-1.

8.7.2.1 Inject 50 ng of DFTPP, pentachlorophenol, benzidine, and 4,4 DDT under the same chromatographic conditions as the regular sample analysis. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. Internal standard may be added to assist in quantitating DDT, DDD and DDE if desired.

8.7.2.2 Evaluate the spectrum of DFTPP. Ion abundance criteria given in Table C-1 must be met. Averaging scans across the peak and reasonable background subtraction is acceptable. Manipulations which will distort the spectrum, such as excessive background subtraction, are not acceptable.

8.7.2.3 If the ion abundance criteria are not met, re-tune the instrument and re-inject DFTPP.

8.7.2.4 If the ion abundance criteria are met, generate a hard copy of the spectrum, mass abundance table, and ion abundance summary.

8.7.3 Initial Calibration: An initial calibration must be performed before analysis of sample extracts can begin. This consists of a five

point calibration curve for all of the analytes of interest. Standard solutions are prepared at concentrations of 20 ug/mL, 50 ug/mL, 80 ug/mL, 120 ug/mL and 160 ug/mL. Certain com-pounds have been selected to monitor instrument performance. These compounds are identified as System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).
The average response factor for each System Performance Check Compounds (SPCC) MUST be greater than 0.05.
The percent relative standard deviation (%RSD) for each Calibration Check Compound (CCC) MUST be less than 30%. The %RSD for all compounds should also be reviewed. Any values greater than 30% should be evaluated before analyses are continued.

If samples are NOT being analyzed for these specific compounds, the criteria for these compounds need not be met. The fact that these compounds are not in the analyte set should be documented.

See Table C-2 for summary of CCC and SPCC criteria.

8.7.3.1 Prior to tune verification, inject the 80 ng/ul standard to prime the column. After DFTPP has passed tune verification, the five standard solutions should be injected in the following order: 20 ug/mL,
50 ug/mL, 80 ug/mL, 120 ug/mL and 160 ug/mL.

8.7.3.2 Immediately check the area of M/Z 152 for d_4-1,2-dichlorobenzene in the 20 ug/mL standard. The peak area should be between 20,000 and 100,000 counts. This

will minimize saturation in the higher level standards. If the peak area is outside these limits, the analyst should adjust the electron multiplier and re-inject the tuning standard. In this case, the DFTPP must be re-evaluated, meet tune criteria, and saved as the 12-hour tune verification.

8.7.3.3 The analyst should complete the data reduction of the 20 ug/mL standard while the 50 ug/mL standard is running. (see section 8.8).

8.7.3.4 The SPCC limits MUST be verified. If a SPCC RF is <0.05 consult your supervisor to determine if corrective action will be taken or analysis will proceed. Corrective action may include replacement of injection port liner, breaking off the column, or replacing the column. Document corrective action taken or decision to proceed. This documentation will be kept with the output for the initial calibration. If necessary, re-inject the tuning standard, meet tune criteria, save tune documentation and begin calibration again.

8.7.3.5 Review the quantitation list to ensure that the internal standards are correctly identified and that the analytes are properly quantitated. ALWAYS check that all compounds are properly integrated.

8.7.3.6 Check for the correct peak assignment for the sets of structural isomers which are in the standard. Identification is based on elution order.

8.7.3.7 Each of the other standards analyzed should be evaluated in the same manner as

the 20 ug/mL standard.

8.7.3.8 Verify that the CCC and SPCC criteria have been met. Review average response factors of all the other analytes. Investigate the individual components for an average response factor that is greater than 30%.

8.7.3.9 If compounds are still outside acceptable limits, consult a supervisor.

8.7.3.10 All SPCC and CCC criteria must be met. If these criteria are not met and the decision is made to continue analysis, the rationale must be documented by the individual making that decision. This documentation must be kept on file with the initial calibration record.

8.7.3.11 Once all calibration QA/QC criteria have been met in the initial five point calibration, the average response factor for each compound is now used for analyte concentration calculations.

8.7.4 Continuing Calibration: The 80 ug/mL standard is used as the continuing calibration standard. It MUST be analyzed for each twelve hour period immediately following a successful DFTPP analysis.

The response factor of each CCC compound should be compared to the initial calibration. The percent difference for each CCC compound should be less than 30%. Response factors for all analytes should be reviewed. Any significant deviations from the initial calibration should be evaluated before analysis are continued. (e.g. deviations of greater than 30%)

All SPCC criteria should be met (i.e. RF > 0.05).

8.7.4.1 Inject 1 uL of the 80 ug/mL standard.

The concentration of acid surrogate compounds is 80 ug/mL. The concentration of base/neutral surrogate compounds is 80 ug/mL. The concentration of internal standard compounds is 40 ug/mL.

8.7.4.2 Process the data using the systems software.

8.7.4.3 Review the quantitation list to ensure that the internal standards are correctly identified and that the analytes are properly quantitated. ALWAYS check all compounds for proper integration.

8.7.4.4 Check for the correct peak assignment for the sets of structural isomers which are in the standard. Identification is based on elution order.

8.7.4.5 Compare the continuing calibration standard to the initial calibration. Evaluate the CCC and SPCC compounds as outlined in section 8.8.3. Review the RF and percent deviations from the initial calibration of all the other compounds. If any large deviations occur (e.g. deviations >30%), recheck peak assignment and integration.

8.7.4.6 If the standard evaluation criteria are NOT met, corrective action must be taken. Corrective action may include replacement of injection port liner, breaking off the column, or replacing the column. Re-inject the continuing calibration

standard and/or prepare a new initial calibration. (See section 8.8.2.)

8.7.4.7 If these criteria are not met and the decision is made to continue analysis, the rationale must be documented by the individual making that decision. This documentation must be kept on file with the continuing calibration record.

8.7.4.8 If the standard evaluation criteria have been met, continue to use the average RF from initial calibration for quantitation.

8.8 Sample Analysis:

8.8.1 Scheduling

8.8.1.1 Analyses are scheduled by the supervisor or a senior operator.

8.8.1.2 The analyst will determine the type of analysis requested by reviewing the sample management record. Modifications to the normal analytical protocol such as low detection limits, special compounds or special criteria will be indicated on the record.

8.8.2 Extract Preparation:

8.8.2.1 Extracts are stored in the extract refrigerator.

8.8.2.2 Locate appropriate sample vials. Water samples will have separate vials for acid, base/neutral and combined fractions. Unless otherwise instructed, the analyst will only need the combined fractions. Soil samples will have only

one vial.

8.8.2.3 Add 10 uL of the internal standard solution to the pre-prepped vials containing the sample extract at a final volume of 1.0 mL. Transfer the prepared extract containing the internal standard to a 100 uL insert and slip into an auto-sampler vial. Cap the vial. The vial is now ready to be loaded on the auto sampler.

8.8.2.4 Carefully rinse the syringe

8.8.3 Data Acquisition:

8.8.3.1 Samples are analyzed using the same instrument parameters as the calibration standards. Verify that the conditions specified in section 8.7 are set.

8.8.3.2 Enter the auto sampler software, and set it up.

8.8.3.3 Enter the accounting parameters for each sample.

8.8.3.4 Record sample number and dilutions in the instrument logbook.

8.8.3.5 If auto samplers are being used, refer to section 8.8.5.

8.8.4 Analysis Sequence:

8.8.4.1 Method blanks and duplicate control samples will be analyzed first. Method blank and LCS sample results must be verified before samples can be analyzed. See section 8.9 for data processing. See section 9.0 for QC criteria for Method

blank and LCS samples.

8.8.4.2 If the QC criteria are met, the samples will be analyzed according to the scheduling sheet. Matrix spike and matrix spike duplicates when available are analyzed in conjunction with the associated sample.

8.8.5 Data Acquisition And Processing Using Auto samplers.

8.8.5.1 Record sample numbers and dilutions in the instrument run log book.

8.8.5.2 Samples are placed in the auto sampler rack and their order is compared with sample numbers in the log book. See section 8.8.4 for analysis sequence. NOTE: QC DATA MUST BE VERIFIED BEFORE SAMPLES ARE ANALYZED. SEE SECTION 9.0.

8.8.5.3 Start the auto sampler program.

8.8.5.4 Data acquisition, file management, disk space management, and auto sampler control are performed by the system software program from the information entered in the auto-sampler program.

8.9 Data Processing For Manual Injections:

8.9.1 Review the internal standard retention times. No internal standard retention time should vary by more than 30 seconds from the daily standard. If this occurs, the chromatographic system should be checked and corrections made as necessary. Affected samples will be re-analyzed.

8.9.2 Review the internal standard areas. The areas should not vary by more than a factor of two (-50% to +100%). If the areas do vary by more than a factor of two, the analyst should first check to see if the peak has been correctly integrated. If the area is still outside the limits, the system should be checked and corrected if necessary. The sample will be re-analyzed. If, upon verification that the instrument is operating properly, the areas are still outside of the limits submit both analyses with the data package and document the actions taken.

8.9.3 Verify that the sample was analyzed at the proper dilution. If any sample contains target compounds that are outside the range of the calibration curve (over 160 on the QUANT report), the sample should be diluted by the appropriate factor and re-analyzed. The dilution should be performed from the remaining sample aliquot that does not contain internal standard if this is available. Any sample that has been diluted should contain levels of compounds (either target or non-target compounds) that are high enough to justify the dilution. target compounds should be at least 50 on the quant sheet. In the absence of target compounds, the peak height of non-target compounds should be approximately greater than or equal to the peak height of the internal standard d_{10} - phenanthrene. If not, the extract should be returned to the extractions group to be concentrated for re-analysis.

8.9.4 Check to verify that all target compounds identified have been properly integrated.

8.9.5 Check to see if any target compounds were missed. Use the total ion chromatogram and

the mass chromatograms.

8.9.5.1 Evaluate surrogate recoveries.

8.9.5.2 Enter the appropriate units. "ug/L" for water samples or "ug/kg" for soil samples.

8.9.5.3 Review the results.

8.9.6 Verify Spectra.

8.9.6.1 Check the quant report to verify the spectra needed to be searched in the Data base library for verification.

8.9.6.2 Obtain copies for the corresponding standard spectra for each of the compounds. Each spectrum should be compared to the standard spectrum. The EPA criteria for comparing spectra are:

1) All ions present in the standard spectrum at a relative intensity greater than 10% of the base peak MUST be present in the sample spectrum.

2) The relative intensities of the ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%.)

3) Ions greater than 10% in the sample spectrum, but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. If the analyst can easily identify a co-eluting compound (e.g. an alkane or a

surrogate spike compound) then the sample spectrum should be labelled with the contaminant.

8.9.6.3 Any spectra that meet these criteria should be initialed by the analyst. Any spectra that do not meet these criteria should be noted as a bad spectrum and initialed by the analyst. The corresponding entry on the quant list should be lined out with a "NO" notation written next to it. If a compound cannot be verified by all of the criteria listed above, but in the technical judgment of the analyst the identification is correct, the compound will be reported. If the analyst is uncertain of an identification, a senior operator or a supervisor should be consulted.

8.9.7 Library Searches (optional). Some clients will include the request for mass spectral library searches for non-target compounds (excluding surrogates and internal standards.) The 20 largest unidentified peaks that are greater than 10% of the peak height of the nearest internal standard will be searched against the NBS library. The peak identification requests may be client specific.

NOTE: DO NOT PERFORM LIBRARY SEARCHES ON MATRIX SPIKE SAMPLES.

8.9.7.1 Look through the sample and search for peaks that have not been identified.

8.9.7.2 When all of the library comparisons have been printed out, a summary sheet listing each peak with the best library fit will print out. The operator should go

through each comparison, determine the probability that the match is correct, and assign a grade based on that probability.

8.9.7.3 The EPA criteria to be used for making these decisions for tentative identifications are as follows:

1) Relative intensities of major ions present in the library spectrum at a relative intensity greater than 10% of the base peak should be present in the sample spectrum.

2) The relative intensities of the ions specified in (1) must agree within plus or minus 20% between the library and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%.)

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

4) Ions present in the sample spectrum, but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. If the analyst can easily identify a co-eluting compound (e.g. an alkane or a surrogate spike compound) then the sample spectrum should be labelled with the contaminant.

5) Ions present in the library spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background

contamination or collating compounds.

8.9.7.4 If in the technical judgment of the analyst, no valid tentative identification can be made, the compound should be reported as unknown. If possible, assign additional compound class information (e.g. unknown hydrocarbon). The analyst should consult with a more experienced analyst or a supervisor if there are questions concerning compound identi- fication.

8.9.8 Label the reconstructed ion chromatogram (RIC) to identify the internal standards, surrogate compounds, and DFTPP. If the sample is particularly dirty and the peaks are buried in other peaks, they need not be labeled. If surrogate compounds are not detected due to sample dilution label only the internal standards and DFTPP.

8.9.8.1 If the blank value lies above the reporting limit, the supervisor is consulted to schedule the blank and all samples associated with the blank for re-preparation and/or reanalysis. With the exception of Phthalates.

8.9.9 When all data review has been completed the analyst should sign and assemble the data package. The DFTPP output and continuing calibration output should be on top of the data package. Standards do not require spectra or library searches.

8.9.10 Upon completion of the data package assembly and review, the data package is passed on to the GC/MS supervisor for review and sign-off.

9 QA/QC REQUIREMENTS - (SEE ET-QAP)

9.1 A method blank is analyzed with every analytical batch of samples. An analytical batch for extractable organics is defined as samples extracted or prepared at the same time.

Method blank components and spike concentrations are given in Appendix D.

For aqueous samples, the method blank components are spiked into organic-free water. For solid samples, the method blank components are spiked onto an extraction thimble. No solid matrix (sand or Celite) is incorporated since there is no true representative solid matrix.

9.2 Surrogates Spiked into Samples. Surrogate compounds are required to be spiked into all samples and QC samples for this method. Surrogates and spike concentrations are given in Appendix D (table D-1).

9.3 Matrix specific QC. Matrix spike (MS) and matrix spike duplicates (MSD) are performed with every analytical batch of samples. Matrix spike compounds will be the same as those in Appendix D. These compounds will be spiked into aliquots of the sample, which may or may not be, specified by the client at the concentration level listed in Appendix D

9.4 Data acceptability is based upon the results of the Laboratory Control Samples unless otherwise negotiated with the client. QC data must fall within established control limits in order for the laboratory to be considered "in control" when samples from the QC lot were analyzed.

9.4.1 All of the recovery data, should be within established control limits in order of the laboratory to be considered "in control". Method blank values must be acceptable.

Outlier surrogate and matrix spike recoveries may be considered acceptable if matrix problems are well documented and supervisor approves the release of the data.

9.5 Control Limits: At a minimum, 8270 limits must be met. These limits are listed in Table D-2. Current historical limits generated by the laboratory will be available through the Quality Assurance department.

10 CALCULATIONS

10.1 Calculations required to run data processing programs

10.1.1 ACID and B/N CONCENTRATION FACTORS (CF):
CF = [F.V.(mL)/INIT. VOL. (g or mL)] x 1000
FV = Final Volume
Where INIT. VOL. = Initial Volume

10.1.2 ACID and B/N SURROGATE CONCENTRATION FACTORS (SCF).
SCF = (FINAL VOLUME X 100) / AMOUNT SPIKED

10.2 Calculations required to verify automated data reduction

10.2.1 Response Factors:

$$RF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the internal standard (ng/uL).

C_x = Concentration of the compound to be measured (ng/uL).

10.2.2 Average response factor:

$$RF_{ave} = (RF_{20} + RF_{50} + RF_{80} + RF_{120} + RF_{160} +) \ /5.$$

Where: RF_x = Response factor of a compound in each of the calibration solutions.

10.2.3 Percent Relative Standard Deviation:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

Where:

RSD = Relative Standard Deviation

SD = Standard Deviation of initial response factors (per compound)

Where : $$SD = \sqrt{\sum_{N=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

RF_{amve} = mean of initial response factors (per compound)

10.2.4 Percent Deviation from average response factor.

$$\% \text{ Difference} = \frac{RF_I - RF_C}{RF_I} \times 100$$

Where:

RF_I = Average response factor from initial calibration

RF_c = response factor from current calibration check standard.

10.2.5 Percent Recovery:

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike Sample Results
SR = Sample Result
SA = Spike Added from Spiking Mix

10.2.6 Relative Percent Difference:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

10.2.7 Percent Moisture:

$$\frac{\text{Wet (sample+dish)} - \text{dry (sample+dish)}}{\text{wet (sample+dish)}} \times 100 = \% \text{ moisture}$$

10.2.8 Analyte concentration in an aqueous sample:

$$\text{Concentration ug/L} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{i\,s})\ (RF)\ (V_o)\ (V_i)}$$

A_x = Area of the characteristic ion for the compound to be measured.

$A_{i\,s}$ = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard injected in nanograms (ng)

RF = Response factor for the compound being measured, determined from the 50 ug/mL calibration solution.

V_o = Volume of water extracted in milliliters (mL)

V_t = Volume of total extract in micro liters, taking into account dilutions (i.e. a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2000.)

10.2.9 Analyte concentration in a soil sample (dry weight)

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{i\,s})\ (RF)\ (V_i)\ (W_s)\ (D)}$$

Where:

$A_x, I_s, A_{i\,s}, RF, V_t$ = Same as given for water, above

V_i = Volume of extract injected (uL)

$$D = \frac{100 - \% \text{ moisture}}{100}$$

W_s = Weight of sample extracted (grams)

10.2.10 Analyte concentration in a soil sample (wet weight)

$$\text{Concentration ug/Kg} = \frac{(A_x)\ (I_s)\ (V_t)}{(A_{is})\ (RF)\ (V_i)\ (W_s)}$$

Where:

$A_x, I_s, A_{is}, RF, V_t$ = Same as given for water, above
V_i = Volume of extract injected (uL)
W_s = Weight of sample extracted (grams)

11 REPORTING REQUIREMENTS

11.1 Units: Aqueous samples will be reported in ug/L solid and sludge samples will be reported in ug/Kg on a wet weight basis, unless requested otherwise by the client.

11.2 Reporting limits: See Appendix A.

11.3 Significant figures: All data <10 ug/L will be reported with one significant figure. All other data will be reported with two significant figures.

12 REFERENCES

12.1 Method Source: Method 8270, SW-846 Third Edition, USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460, September 1986.

12.2 Deviations from Source Methods

12.2.1 Column performance is monitored through the response factors of the system performance check compounds.

12.2.2 Deviations from the specified criteria for initial and continuing calibration are allowed, provided the rationale is documented.

12.2.3 An internal QA/QC program has been adopted by ET Lab. This is described in ET Lab's "Quality Assurance Program Plan. The laboratory control samples generated in this program are used to monitor method performance. Matrix spikes are performed at the request of the client.

APPENDIX A--TABLES OF ANALYTE LISTS TO INCLUDE ANALYTE NAME AND REPORTING LIMIT.

TABLE A-1: List of compounds analyzed by this method and reporting limits.

COMPOUND	WATER MDL	SOLID MDL
N-Nitrosodimethylamine	15	660
Pyridine	10	**
Phenol	10	660
Aniline	15	660
Bis(2-chloroethyl)ether	10	660
2-Chlorophenol	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
Benzyl Alcohol	20	1300
1,2-Dichlorobenzene	10	660
2-Methylphenol	10	660
Bis(2-chloroisopropyl)ether	10	660
4-Methylphenol	10	660
N-Nitroso-di-n-propylamine	10	660
Hexachloroethane	10	660
Nitrobenzene	10	660
Isophorone	10	660
2-Nitrophenol	10	660
2,4-Dimethylphenol	10	660
Bis(2-chloroethoxy)methane	10	660
Benzoic acid	120	3300

2,4-Dichlorophenol	10	660
1,2,4-Trichlorobenzene	10	660
Naphthalene	10	660
4-Chloroaniline	20	1300
Hexachlorobutadiene	10	660
4-Chloro-3-methylphenol	20	1300
2-Methylnaphthalene	10	660
Hexachlorocyclopentadiene	10	660
2,4,6-Trichlorophenol	10	660
2,4,5-Trichlorophenol	10	660
2-Chloronaphthalene	10	660
2-Nitroaniline	50	3300
Dimethyl phthalate	10	660
Acenaphthylene	10	660
2,6-Dinitrotoluene	10	660
3-Nitroaniline	50	3300
Acenaphthene	10	660
2,4-Dinitrophenol	50	3300
4-Nitrophenol	50	3300
Dibenzofuran	10	660
2,4-Dinitrotoluene	10	660
Diethyl phthalate	10	660
Fluorene	10	660
4-Chlorophenylphenylether	10	660
4-Nitroaniline	50	660
2-Methyl-4,6-dinitrophenol	50	3300
N-Nitrosodiphenylamine	10	660
Azobenzene	10	660
4-Bromophenylphenylether	10	660
alpha-BHC	10	2000
Hexachlorobenzene	10	660
gamma-BHC	10	2000
Pentachlorophenol	50	3300
beta-BHC	10	2000
Phenanthrene	10	660
Antharacene	10	660
delta-BHC	10	2000
Heptachlor	10	2000
Di-n-butyl phthalate	10	2000
Aldrin	10	2000
Heptachlor epoxide	10	2000

Fluoranthene	10	660
Endosulfan I	10	2000
Benzidine	60	3300
Pyrene	10	660
4,4'-DDE	10	2000
Dieldrin	10	2000
Endrin	10	2000
Endosulfan II	15	2000
4,4'-DDD	15	2000
Butyl benzyl phthalate	10	660
4,4'-DDT	10	2000
3,3'-Dichlorobenzidine	20	2000
Benzo(a)anthracene	10	660
Chrysene	10	660
Endosulfan sulfate	10	2000
Bis(2-ethylhexyl)phthalate	25	2000
Di-n-octyl phthalate	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzo(a)pyrene	10	660
Indeno(1,2,3-c,d)pyrene	10	660
Dibenzo(a,h)anthracene	10	660
Benzo(g,h,i)perylene	10	660

** Compound is not analyzed in solid samples.

Appendix B TABLES OF STANDARD SOLUTIONS USED IN THIS METHOD, INCLUDING AN ANALYTE LIST, CONCENTRATION OF SOLUTION, AND AMOUNT TO USE TO SPIKE SAMPLES OR INJECT.

TABLE B-1 SURROGATE STANDARD SPIKING SOLUTION
TABLE B-2 MATRIX STANDARD SPIKING SOLUTION
TABLE B-3 INTERNAL STANDARD SOLUTION
TABLE B-4 CALIBRATION STANDARD SOLUTIONS PURCHASED BY VENDORS
TABLE B-5 CALIBRATION STANDARD SOLUTIONS PREPARED FROM NEAT COMPOUNDS

TABLE B-1: SURROGATE STANDARD SPIKING SOLUTION

Acid Surrogate List:

Compound	Standard conc.	Conc. After Spiking
Phenol-d5	2000 ug/ml	100 ug/ml
2-Fluorophenol	2000 ug/ml	100 ug/ml
2,4,6-Tribromophenol	2000 ug/ml	100 ug/ml

Base/Neutral Surrogate List:

Compound	Standard conc.	Conc. After Spiking
Nitrobenzene-d5	1000 ug/ml	50 ug/ml
2-Fluorobiphenyl	1000 ug/ml	50 ug/ml
p-Terphenyl-d14	1000 ug/ml	50 ug/ml

TABLE B-2: MATRIX SPIKE STANDARD SPIKING SOLUTION

Acid Matrix Spiking List:

Compound	Standard conc.	Conc. After Spiking
Pentachlorophenol	2000 ug/ml	100 ug/ml
Phenol	2000 ug/ml	100 ug/ml
2-Chlorophenol	2000 ug/ml	100 ug/ml
4-Chloro-3-methylphenol	2000 ug/ml	100 ug/ml
4-Nitrophenol	2000 ug/ml	100 ug/ml

Base/Neutral Matrix Spiking List:

Compound	Standard conc.	Conc. After Spiking
1,2,4-Trichlorophenol	1000 ug/ml	50 ug/ml
Acenaphthene	1000 ug/ml	50 ug/ml
2,4-Dinitrotoluene	1000 ug/ml	50 ug/ml
Pyrene	1000 ug/ml	50 ug/ml
N-Nitroso-di-n-propylamine	1000 ug/ml	50 ug/ml
1,4-Dichlorobenzene	1000 ug/ml	50 ug/ml

TABLE B-3: INTERNAL STANDARD SOLUTION

Compound	Standard conc.	Conc. After Spiking
1,4-Dichlorobenzene-d4	4000 ug/ml	40 ug/ml
Naphthalene-d8	4000 ug/ml	40 ug/ml
Acenaphthene-d10	4000 ug/ml	40 ug/ml
Phenanthrene-d10	4000 ug/ml	40 ug/ml
Chrysene-d12	4000 ug/ml	40 ug/ml
Perylene-d12	4000 ug/ml	40 ug/ml

TABLE B-4: CALIBRATION STANDARD SOLUTIONS PURCHASED BY VENDORS

Vendor: Ultra Scientific
Final Volume: 5 ml

Standard Mix Name	Standard conc.	Amt spiked for high std	Final conc.
Base/Neutrals Mix #1	2000 ug/ml	400 ul	160 ug/ml
Base/Neutrals Mix #2	2000 ug/ml	400 ul	160 ug/ml
Toxic Substances Mix #1	2000 ug/ml	400 ul	160 ug/ml
Toxic Substances Mix #2	2000 ug/ml	400 ul	160 ug/ml
Benzidines	2000 ug/ml	600 ul	240 ug/ml
PAH Mixture	2000 ug/ml	400 ul	160 ug/ml
Phenols Mixture	2000 ug/ml	400 ul	160 ug/ml
Organochlorine Pesticides	2000 ug/ml	800 ul	320 ug/ml
Acid Surrogate Standard	2000 ug/ml	400 ul	160 ug/ml
Base/Neutral Surr. Std.	1000 ug/ml	800 ul	160 ug/ml

Vendor: Supelco Supelpreme-HC Mixes
Final Volume: 5 ml

Standard Mix Name	Standard conc.	Amt spiked for high std	Final conc.
Base-Neutrals Mix 1	2000 ug/ml	400 ul	160 ug/ml
Base-Neutrals Mix 2	2000 ug/ml	400 ul	160 ug/ml
Hazardous Sub. Mix 1	2000 ug/ml	400 ul	160 ug/ml
Hazardous Sub. Mix 2	2000 ug/ml	400 ul	160 ug/ml
Benzidines	2000 ug/ml	600 ul	240 ug/ml
PAH Mixture	2000 ug/ml	400 ul	160 ug/ml
Phenols Mixture	2000 ug/ml	400 ul	160 ug/ml
Organochlorine Pesticides	2000 ug/ml	800 ul	320 ug/ml
Acid Surrogate Standard	2000 ug/ml	400 ul	160 ug/ml
B/N Surrogate Std	1000 ug/ml	800 ul	160 ug/ml

FIVE POINT CALIBRATION STANDARDS:

2250 ul of the 160 ug/ml calibration standard diluted to 3 ml yields the 120 ug/ml calibration standard.

2000 ul of the 120 ug/ml calibration standard diluted to 3 ml yields the 80 ug/ml calibration standard.

1875 ul of the 80 ug/ml calibration standard diluted to 3 ml yields the 50 ug/ml calibration standard.

400 ul of the 50 ug/ml calibration standard diluted to 1 ml yields the 20 ug/ml calibration standard.

TABLE B-5: CALIBRATION STANDARD SOLUTIONS PREPARED FROM NEAT COMPOUNDS

Final Volume: 10 ml

Compound	Density	Amt spiked for stock std	Final conc.
Pyridine	0.978	20.4 ul	2000 ug/ml

Appendix C

TABLE C-1

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

TABLE C-2

Initial Calibration: The percent relative standard deviation for each compound listed below should be <30%.

Continuing Calibration: The percent deviation from the average response factor determined in the initial calibration should be <30% for each compound listed below.

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-Methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Phentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

SYSTEM PERFORMANCE CHECK COMPOUNDS

Initial Calibration: The average response factor for each compound listed below should be >0.05.

Continuing Calibration: The response factor for each compound listed below should be >0.05.

Base/Neutral Fraction	Acid Fraction
N-Nitroso-Di-n-Propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

Appendix D

TABLE D-1

SPIKE LEVELS FOR LABORATORY CONTROL SAMPLES

MATRIX SPIKE/MATRIX SPIKE DUPLICATE

Pentachlorophenol	100
Phenol	100
2-Chlorophenol	100
4-Chloro-3-cresol	100
4-Nitrophenol	100
1,2,4-Trichlorobenzene	50
Acenaphthene	50
2,4-Dinitrotoluene	50
Pyrene	50
N-Nitroso-di-N-propylamine	50
1,4-Dichlorobenzene	50

METHOD BLANK

Phenol-d_5	100
2-Fluorophenol	100
2,4,6-Tribromophenol.	100
Nitrobenzsene-d_5	50
2-fluorobihenyl	50
Terphenyl-d_{14}	50

Surrogates added to samples

Same as method blank

TABLE D-2

8270 CONTROL LIMITS

	Minimum Control Limit			
	WATER		SOIL	
MS/MSD	MS/MSD	RPD	MS/MSD	RPD
Pentachlorohenol	9-103	50	17-109	47
Phenol	12-89	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
4-Chloro-3-cresol	23-97	42	26-103	33
4-Nitrophenol	10-80	50	11-114	50
1,2,4-Trichlorobenzene	39-98	28	38-107	23
Acenaphthene	46-118	31	31-137	19
2,4-Dinitrotoluene	24-96	38	28-89	47
Pyrene	26-127	31	35-142	36
N-Nitroso-di-N-propylamine	41-116	38	41-126	38
1,4-Dichlorobenzene	36-97	28	28-104	27
SURROGATE/METHOD BLANK RECOVERIES	SURROGATE RECOVERY		SURROGATE RECOVERY	
Phenol-d_5	10-94		24-113	
2-Fluorophenol	21-100		25-121	
2,4,6-Tribromophenol	10-123		19-122	
Nitrobenzsene-d_5	35-114		23-120	
2-Fluorobiphenyl	43-116		30-115	
Terphenyl-d_{14}	33-141		18-137	

Subject or Title:

ICP Analysis of Metals using SW-846 Method 6010

SOP No.	Revision No.:	Effective Date:
ETASD-4001	original	May 17, 1991

Supercedes: None

1 FILING INSTRUCTIONS

1.1 This document shall be filed at ETASD as documt ET-ASD 4001 in the 4000 section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 Analytes: Secioy 3.2

2.2 Detection Limits: Section 3.2

2.3 Applicable matrices: water, soil or sludge

2.4 Linear Range of Instrument: section 3.2

2.5 Analysis

2.5.1 Sample prep requires at least one day for completion.

2.5.2 Analysis time is approximately 3 minutes per sample or standard.

3 Method SUMMARY

3.1 Samples are digested with hydrogen peroxide, nitric and hydrochloric acid. Analysis is performed using an inductively coupled argon plasma spectrometer.

Prepared by: Date:

Management Approval: Date:

Arthur Marley 6-7-93

QA Officer: Date:

3.2 Reporting limits for the target parameters are presented in the following tables:

Analyte	Reporting Limit (PQL)	Linear Range
Arsenic	0.1 mg/L	100 mg/L
Barium	0.1 mg/L	100 mg/L
Cadmium	0.1 mg/L	100 mg/L
Chromium	0.1 mg/L	100 mg/L
Lead	0.1 mg/L	100 mg/L
Mercury	0.1 mg/L	100 mg/L
Selenium	0.1 mg/L	100 mg/L
Silver	0.1 mg/L	100 mg/L

4 COMMENTS

4.1 In order to minimize analytes from interferening one another, computer aided software aids the analyst by applying interelemental corrections.

5 SAFETY

5.1 Chemicals used in this method 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 data handling sheet should also be made available to all personnel involved in the chemical analysis. Additional references material is available.

5.2 Minimum Safety requirements:

5.2.1 Lab coat;
5.2.2 Safety glasses or goggles;
5.2.3 All work must be performed in a fume hood;
5.2.4 Acid resistant gloves must be worn at all times; and

5.2.5 Face shield must be worn when work is being performed in the hood.

6 SAMPLE COLLECTION, PRESERVATION AND HOLDING TIMES

6.1 Soil/Sludge

6.1.1 Grab samples must be collected in either a borosilica glass jar or polyethylene bottle. Conventional sampling practices should be followed, except that the bottle must not be pre-rinsed with sample before collection. Samples must be stored at 4°C until sample prep (EPA's SW-846 protocol).

6.2 Water

6.2.1 Grab samples must be collected in either a borosilica glass jar or a polyethylene bottle, acidify with nitric acit to pH < 2. Store at 4°C.

7 APPARATUS

7.1 Hot plate: Capable of maintaining 100°C.

7.2 Funnel rack: Filtering a maximum of eight samples.

7.3 Balance: Analytical capable of accurately weighing 0.01g.

7.4 Funnel: Poly-Methylpentene or equivalent.

7.5 Griffin beakers: 250 mL.

7.6 Watch glasses: Ribbed and plain.

7.7 Qualitative filter paper: 7 uM or equivalent.

7.8 Pipettors: 1 to 10 mL

7.9 Inductively coupled argon plasma atomic emission spectrometer:

7.9.1 Computer-controlled emission spectrometer with background correction, and able to compensate for interelement correction factors.

7.9.2 Argon gas supply: Technical grade or equivalent.

8 REAGENTS AND STANDARDS

8.1 *Reagent water:* Reagent water is defined as a water in which an interference is not observed at the method detection limit of each parameter of interest.

8.2 *Concentrated Nitric acid.*

8.3 *Hydrochloric acid (1:1):* Add 500 ml concentrated HCl to 400 ml reagent water and dilute to 1 liter.

8.4 *Nitric acid (1:1):* Add 500 ml concentrated HNO_3 to 400 ml of reagent water and dilute to volume.

8.5 *Standard stock solution:* May be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hr. at 105°C, unless otherwise specified.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{Volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{Volume}}$$

8.5.1 Arsenic solution: 1000 ppm

8.5.2 Barium solution: 1000 ppm
8.5.3 Cadmium solution: 1000 ppm
8.5.4 Chromium solution: 1000 ppm
8.5.5 Lead solution: 1000 ppm
8.5.6 Mercury solution: 1000 ppm
8.5.7 Selenium solution: 1000 ppm
8.5.8 Silver solution: 1000 ppm
8.5.9 Copper solution: 1000 ppm
8.5.10 Cobalt solution: 1000 ppm
8.5.11 Aluminum solution: 1000 ppm
8.5.12 Calcium solution: 1000 ppm
8.5.13 Magnesium solution: 1000 ppm
8.5.14 Iron solution: 1000 ppm
8.5.15 Molybdenum solution: 1000 ppm
8.5.16 Vanadium solution: 1000 ppm
8.5.17 Nickel solution: 1000 ppm
8.5.18 Zinc solution: 1000 ppm
8.5.19 Beryllium solution: 1000 ppm
8.5.20 Antimony solution: 1000 ppm
8.5.21 Primary ICP Drinking Water Mix standard
8.5.22 Interference check standard #1

9 PROCEDURE

9.1 Method Summary

9.1.1 This method is applicable to the determination of metals. Either 1 gram of soil/sediment or 100 ml of water is acid digested (refluxed) using various concentrated acids. Once digested, samples are diluted to appropriate volume and filtered. The filtrate is analyzed using an inductively coupled argon plasma spectrometer.

9.2 Digestion of Soil/Sediment Samples

9.2.1 A representative 1.00 to 2.00 gram (wet weight) sample is weighed to the nearest 0.01 gram in a 250 ml Griffin beaker.

9.2.2 Add 10 ml of 1:1 nitric acid (HNO_3)/Water solution. Mix the slurry and cover with a watch glass.

9.2.3 Reflux sample for 10-15 minutes at 95°C without boiling. Allow sample to cool to room temperature.

9.2.4 Add 5 ml of concentrated nitric acid. Mix the slurry and reflux for 30 minutes. Allow sample to cool to room temperature. Note: Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

9.2.5 Add 2 ml of reagent water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, remove beaker and allow to cool to room temperature.

9.2.6 Continue to add 30% hydrogen peroxide in 1 ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Note: the maximum amount of 30% hydrogen peroxide per sample is 10 ml. Allow the sample to cool to room temperature.

9.2.7 Dilute the sample to the appropriate volume with reagent water.

9.2.8 Filter sample and collect filtrate for analyzes. Complete digestion prep sheet.

9.3 Digestion of Aqueous Samples

9.3.1 Transfer a 50 mL representative aliquot of the well-mixed sample to 250 ml Griffin beaker.

9.3.2 To the sample, add 2 ml of 1:1 HNO_3/Water and 10 ml of 1:1 Hydrochloric acid (HCl)/Water.

9.3.3 Cover beaker with watch glass and reflux for 2 hours at 95°C. Note: at all times the sample must not boil or evaporate to less than 25 ml. Allow the sample to cool to room temperature.

9.3.4 Add reagent water to the Griffin beaker to the appropriate level. Filter and analyze.

9.3.5 Complete digestion prep log sheet.

9.4 Percent Solids

9.4.1 Weigh 5 grams of soil to the nearest 0.1 gram in a disposable glass test tube.

9.4.2 Place test tube in drying oven at 105°C for 24 hours.

9.4.3 Remove sample and place in dessicator.

9.4.4 Re-weigh sample.

9.4.5 Calculations

$$\frac{\text{(sample wt. after drying)}}{\text{(sample wt. before drying)}} \times 100 = \% \text{ Moisture}$$

9.5 ANALYSIS

9.5.1 Calibration of Instrument

9.5.1.1 A minimum of one wavelength calibration

is performed after instrument start-up.

9.5.1.2 Calibration standards are run at 2 levels, of which one is a blank. A calibration curve is generated for each analyte.

9.5.1.3 After standardization, the high standard is rerun and must be within 5%. An Initial Calibration Verification (ICV/QCS) and an Initial Calibration Blank (ICB) are analyzed. Each element must not exceed +/- 10% of the ICV concentration. In the event the ICV fails, the analyst must either recalibrate the instrument or remake calibrating solutions. Note: if ICV still fails after corrective actions, the Q.A. Officer must be informed immediately. All actions must be well documented.

9.5.1.4 A Continuing Calibration Verification (CCV/LPC) and a Continuing Calibration Blank (CCB) must be analyzed after a maximum of 10 samples. If the CCV/LPC fails, recalibrate and all samples since the last acceptable calibration are reanalyzed.

10 QC/QA REQUIREMENTS

10.1 For each batch of samples (maximum of 20) digested, the minimum QA/QC required is:

10.1.1 Prep Blank
10.1.2 LCS (SCS)
10.1.3 Matrix Spike (MS)
10.1.4 Matrix Spike Duplicate (MSD)

11 Calculations

11.0.1 Water

11.0.1.1 Water Conc. (mg/L)

11.0.2 Soil/Sludge

11.0.2.1 Soil/Sludge (mg/kg) = $\frac{(V) \times (C)}{(W) \times (S)}$

V = Final Volume in ml
C = Concentration in mg/L
W = Sample Weight in grams
S = % Solids /100

12 REFERENCES

12.1 Method Source:

12.1.1 "Test Methods for Evaluating Solid Waste", 3rd Edition (1986), Office of Solid Waste and Emergency Response, U.S. EPA.

12.1.2 "Standard Methods for the Examination of Water and Wastewater", 17th Edition, American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington D.C. (1989).

13 CORRECTIVE ACTIONS

13.1 In case of difficulties consult your supervisor.

TABLE 1

##	Elem	PQL	LRS	Solution	##	Elem	PQL	LRS	Solution
1	Al	0.10	50	Al 1000 ppm	19	Mn	0.10	50	SPEX QC-19
2	Sb	0.10	50	SPEX QC-19	20	Hg	0.10	50	Hg 1000 ppm
3	As	0.10	50	SPEX QC-19	21	Mo	0.10	50	SPEX QC-19
4	Ba	0.10	50	Ba 1000 ppm	22	Ni	0.20	50	SPEX QC-19
5	Be	0.10	50	SPEX QC-19	23	P	0.10	50	P 10000 ppm
6	Bi	0.10	50	Bi 10000 ppm	24	K	0.50	50	K 10000 ppm
7	B	0.10	50	B 1000 ppm	25	Se	0.20	50	SPEX QC-19
8	Ca	0.10	50	SPEX QC-19	26	Si	0.10	50	Si 1000 ppm
9	Cd	0.10	50	SPEX QC-19	27	Ag	0.10	50	Ag 1000 ppm
10	Cr	0.10	50	SPEX QC-19	28	Na	0.10	50	Na 1000 ppm
11	Co	0.10	50	SPEX QC-19	29	Sc	0.10	50	Sc 10000 ppm
12	Cu	0.10	50	SPEX QC-19	30	Sr	0.10	50	Sr 10000 ppm
13	Ga	0.10	50	Ga 10000 ppm	31	Sn	0.10	50	Sn 10000 ppm
14	Fe	0.10	50	SPEX QC-19	32	Ti	0.10	50	SPEX QC-19
15	Pb	0.10	50	SPEX QC-19	33	Tl	0.20	50	SPEX QC-19
16	La	0.10	50	La 10000 ppm	34	V	0.10	50	SPEX QC-19
17	Li	0.10	50	Li 10000 ppm	35	Zn	0.10	50	SPEX QC-19
18	Mg	0.10	50	SPEX QC-19	36	Zr	0.10	50	Zr 1000 ppm

Subject or Title:

Mercury analysis in Water and Wastewater.

SOP No.:	Revision No.:	Effective Date:
ETASD-4010	original	May 17, 1992

Supersedes: None

1 FILING INSTRUCTIONS:

1.1 This document shall be filed at ETASD as document ETASD-4010 in the 4000 section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system.

2.2 Reporting Limits:

2.2.1 The reporting limits for each sample will be reported 0.2 ug/L.

2.3 Applicable Matrices:

Prepared by: Ajit Joshi	Date: November 5, 1992
Management Approval: Arthur Dailey	Date: 6-7-93
QA Officer Approval:	Date:

2.3.1 This method is applicable to drinking water and waste water.

2.4 Dynamic Range:

2.4.1 The dynamic range for method is 0.1 to 50 ug/L.

2.5 Analysis time:

2.5.1 5 minutes per sample, after 30 minutes of prep and 2½ hour digestion.

3 METHOD SUMMARY

3.1 The flame-less AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration, and recorded in the usual manner.

4 COMMENTS

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere.

4.2 Copper has also been reported to interfere; however, copper concentration as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the

cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

5 SAFETY ISSUES

5.1 Eye ware, lab coat, and gloves should be worn at all times.

5.2 Refer to Chemical Hygiene Plan for further information.

6 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

6.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

7 APPARATUS

7.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Thermo Jarell Ash Model SH 4000.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available, and may be substituted for the atomic absorption spectrophotometer.

7.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

7.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

7.4 Absorption Cell: Standard spectrophotometer cells 10 cm. long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing,

1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place.

The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

7.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

7.6 Automatic Vapor Accessory: Model 880 Thermo Jarell Ash. (Optional)

7.7 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

7.8 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

7.9 Drying Tube: 6" X 3/4" diameter tube containing 20 g. of magnesium perchlorate (See Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell, maintaining the air temperature in the cell about 10°C above ambient.

8 REAGENTS AND STANDARDS

8.1 *Concentrated Sulfuric Acid Conc:* Reagent grade.

8.2 *0.5N Sulfuric acid:* Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

8.3 *Concentrated Nitric Acid:* Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

8.4 *Stannous chloride:* Dissolve 25 g. stannous chloride to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension, and should be stirred continuously during use. (Stannous sulfate may be used in place of stannous chloride).

8.5 *Sodium Chloride-Hydroxylamine Sulfate Solution:* Dissolve 12 g. of sodium chloride and 12 g. of hydroxylamine sulfate in distilled water, and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate).

8.6 *Potassium Permanganate, 5% solution:* Dissolve 5 g. of potassium permanganate in 100 mL of distilled water.

8.7 *Potassium Persulfate, 5% solution:* Dissolve 5 g. of potassium persulfate in 100 mL of distilled water.

8.8 *Mercury Stock Solution:* Dissolve 0.1354 g. of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1mL = 1 mg Hg. Alternatively use commercially available standards.

8.9 *Mercury Standard Solution:* Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

9 PROCEDURE

9.1 Standards:

9.1.1 Transfer 0, 0.5, 1, 5, 10 mL aliquot of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL.

9.2 Samples:

9.2.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle.

9.3 Mix thoroughly and add 5 mL of conc. sulfuric acid, and 2.5 mL of conc. nitric acid to each bottle.

9.4 Add 15 mL of KM_nO_4 solution to each bottle, and allow to stand at least 15 minutes. For sewage samples additional KMnO4 must be added. Add same amount to standards. (0.25 gr. of solid KM_nO_4 may be substituted for KM_nO_4 solution).

9.5 Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs.

9.6 Allow bottles cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Continue to add 1 mL aliquat until all KMnO4 is removed.

9.7 Analysis:

9.7.1 Calibration:

9.7.1.1 If using Jarell Ash SH4000 Atomic Absorption, follow the manufacturers specifications, calibrate using the digested standards.

9.7.1.2 Data is transfered in "Real Time" to a IBM compatible computer, the software is

able to generate a calibration curve, and calculate concentration based on that curve.

9.7.2 Manual vapor generation:

9.7.2.1 Add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

9.7.2.2 The circulating pump, which has previously been adjusted to a rate of 1 liter per minute is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards, and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood, or pass the vapor through some absorbing media, such as:

a) Equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4 or

b) 0.25% iodine in a 3% a KI solution. A specially treated charcoal that will absorb mercury vapor is available.

9.7.3 Automatic Vapor Generation:

9.7.3.1 In place of the manual vapor generation, a automatic vapor Accessory such as Jarell Ash Model 880 AVA, can be used.

9.7.3.2 Transfer a small aliquot (25 ml's) into a beaker and insert the sipper probe of the AVA, and allow the sample to flush for 2 minutes, the sample gas has now reached the absorption cell and a peak height reading may be taken at this time.

10 QA/QC REQUIREMENTS

10.1 A five point standard curve must be plotted (correlation coefficient to 0.995 or better),

10.2 Initial Calibration Verification, ICV must be analyzed and should be within 15% of the mean.

10.3 A reagent blank and laboratory control sample must be run for a batch of 20 samples.

10.4 Continuing Calibration Verification, CCV must be analyzed every 10 samples or less, and must be within 15% of the mean.

11 CALCULATIONS

11.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

11.2 Calculate the mercury concentration in the sample by the

formula:

$$\text{ug Hg/L} = \text{ug Hg in aliquot} \times \frac{1{,}000}{\text{volume of aliquot in mL}}$$

11.3 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L, the standard deviations were +/- 0.027, +/- 0.0006, +/- 0.01 and +/-0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

11.4 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

12 REFERENCES

12.1 Kopp, J.F., Longbottom, M.C. and Lobring, L.B. "Cold Vapor Method for Determining Mercury", AWWA, vol. 64, p. 20, Jan. 1972.

12.2 Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p. 343, (1976).

12.3 Standard Methods for the Examination of Water and Wastewater 17th Edition.

13 CORRECTIVE ACTION

13.1 If the ICV fails, all samples and standards must be redigested and reanalyzed.

13.2 Consult with supervisor if further problems develop.

Subject or Title:

Mercury Analysis in Soil/Sediment by Manual Cold Vapor Technique
MERCURY (In sediments)/Method 245.5 CLP-M*
(Manual Cold Vapor Technique)

SOP No.:	Revision No.:	Effective Date:
ETASD-4011	original	July 31, 1991

Supersedes: None

1. SCOPE AND APPLICATION

1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2. METHOD SUMMARY

2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2 An alternate digestion involving the use of an autoclave is described in (8.2).

*CLP-M modified for the Contract Laboratory Program.

Prepared by: Date:

Management Approval: Date:
Arthur Neeley 8/23/91

QA Officer Approval: Date:
Kenneth C. Hon 8/23/91

3. COMMENTS

3.1 The same types of interferences that may occur in water samples are also possible with sediments (i.e. sulfides, high copper, high chlorides, etc.).

3.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

4. SAFETY ISSUES

4.1 Not applicable.

5. SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

5.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or airborne mercury contamination.

5.2 Refrigerate solid samples at 4°C (+/- 2°) upon receipt until analysis (See Exhibit D, Section II).

5.3 The sample should be analyzed without drying. A separate percent solids determination is required (Part F).

6. APPARATUS

6.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

6.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.4 Absorption Cell: Standard spectrophotometer cells 10 cm. long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give a maximum transmittance. Two 2" by 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

6.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory (Regulated compressed air can be used in an open one-pass system).

6.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

6.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

6.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g. of magnesium perchlorate (See Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

7. REAGENTS AND STANDARDS

7.1 Sulfuric acid, conc.: Reagent grade of low mercury content.

7.2 Nitric acid, conc.: Reagent grade of low mercury.

7.3 Stannous Sulfate: Add 25 g. stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

7.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 3) Solution: Dissolve 12 g. of sodium chloride and 12 g. of hydroxylamine sulfate in distilled water and dilute to 100 mL.

NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

7.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g. of potassium permanganate in 100 mL of distilled water.

7.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g. of potassium persulfate in 100 mL of distilled water.

7.7 Stock Mercury Solution: Dissolve 0.1354 g. of mercuric chloride in 75 mL of distilled water. Add mL of conc, nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg. Hg.

7.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

8. PROCEDURE

8.1 Transfer 0, 1, 2.5, 5, and 10 mL aliquots of the working mercury solution (6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of conc. H_2SO_4 (6.1) and 2.5 mL of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (6.5) and 8 mL of potasium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is

allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (See Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor though some absorbing media, such as:

a) Equal volumes of 0.1 N $KMnO_4$, and 10% H_2SO_4 or

b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is available.

8.2 Weight a representative 0.2 g. portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat tow minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potasium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium

chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, purge the head space of the sample bottle for at least one minute, and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.3 An alternate digestion procedure employing an autoclave may also be used. In this method 5 mL of conc. H_2SO_4 and 2 Ml of conc. HNO_3 are added to the 0.2 g. of sample. 5 mL of saturated $KMnO_4$ solution and 8 Ml of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. {urge the head space of the sample bottle for at least one minute and continue as described under (7.1).

9. QA/QC REQUIREMENTS

9.1 Not applicable.

10. CALCULATIONS

10.1 Measure the peak height of the unknown from the chart an read the mercury value from the standard curve.

10.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in aliquot}}{\text{wt of the aliquot in gms (based upon dry wt of the sample)}}$$

10.3 Report mercury concentrations as described for aqueous mercury samples converted to units of mg/kg. The sample result or the detection limit for each sample must be corrected for sample weight and % solids before reporting.

11. REFERENCES

11.1 Bishop, J.N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.

11.2 Salma, M., private communication, EPA Cal/Nev. Basin Office, Almeda, California.

11.3 "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue", USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.

11.4 Op. cit (#3), Methods 245.1 or 245.2.

12. CORRECTIVE ACTION

12.1 Not applicable.

STANDARD OPERATION PROCEDURE

Subject or Title:

Sulfate - Turbidimetric Method

SOP NO.:	Revision No.:	Effective Date:
ETASD-4012	1992-7	July 30, 1992

Supersedes: Original

1 FILING INSTRUCTIONS

1.1 This procedure shall be filed at ETASD as document number ETASD-4012 in the 4000 series section of the SOP Manual.

2 SCOPE AND APPLICATION

2.1 Analytes: SO_4^{-2}

2.2 Reporting Limits: 1 mg. SO_4^{-2}/Liter

2.3 Applicable matrices: Water or Wastewater

2.4 Linear range of instrument:

2.4.1 Calibration standards are run at 5 concentration levels, of which one is a blank.

2.5 Analysis

2.5.1 Each sample requires seven minutes from sample prep to analysis.

Prepared by: Date:

Management Approval: Arthur Beeley Date: 8-19-92

QA Officer Approval: Laura Hanson Date: 8-19-92

3 SUMMARY

3.1 Principle sulfate ion (SO_4^{-2}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the (SO_4^{-2}) concentration is determined by comparison of the reading with a standard curve.

4 COMMENTS

4.1 Not Applicable

5 SAFETY

5.1 Safety glasses or goggles, coat and gloves

6 SAMPLE COLLECTION, PRESERVATION AND HOLDING TIMES

6.1 Water/Wastewater

6.1.1 Grab samples must be collected in either a polyethylene or borosilica glass bottle and stored at 4°C.

6.1.2 Samples must be analyzed with 28 days of sample collection.

7 APPARATUS

7.1 Stir plate with assorted stir bars

7.2 Nephelometer

7.3 Electric Timer

7.4 Spatula

7.5 125 ml Erlenmeyer flash or equivalent

7.6 Volumetric pipets - borosilica glass or equivalent

8 REAGENTS AND STANDARDS

8.1 Reagent water: Reagent water is defined as a water in which an interference is not observed at the method detection limit.

8.2 Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) or 51% w/v $MgCl_2$ in water

8.3 Sodium acetate ($CH_3COONa.3H_2O$)

8.4 Potassium nitrate (KNO_3)

8.5 Glacial acetic acid, 99% (CH_3COOH)

8.6 Anhydrous sodium sulfate

8.7 Standardized (0.02 N) sulfuric acid

8.8 Barium chloride, $BaCl_2$, crystals 20 to 30 mesh

8.9 100 ppm sulfate standard

8.9.1 10.4 ml of 0.02 N H_2SO_4 and dilute to 100 ml.

8.9.2 Dissolve 0.1479 g of anhydrous sodium sulfate to 1 liter.

8.10 Buffer Solution: Dissolve 30 g. Magnesium Chloride, hexahydrate or 59 ml $MgCl_2$ 51%, 5 g. sodium acetate, 1.0 g. potassium nitrate, and 20 mL acetic acid in 1 L water.

9 PROCEDURE

9.1 Measure 100 ml of sample in a 125 ml erlenmeyer flask.

9.2 Add 10 ml of buffer solution and mix.

9.3 While stirring, add a spoon full of barium chloride and mix for 60 ± 2 seconds.

9.4 After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5 ± 0.5 minutes. (See SOP for operation of Turbidity-Nepholmeter).

10 ANALYSIS

10.1 Plot concentration of standard against LCD reading. Apply a linear regression curve based on 5 standards, of which one is a blank. A minimum of 0.995 (r) is required for this method.

10.2 Note: Sulfate at a concentration of 40 mg/L, or greater decreases the reability of curve.

11 QA/QC REQUIREMENTS

11.1 For each batch of samples, the following is required

11.1.1 Prep blank

11.1.2 EPA QC (Note: If EPA QC is unavailable, prep mid-range sulfate standard using anhydrous sodium sulfate). QC requirements for Na_2SO_4 standard ± 10% for true value.

11.1.3 Samples (3-5)

11.1.4 QC (Continuing Calibration Verification).

12 REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater", 17th edition, American Public Health Associates, American Water Works Associates, Water Pollution Central Federation, Washington, D.C. (1989).

13 CORRECTIVE ACTIONS

13.1 If standard curve correlation coefficient is < 0.995; investigate nephelometer operation, reprep standards if necessary and recalibrate.

13.2 If QC check is outside of acceptance limits, investigate and reprep QC check, if necessary.

Subject or Title:		
Fluoride by Ion Selective Electrode.		
SOP No.: ETASD-4019	Revision No.: original	Effective Date: July 30, 1992
Supersedes: None		

1 FILING INSTRUCTIONS:

1.1 This document shall be filed at ETASD as document ETASD-4019 in the 4000 section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 This method is suitable for the determination of Fluoride by Ion Selective Electrode.

2.2 Reporting Limits:

2.2.1 The reporting limits for each sample will be reported in 0.2 mg/ L F-.

2.3 Applicable Matrices:

2.3.1 The applicable matrix is liquid.

2.4 Dynamic Range:

2.4.1 The dynamic range for method is 100 mg/L F-.

2.5 Analysis Time:

2.5.1 5 minutes per sample, not including calibration.

3 METHOD SUMMARY

3.1 The fluoride electrode is an ion-selective electrode, and

Prepared by:	Date:
Management Approval: [signature]	Date: 8-18-92
QA Officer Approval: [signature]	Date: 8-17-92

measures the ion activity of fluoride in solutions rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts pH, and breaks up complexes so that, in effect, the electrode measures concentration.

4 COMMENTS: None

5 SAFETY ISSUES

5.1 A minimum of safety glasses, lab coat and protective gloves are required.

6 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Samples should be collected in polyethylene containers.

6.2 Samples should be stored at 4°C.

6.3 Samples must be analyzed within 28 days from the date sampled.

7 APPARATUS

7.1 Ion selective meter.

7.2 Fluoride electrode with reference electrode or fluoride combination electrode.

7.3 Magnetic stirrer, with TFE-coated stirring bar.

8 REAGENTS AND STANDARDS

8.1 *Stock fluoride solution:* Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in DI water and dilute to 1 L; 1.00 mL = 100 ug F-, or use commercially certified solutions.

8.2 *Standard fluoride solution:* Dilute 100 mL stock fluoride solution to 1 L with DI water; 1.00 mL = 10.0 ug F-.

8.3 *Fluoride buffer:* TISAB powder pillows (HACH).

9 PROCEDURE

9.1 *Instrument calibration.*

9.1.1 Remove existing pH probe from ISE meter and connect fluoride electrode, press the mode button so that the mV light flashes.

9.2 *Preparation of fluoride standards and samples:*

9.2.1 Prepare a series of standards by diluting with DI water 5.0, 10.0, and 20.0 mL of standard fluoride solution to 100 mL with DI water. These standards are equivalent to 0.5, 1.0, and 2.0 mg F- /L.

9.2.2 In 100 mL beakers add by volumetric pipet from 10 to 25 mL standard or sample. Allow samples and standards to come to room temperature. Add 1 (one) powder pillow, by using nail clippers clip the pillow on top and pour out the contents into the beaker.

9.2.3 Place a stirring bar and dip the electrode into the solution and start the stirrer, measure the developed potential. Let electrode remain in the solution for 3 min. (or until the reading is stable) before taking the final mV reading. Withdraw electrode, rinse with DI water, and blot dry between readings.

9.2.4 When using an expanded-scale pH meter or selective-ion meter, frequently recalibrate the electrode by checking the potential reading of the 1.00 mg F- /L.

10 QA/QC REQUIREMENTS

10.1 The method blank is mandatory and must be performed for

every set, and every 20 samples, when an sample batch exceeds 20 samples. The method blank for this method is 100 mL of nanopure water.

10.2 For each batch of samples (20 sample max.), a minimum of one matrix duplicate is required.

11 CALCULATIONS

11.1 Plot potential measurement of fluoride against concentration on a one-cycle semilogarithmic graph paper, (attachment 1). Plot mg F- /L on the logarithmatic axis (ordinate), with the lowest concentration on the bottom of the graph. Plot the mV on the abscissa. From the potential measurement for each sample, read the corresponding fluoride concentration from the standard curve.

11.2

$$\text{mg F- /L} = \frac{\text{ug F-}}{\text{mL sample}}$$

12 REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, 17th Edition,

13 Corrective Actions:

13.1 If readings are unstable check the manufacturers instructions for checking the ISE probe.

13.2 If QC limits are exceeded, analysis must be terminated and investigated for the problem.

STANDARD OPERATING PROCEDURE

Subject or Title:

Nitrate By HACH Test Kit.

SOP No.:	Revision No.:	Effective Date:
ETASD-4021	original	July 30, 1992

Supersedes: None

1 FILING INSTRUCTIONS:

1.1 This document shall be filed at ETASD as document ETASD-4021 in the 4000 section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 This method is suitable for the determination of Nitrate by HACH powder pillow/color comparator.

2.2 Reporting Limits:

2.2.1 The reporting limits for each sample will be reported in 0.01 mg/L NO3.

2.3 Applicable Matrices:

2.3.1 The applicable matrix is liquid.

2.4 Dynamic Range:

2.4.1 The dynamic range for method is 50 mg/L NO3.

2.5 Analysis Time:

2.5.1 3 minutes per sample for NO3.

3 METHOD SUMMARY

3.1 The Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium

Prepared by: Date:

Management Approval: Date:

Cathryn Deeley 8-18-92

QA Officer Approval: Date:

Diane Thurston 8-18-92

with sulfanilic acid to form an intermediate diazonium salt. This salt couples to gentisic acid to form an amber-colored product, which is then compared on the colored wheel.

4 COMMENTS

4.1 Interferences:

4.1.1 Strong oxdizing and reducing substances will interfere. Ferric iron causes high results and must be absent. Chloride concentration above 100 mg/L will cause low results.

4.1.2 Add Bromine water, 30 g/L, drop-wise to the sample before the addition of powder pillow, until a yellow color remains. Add one drop of phenol solution, 30 g/L, to destroy the color. Proceed with the addition of powder pillow.

4.2 Dilution

4.2.1 Samples containing more than 50 mg/L of nitrate nitrogen can be tested by diluting the sample before running test. a 1-to-5 dilution can be made by diluting 1 mL of water sample to 5 mL, use the calibrated dropper provided in the kit. Dilute with DI water.

5 SAFETY ISSUES

5.1 A minimum of safety glasses, lab coat and protective gloves are required.

6 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Samples should be collected in plastic or glass bottles.

6.2 Store at 4°C (39°F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before analysis. For longer storage periods, up to 14 days, adjust sample pH to 2 or less with sulfuric acid

(about 2 mL per L), store at 4°C. Before analysis neutralize the sample with 5N NaOH.

7 APPARATUS

7.1 HACH Nitrate-Nitrite Test Kit Model NI-12.

8 REAGENTS AND STANDARDS

8.1 Refer to Test Kit.

9 PROCEDURE

9.1 Rinse a color viewing tube several times with the water to be tested. Fill to the 5 mL mark with the water sample.

9.2 Use the clippers to open 1 (one) NitraVer 5 Nitrate Reagent Powder Pillow. Add the contents of the pillow to the sample, stopper the tube, and shake vigorously for exactly one minute. An amber color will develop if nitrate nitrogen is present in the sample. Allow the sample to stand undisturbed for one minute to complete color development.

9.3 Place the prepared sample in the right top opening of the color comparator (see attachment 1), fill the other viewing tube to the 5 mL mark with untreated water sample. Place this tube in the left top opening of the comparator.

9.4 Hold the comparator up to a light source and view through the openings in front. Rotate the disk to obtain a color match. Read mg/L nitrate nitrogen (N) through the scale window.

10 QA/QC REQUIREMENTS

10.1 To check reagent accuracy, use a reliable standard such as Nitrogen, Nitrate, Standard solution 100 mg/L as N. Follow steps 9.1 to 9.4 .

10.2 The method blank is mandatory and must be performed for every set, and every 20 samples, when an sample batch exceeds 20 samples. The method blank for this method is 5 mL of nanopure water.

10.3 For each batch of samples (20 sample max.), a minimum of one matrix duplicate is required.

11 CALCULATIONS

11.1 The reading on the comparator wheel is expressed in mg/L nitrate nitrogen (N), to convert mg/L nitrate (NO3) multiply the reading by 4.4.

mg NO3 /L = mg (N) /L x 4.4 x Dilution Factor

12 REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, 17th Edition.

12.2 HACH Water Analysis Handbook.

13 Corrective Actions:

13.1 In case of difficulty consult with your supervisor.

STANDARD OPERATING PROCEDURE

Subject or Title: Page 1 of 4

Nitrite By HACH Test Kit.

SOP No.:	Revision No.:	Effective Date:
ETASD-4022	original	July 30, 1992

Supersedes: None

1 FILING INSTRUCTIONS:

1.1 This document shall be filed at ETASD as document ETASD-4022 in the 4000 section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 This method is suitable for the determination of Nitrite by HACH powder pillow/color comparator.

2.2 Reporting Limits:

2.2.1 The reporting limits for each sample will be reported in 0.01 mg/L NO2.

2.3 Applicable Matrices:

2.3.1 The applicable matrix is liquid.

2.4 Dynamic Range:

2.4.1 The dynamic range for method is 1.0 mg/L NO2.

2.5 Analysis Time:

2.5.1 15 minutes per sample for NO2.

3 METHOD SUMMARY

3.1 Nitrite in the sample reacts with sulfanilic acid to form

Prepared by: Date:

Management Approval: Date:

Arthur J. Beeley 8-18-92

QA Officer Approval: Date:

Laura Hinson 8-17-92

an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

4 COMMENTS

4.1 Interferences:

4.1.1 Strong oxdizing and reducing substances will interfere. Cupric and Ferrous ions causes low results. Ferric , mercurous, silver, bismuth, antimonous, lead, auric, chloroplatinate and metavanadate ions interfere by causing precipitation.

4.2 Dilution

4.2.1 Sample containing more than 0.5 mg/L of nitrite nitrogen can be tested by diluting the sample before running test. a 1-to-5 dilution can be made by diluting 1 mL of water sample to 5 mL, use the calibrated dropper provided in the kit. Dilute with DI water.

5 SAFETY ISSUES

5.1 A minimum of safety glasses, lab coat and protective gloves are required.

6 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Samples should be collected in plastic or glass bottles.

6.2 Store at 4°C (39°F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before analysis. For longer storage periods, up to 14 days, adjust sample pH to 2 or less with sulfuric acid (about 2 mL per L), store at 4°C. Before analysis neutralize the sample with 5N NaOH.

7 APPARATUS

7.1 HACH Nitrate-Nitrite Test Kit Model NI-12.

8 REAGENTS AND STANDARDS

8.1 Refer to Test Kit.

9 PROCEDURE

9.1 Rinse a color viewing tube several times with the water to be tested. Fill to the 5 mL mark with the water sample.

9.2 Use the clippers to open 1 (one) NitraVer 3 Nitrite Reagent Powder Pillow. Add the contents of the pillow to the sample, stopper the tube, and shake vigorously for exactly one minute. An red color will develop if nitrite nitrogen is present in the sample. Allow the sample to stand undisturbed for 10 minutes to complete color development.

9.3 Place the prepared sample in the right top opening of the color comparator (see attachment 1), fill the other viewing tube to the 5 mL mark with untreated water sample. Place this tube in the left top opening of the comparator.

9.4 Hold the comparator up to a light source and view through the openings in front. Rotate the disk to obtain a color match. Read mg/L nitrite nitrogen (N) through the scale window.

10 QA/QC REQUIREMENTS

10.1 To check reagent accuracy, using a reliable standard such as Nitrogen, Nitrate, Standard solution 100 mg/L as N. Follow steps 9.1 to 9.4 .

10.2 The method blank is mandatory and must be performed for every set, and every 20 samples, when an sample batch exceeds 20 samples. The method blank for this method is 5 mL of nanopure water.

10.3 For each batch of samples (20 sample max.), a minimum of one matrix duplicate is required.

11 CALCULATIONS

11.1 The reading on the comparator wheel is expressed in mg/L nitrite nitrogen (N), to convert mg/L nitrite (NO_2) multiply the reading by 3.3.

mg NO_2 /L = mg (N) /L x 3.3 x Dilution Factor

12 REFERENCES

12.1 Standard Methods for the Examination of Water and Wastewater, 17th Edition.

12.2 HACH Water Analysis Handbook.

13 Corrective Actions:

13.1 In case of difficulty consult with your supervisor.

STANDARD OPERATION PROCEDURE

Subject or Title:

Chloride - Argentometric Method

SOP NO.:	Revision No.:	Effective Date:
ETASD-4028	1992-7	July 31, 1992

Supersedes: None

1 FILING INSTRUCTIONS

1.1 This procedure shall be filed at ETASD as document number ETASD-4028 in the 4000 series section of the SOP manual.

2 SCOPE AND APPLICATION

2.1 Analytes: Cl^-

2.2 Reporting Limits: 0.5 mg Cl^-/Liter

2.3 Applicable matrices: Water or wastewater

2.4 Linear range: sample is analyzed undiluted if chloride concentration required 10 mls. $AgNo_3$ titrant or less.

2.5 Analysis time: approximately 5-8 minutes per titration.

3 SUMMARY

3.1 Principle: In a neutral or slightly alkaline solution, potassium chromate can indicate the endpoint of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

3.2 Interferences: Substances in amounts normally found in potable waters will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations.

Prepared by: Date:

Management Approval: Date:
Gillian Reeley 8-19-92

QA Officer Approval: Date:
Laura Johnson 8-19-92

Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide. Orthophosphate in excess of 25 mg/L interferes by precipitating as silver phosphate. Iron in excess of 10 mg/L interferes by masking the endpoint.

4 COMMENTS

5 SAFETY

5.1 Safety glasses or goggles, coat and gloves

6 SAMPLE COLLECTION, PRESERVATION AND HOLDING TIMES

6.1 Water/wastewater

6.1.1 Grab samples must be collected in either a polyethylene or borosilica glass bottle and stored at 4°C.

6.1.2 Samples must be analyzed within 28 days of sample collection.

7 APPARATUS

7.1 Stir plate with assorted stir bars

7.2 10 ml micro buret

7.3 250 ml beaker or equivalent

7.4 pH paper 0-14 range

8 REAGENTS AND STANDARDS

8.1 Reagent water: Reagent water is defined as a water in which an interference is not observed at the method detection limit.

8.2 Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in a small amount of DI water. Add $AgNO_3$ until a

definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 L with DI water. Prepared indicator may also be purchased from vendors.

8.3 Standard silver nitrate titrant, (0.0141 N): Dissolve 2.395 g $AgNO_3$ in DI water and dilute to 1L. Standardize against NaCl. Vendor standardized $AgNO_3$ may be used if the standardized normality is close to 0.0141 N.

8.4 Standard sodium chloride, (0.0141 N): Dissolve 824.0 mg NaCl (dried at 140°C) and dilute to 1L 1 ml = 500 ug/ Cl^-. Standardization solution is unnecessary if using vendor standardized $AgNO_3$.

8.5 Special reagents for interference removal:

8.5.1 Aluminum hydroxide suspension. Dissolve 125 g aluminum potassium sulfate ($AlK(SO_4)_2 \cdot 12H_2O$) or aluminum ammonium sulfate ($AlNH_4(SO_4)_2 \cdot 12_2O$) in 1 L DI water. Warm to 60°C and add 55 ml concentrated ammonium hydroxide (NH_4OH) slowly with stirring. Let stand about 1 hour, transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with distilled water, until free from chloride.

8.5.2 Sodium hydroxide, NaOH, 1 N: Dissolve 40 g NaOH in DI water, cool, and dilute to 1L.

8.5.3 Sulfuric acid, H_2SO_4, 1N: Dilute 28 ml concentrated H_2SO_4 to 1L.

9 PROCEDURE

9.1 Measure 100 ml of sample into a 250 ml beaker.

9.2 If sample is highly colored, add 3 ml $Al(OH)_3$ suspension, mix, let settle, and filter.

9.3 If sulfide, sulfite, or thiosulfate is present, add 1 ml H_2O_2 and stir for 1 minute.

9.4 Check sample pH. Sample must be titrated in the 7.10 range. If sample is out of this range, adjust with H_2SO_4 or NaOH.

9.5 Add 1 ml K_2CrO_4 and titrate with standardized $AgNO_3$ to pinkish yellow endpoint. Endpoint is not sharp, so be consistent in endpoint recognition. Look for the red color to stay as the endpoint.

9.6 Analyze reagent water as outlined above. A blank of 0.2 to 0.5 ml is usual.

10 QA/QC REQUIREMENTS

10.1 For each batch of samples, the following is required:

10.1.1 Prep blank

10.1.2 EPA QC (Note: If EPA QC is unavailable, prep the standard sodium chloride solution as described in 8.4 and analyze 100 ml. 100 ml = 50 mg Cl^-). QC requirements for NaCl standard is ± 10% for true value.

11 CALCULATIONS

$$\text{mg } Cl^-/L = \frac{(A-B) \times N \times 35450}{\text{mL sample}}$$

Where: A = mL titration for sample
B = mL titration for blank
N = normality of $AgNO_3$

$$\text{mg NaCl/L} = (\text{mg } Cl^-/L) \times 1.65$$

12 REFERENCES

12.1 "Standards Methods for the Examination of Water and Wastewater", 17th edition, American Public Health Associates, American Water Works Associates, Water Works Associates, Water Pollution Central Federation, Washington, D.C., (1989).

13 CORRECTIVE ACTIONS

13.1 If problems occur contact the supervisor.

EXPIRES 9/30/93

COPY

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF TOTAL ORGANIC CARBON/PURGEABLE ORGANIC CARBON

1.0 SUMMARY, SCOPE, APPLICATION

1.1 Scope and Application

The autosampler is used for water samples, the furnace for soils, sludges, etc. The reaction occurring is as follows:

$$C_xH_yO_z + K_2S_2O_8 + H^+ \xrightarrow{UV} CO_2 + H_2O$$

Any carbon containing organic compound which can be oxidized, given the conditions in the reaction above, may be analyzed. The sample must be completely purged of CO_2 and there must be no competing reactions either adding to the production of CO_2, or preventing oxidation to CO_2 and H_2O.

The Method Detection Limit (MDL) is a function of the amount of carbon containing organic material present in the water used for the test. The linear working range is instrument dependent and is generally 8000 ppm, although it is desireable to keep the sample concentration at less than 400 ppm through dilution.

1.2 Summary

1.2.1 Water Samples

Samples are prepared for analysis by adding concentrated H_3PO_4 to adjust the pH to <2, after being placed into 10 x 150 mm disposable borosilicate test tubes, which are then loaded on the autosampler wheel. The samples are purged with Ultra High Purity (UHP) Oxygen (O_2) and a 200 ul aliquot is drawn, by the instrument, out of the test tube. The sample enters an in-line reaction vessel where it is mixed with Potassium Peroxydisulfate ($K_2S_2O_8$) at pH<2. The mixture is illuminated with UV light which initiates the oxidation process. As CO_2 is evolved, it is detected in the instrument by Infrared absorption, and quantitated.

1.2.2 Soil Samples

Soil samples are individually loaded into a Platinum boat, then treated with HCL to generate any CO_2 which may be created by inorganic carbon. The Platinum boat is then placed in a quartz tube, the tube is sealed, purged with UHP O_2, and the sample combusted. The resulting CO_2 is detected using Infrared absorption, and the amount of Organic Carbon is quantitated.

2.0 DISCUSSION/COMMENTS

Samples containing significant amounts of particles must be filtered prior to the of H_3PO_4. After the instrument power is turned on, the instrument will beep when it is ready for standardization. Assure that the baseline is at approximately 0.150 units before injecting standards. In order to be certain there will be no air bubbles in the syringe make sure the standards are at room temperature prior to injecting. The chamber door should not remain open for extended periods.

The concentration of TOC in the 10 ppm TOC standard has a tendency to increase with time. This standard should be prepared as often as possible, at least every two weeks.

Whenever standards are run, the first standard of the day should be injected at least two times before the instrument is calibrated. If the standard value determined by the instrument, using the previous calibration, differs greatly from the expected or true value, it should be re-injected. This should be done until the value determined by the instrument is close to the expected or true value of the standard, then the instrument may be recalibrated.

Frequently water will get into the teflon lines through which the gasses flow. When this occurs, the flow of CO_2 from the sample to the infrared detector is stopped. The autosampler should be stopped before an aliquot is taken from the next sample. An examination of the printout for TOC values will indicate which samples were affected and need to be rerun. The affected teflon lines containing the water should be disconnected, the water vacuumed out and the lines dried. If the problem persists after reconnecting the lines, check the tin and copper scrubbers for moisture build up in the glass wool or for lumps in the metal. The instrument should be closely monitored, and pump lines should be checked daily and replaced as necessary.

3.0 REAGENTS AND APPARATUS

3.1 Reagents

3.1.1 Concentrated H_3PO_4

3.1.2 2% Potassium Peroxydisulfate: 20 grams/liter acidified with 1 ml concentrated HNO_3.

3.1.3 Organic Free H_2O - Double carbon filtered.

3.1.4 Potassium Biphthalate ($K_2HC_8H_4O_4$)

3.1.5 For high salt containing samples an oxidizing solution is prepared as follows:

8.2 grams Mercuric Chloride ($HgCL_2$)
9.6 grams Mercuric Nitrate monohydrate
Dissolve in 400 mls TOC water

Then add:
20 grams $K_2S_2O_8$ (Potassium Peroxydisulfate)
5 mls concentrated HNO_3

Mix well and dilute to 1.0 liter with TOC water.

3.1.6 Copper, granular 20-30 mesh.

3.1.7 Lithium Hydroxide (LiOH)

3.1.8 Tin, granular 20 mesh

3.1.9 Copper Oxide (wire needle type)

3.1.10 Organic Carbon Stock Solution: In a 1000 ml volumetric flask, dissolve 4.2508 g of dried Potassium Biphthalate ($K_2HC_8H_4O_4$) in carbon-free (Nanopure) water. Bring to volume. The solution contains 2000 mg/l organic carbon.

3.1.11 Standard Solution of KHP:

3.1.11.1 2000 ppm C standard - 850mg/200 ml, acidify with 0.2 ml HNO_3(conc). Prepare fresh monthly.

3.1.11.2 400 ppm C standard - dilute a 40 ml aliquot of 2000 ppm C standard to 200 ml. Prepare fresh weekly.

3.1.11.3 10 ppm C standard - dilute a 1.0 ml aliquot of 2000 ppm C standard to 200 ml. Prepare fresh weekly.

3.1.12 Ultra High Purity Oxygen (UHP O_2 - 99.99% pure)

3.2 Apparatus

3.2.1 Dohrmann DC-80 Carbon Analyzer equipped with autosampler, reaction vessel and IR detector.

3.2.2 Pump hoses

3.2.3 Teflon Tubing - 1/8" OD x 1/16" ID, 1/16" OD x 1/32" ID.

3.2.4 Glass Spargers

3.2.5 18 x 150 mm borosilicate test tubes.

3.2.6 1/4" teflon coated septa with one hole

3.2.7 3/8" silicone septa (solid)

3.2.8 Platinum boat

3.2.9 Quartz wool

3.2.10 #000 1-hole rubber stopper

3.2.11 Amber reagent bottles - 250 ml, 1000 ml

4.0 PROCEDURE

Set gas (O_2) pressure to 35 psi and leave on all the time.

4.1 Calibration - TOC Water Samples

4.1.1 Push white power button on analyzer unit to the left.

4.1.2 Turn autosampler counter-clockwise only to start the flow of $K_2S_2O_8$ solution to the reaction vessel.

4.1.3 Wait for the instrument to beep prior to running the standards.

4.1.4 Turn the selection dial to the TOC or POC mode, depending upon the analysis to be performed. Check to see that the teflon lines are plumbed according to the diagram on page 5-5 of the Dohrman TOC manual.

4.1.5 Position the sample volume knob at the 40 ul setting for injection of the 2000 ppm standard.

4.1.6 Inject 40 ul of the 2000 ppm standard into the port by pushing the start button. The port is positioned below the three white buttons labeled from the top power pump lamp. These buttons need not be pushed, as they are on when the main power button is pushed.

4.1.7 Observe the ppm value on the digital readout. It should be close to 2000 $\pm$ 250. If this is the case, lift the cover on the calibrate button and push it quickly. Do not depress the button longer than one second or it will erase previous calibrations.

4.1.8 Repeat 4.1.6-4.1.7 until the standard value meets acceptance criteria.

4.1.9 Position the sample volume knob at the 200 ul setting and inject 200 ul of the 400 ppm C Standard. Push the start button and observe the readout. If the value is 400 ppm ± 50, press the calibrate button.

4.1.10 Repeat step 4.1.9. If the value is within acceptance criteria, continue to 4.1.11.

4.1.11 Position the sample volume knob at the 1.0 ml setting and inject 1.0 ml of the 10 ppm C standard. Press the start button and observe the digital readout. If the value is 10 ppm ± 1.25 ppm press the calibrate button.

4.1.12 At this point the instrument is considered calibrated and the sample volume knob should be positioned at the proper setting for the amount of sample to be analyzed (generally 200 ul).

4.1.13 Optional: You can either shoot 200 ul of the QC through the port, or load it on the autosampler as a sample. If you inject it directly, assure the amount injected is the same as the amount selected by the sample volume knob.

4.2 Sample preparation and Set up of the Autosampler

All samples are placed in 10 x 150 mm test tubes.

4.2.1 Begin at the grey plastic circle, and load the labeled test tubes in the following sequence:

1.	BLANK (BLK)
2.	BLANK
3.	BLANK
4.	400 PPM C
5.	400 PPM C
6.	BLANK
7.	BLANK
8-17.	SAMPLES
18.	DUPLICATE
19.	SPIKE OF DUPLICATE SAMPLE
20.	400 PPM C
21.	BLANK
22.	BLANK
23-32.	SAMPLES
33.	ETC.

4.2.2 The QC sample can be placed on the wheel after a set of blanks if it has not been previously run.

4.2.3 Once the samples are loaded on the wheel, they are acidified with 0.2 ml of concentrated H_3PO_4. This is easily accomplished by using an autopipetor and rotating the wheel counter-clockwise while dispensing the reagent in to the samples.

4.2.4 Position the autosampler wheel so that the first three blanks face and sample and purge tubes. Move the tubes until they are positioned directly over the test tubes, centered.

4.2.5 Check the sample volume knob for the appropriate setting (generally 200 ul) and assure that the baseline is approximately 0.0150 units.

4.2.6 Push the red auto button to begin the sampling and purging process. Check to verify that bubbles are passing through the solution in test tubes 2 and 3.

4.2.7 Periodically check the water level in the U-tube for bubbling. If bubbling occurs, wait until the purge and sample tube comes out of the sample it is currently in and begins a decent into the next sample. Before it comes in contact with the next set, push the red auto button, and remove water from the teflon lines going to and from the U-tube water float. Also check the tin and copper scrubbers for lumps or moisture. If moist, repack with new glass wool and copper or tin as necessary.

4.2.8 When the instrument prints the value of the 400 ppm C standard, lift the cover to calibrate and push the button quickly. If, for whatever reason, the instrument has cleared the readout, calibrate both standards after the next 400 ppm C is run.

4.2.9 Periodically check the value printed out and write the corresponding accession number to allow for proper matching of data to samples.

4.2.10 A log book matching the chart paper number to the sample ID number is maintained for each sample run. **Note:** Every time the calibration button is pushed during a run, the instrument resets the chart number to 1.

4.2.11 When the last sample is run, the red auto button can be pushed when the autosampler table moves to an empty space and makes a decent, or the magnet can be placed such that it trips the sensor and shuts off the autosampler. Place the magnet in the same row as the test tubes being analyzed approximately three blank spaces from the last sample to be analyzed.

4.2.12 Upon completion of analysis shut off the main power switch. The calibration standards may or may not be in the next day depending upon the condition of the instrument's battery.

4.3 TOC Procedure for soils, sludges, etc.

4.3.1 Start the instrument as in section 4.1. Run the teflon lines according to the diagram.

4.3.2 Push the button labeled "furnace" located next to the sparger, and let the furnace warm up for approximately 1 1/2 hours. During furnace warm up the standards can be run.

4.3.3 When the furnace has warmed up, push the magnet toward the furnace until the boat is in the oven area. Let it bake for a while. Observe the baseline reading as it bakes, it should calm down after a short time.

4.3.4 Pull the magnet back to the starting position and allow to cool.

4.3.5 Using tweezers, remove the platinum boat and load 10-50 mg of sample into the boat. Add drops of 10% HCl until the sample stops bubbling.

4.3.6 Close the boat in the port latch and insert it halfway into the oven for 1-2 minutes to rid the sample of moisture.

4.3.7 Insert fully into the oven and press the start button. The ready light will come on when stabilized.

4.3.8 The furnace scrubber should be changed as necessary, or when several high concentration samples are encountered in one day. The scrubber is in the furnace and contains quartz wool plugs with CuO wire pieces in the middle. The flow of oxygen should keep it in the proper oxidation state.

4.4 POC Waters Procedure

4.4.1 Start up procedure is the same as section 4.1

4.4.2 After calibration, turn method knob to POC and sample volume knob to 1.0 ml.

4.4.3 Plumb the teflon lines according to the diagram on page 5-5 or the Dohrman TOC manual.

4.4.4 Put about 3 mls of TOC water in the left sparger, humidifier.

4.4.5 Inject 1 ml of the sample to be analyzed into the right sparger and push the green start button.

4.4.6 After the ready light illuminates, remove the sample withy a stopcock syringe and repeat the sample injection.

4.4.7 The value on the digital readout is in ppm assuming no dilutions or volume difference compared to the sample volume knob setting of 1 ml.

5.0 QA/QC

5.1 Initial and Continuing Calibration

The instrument must be calibrated at the beginning of each day of use. The initial calibration consists of running a minimum of three concentrations of organic carbon standard.

5.1.1 Initial calibration standards are made up at the following concentrations:

2000 ppm	high (linear range)
400 ppm	mid-point
10 ppm	low (detection limit)

This defines the linear range of the instrument and also demonstrates our ability to see organic carbon concentrations at the detection limit.

5.1.2 Throughout the course of the days run, the mid-point organic carbon standard is periodically run, to ensure that the instrument calibration has not significantly changed.

5.2 Blank

A blank is run after the initial calibration of the day. The blank consists of organic carbon free water.

5.2.1 The result for the TOC analysis of the blank must be below the Method Detection Limit (MDL).

5.3 Duplicate and Matrix Spike

A sample is analyzed in duplicate for every ten samples analyzed (or once per run if less than ten samples). This same sample is also spiked and run again (matrix spike).

5.4 Blank Spike

A blank spike is analyzed with each run.

5.5 Continuing Calibration Verification

As mentioned ins section 5.1.2, a mid-point standard is analyzed throughout the course of the days run. It is analyzed after each successive ten samples.

5.5.1 If there are less than ten samples to be analyzed, it is analyzed after the last sample.

5.6 Laboratory Control Sample (LCS)

A Quality Control sample or a standard prepared in-house, from a source other than the initial and continuing standards, is analyzed once each day.

5.6.1 The LCS is made up such that it mimics the majority of the samples analyzed in the run. It is made up to contain either a small or large amount of organic carbon.

6.0 CALCULATIONS

6.1 Waters: The printout is in ppm (mg/l), take any dilutions into account when reporting concentrations. The reported units for waters is mg/L.

6.2 Soils: The printout is in ppm assuming the sample volume taken on the 40 ul, 200 ul, 1.0 ml sample volume knob. For example:

$$\frac{\text{Readout x ul knob setting}}{\text{mgrams of sample}}$$

The reported units for Total Organic Carbon in soils is mg/kg.

6.3 For more information refer to procedures section of Dohrmann TOC Manual (page 9).

7.0 SAFETY/WASTE

7.1 Safety

Wear safety glasses, a lab coat and gloves when using this instrument.

Samples with large amounts of volatiles and odor should be purged with oxygen under a fume hood.

7.2 Waste

Waste produced is currently going down the drain.

7.3 For more information regarding safety and waste refer to the procedures section of the Dohrmann TOC Manual (page 9).

8.0 REFERENCES

8.1 Dohrmann TOC Manual

8.2 EPA Method 9060

8.3 Standard Methods, 16th Edition, 1985

EXPIRES: 9/30/93

COPY

TOTAL ORGANIC HALIDE (TOX) DETERMINATION STANDARD OPERATING PROCEDURE

1.0 SCOPE AND APPLICATION

This method determines Total Organic Halides (TOX) as Cl^- in drinking and ground waters, soils, oils, and sludges. It requires that all samples run be particulate free.

It detects all organic halides that are adsorbed by granular activated carbon under the conditions of the method except Fluorine-containing species.

It is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

The method detection limit has been set to 0.008 mg/l assuming a 100 ml H_2O sample. All other MDL are to be determined from this base value. The linear working range is 20-25 micrograms maximum, all values above this range must be rejected and these samples must be re-analyzed with reduced initial volumes.

2.0 DISCUSSION/COMMENTS

2.1 Summary

This method determines the Total Organic Halides from water, soil and oil matrix. Each matrix is treated with a different extraction method for analysis of halide. Water samples containing the halide are passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides. The activated carbon is then analyzed to convert the adsorbed organohalides to halides. The activated carbon is then introduced into a combustion chamber and the halides carried into a titration cell that can measure the titratable species by a microcoulometric detector.

2.2 Interferences

Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

2.2.1 Glassware

Glassware must be scrupulously cleaned. Glassware is cleaned with a dilute chromate cleaning solution, following with a detergent washing in hot water and rinsed with distilled water until all visible detergent and carbon is eliminated. It is drained dry and completely dry in a heating oven to 180°F and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

The use of high purity reagents and gases helps to eliminate or minimize interference problems.

2.2.2 Activated Carbon

Purity of activated carbon must be verified before use. It is suggested that carbon samples that register less than 1000 ng/40 mg should be used. the stock supply of activated carbon should be stored in a glass container with a Teflon seal. Exposure to the air must be minimized. It shall be protected by storing in a vacuum sealed dessicator container and keeping from all sources of halogenated organic vapors. Prepared carbon and packed columns shall be stored in glass containers with teflon seals.

3.0 REAGENTS AND APPARATUS

3.1 Adsorption Module:

a. Granular Activated Carbon (100-200 Mesh)
b. N_2 (UHP) 99.99% Purity set pressure at 30 psi.
c. Glass Column Tubes
d. Cerafelt and Cerafelt punch
e. GAC Column holders upper and lower with swagelok fitting and "O" rings in place at proper location.
f. Dessicator for storage of Granular Activated Carbon.
g. 5000 ppm KNO_3 solution = 8.2 g/l.
h. 0.1 M $NaSO_3$
i. Conc. HNO_3

3.2 Analyzer Module:

a. CO_2 Coleman grade 99.99% pure at 25 psi.
b. O_2 UHP 99.99% pure at 25 psi.
c. 70% Glacial Acetic Acid Reagent Grade

d. Silver Acetate flakes
e. Quartz wool
f. Quartz exit tubes
g. Quartz pyrolysis tube
h. Quartz sample boat
i. O-Rings for att entry and exit connections
j. Two spin clips for ground glass ball joints
k. One #000 one-hole stopper per machine
l. Teflon tubing 1/8" O.D. x 1/16" I.D., and one 1/16" x 1/132".
m. 500 ppm 2,4,6-Trichlorophenol (92.8 mg/100 ml MeOH)
n. Reagent grade Methanol
o. 100 ml graduated cylinder
p. 50 l syringe
q. 5 ml & 10 ml oxford pipets
r. Oxford pipet and 100-1000 1 eppendorf pipet

4.0 PROCEDURE

4.1 Initial Set-up - Adsorption Module and TOX Module

4.1.1 Cleaning

a. The glass columns shall be packed with granular activated carbon before extraction. Care shall be taken when packing the columns not to pack the columns tightly when inserting small sections of cerafelt on the ends of the columns to hold the carbon within the column.

b. Distilled water from the in-house supply shall be cleaned with a two stage carbon filtration step before use in any of the methods.

c. Any particulate matter shall be removed from water samples or extraction solvent by filtration or other appropriate method to ensure flow through the GAC columns.

d. Chlorinated solvents shall not be allowed to enter the work area. Any contaminated supplies or apparatus shall be disposed of.

e. Carbon tube push rods shall be cleaned with a kim-wipe after the carbon is pushed out of the tube for analysis.

f. The titration cell must be rinsed well and kept clean. The cell shall be cleaned daily, when in use with acetone, and after analysis of samples with high halide concentration. The cell electrolyte of 70% acetic acid must be kept at the appropriate level. The level is marked on the titration cell. Periodically monitor the O_2 and CO_2 bubbles going through the electrolyte for proper analysis.

g. Each cylinder of the extraction module must be thoroughly cleaned with deionized water and rinsed with methanol and allowed to dry after each extraction.

4.1.2 TOX module set-up

a. Set furnace temperature at 800°C ± 20°C.

b. Set gas flow to 25 psi CO_2 and 25 psi O_2.

c. Set N_2 pressure to 30 psi.

d. Set N_2 channel pressure to 20 psi.

e. Clean out exit tube with methanol.

f. Clean titration cell with cotton swab and acetone and rinse well with 70% acetic acid, fill with acetic acid to slightly over the fill line.

g. Remove teflon plug from reference cell, allow acetic acid to flow out removing all air bubbles from this area. Replace plug and rinse cell with acetic acid. Remove any air bubbles from other side arms of the titration cell.

h. Fill the titration cell to the full line and switch from gen mode to detector mode on the instrument.

i. Allow baseline to stabilize to the range of 0.00 to 1.00 on the digital readout.

j. Burn the quartz boat without any sample for one complete cycle by switching from detector mode to integrate mode, press the integrator button to zero instrument and then begin burn cycle.

k. When the cycle is complete, switch to detector mode and make sure the digital readout is 0.00 to 1.00.

l. When stabilized, run a carbon blank. This blank ususally runs at between 0.50 to 0.85 g.

m. Record value from blank. If unusually high, run again. If the blank is high a second time, then troubleshoot the instrument.

n. Inject 10 microliters (μl) of 500 ppm 2,4,6 trichlorophenol solution onto a pre-ashed carbon blank on the quartz boat. Run complete burn cycle and digital readout should be 5.00 g $\pm$ 10%.

o. Repeat calibration check on both machines if necessary as above. Record these cal check results.

4.2 Water Sample Preparation and Analysis

4.2.1 Sample Preparation

a. Filter water if necessary.

b. Fill a sufficient amount of glass columns with to analyze all samples and necessary QC samples. The granular activated carbon is held in place with cerafelt plugs on each end. Caution: The carbon in the columns must not be packed too tightly. Fill at least 10 columns.

c. Mount columns onto column holding apparatus and screw together tightly, mount the column holding apparatus onto adsorption module cylinder fitting.

d. Measure out 100 ml of sample H_2O and pour into cylinder on adsorption module.

e. Add 0.2 ml of 0.1 M Na_2SO_3 to remove residual chlorine.

f. Acidify to pH less than 2 with 2 drops concentrated HNO_3.

g. Close top of cylinder with spin fitting.

h. Press the start button to pressurize the cylinder with the samples and begin adsorption process.

i. When finished, disconnect the column from the cylinder and mount onto Nitrate wash cylinder reservoir. Set auto shut off at 2 ml on graduated 10 ml cylinder.

j. Remove upper and lower carbon columns and wrap with foil and label accordingly. Store in a seal container until analyzed.

k. Duplicates and spikes are prepared for each ten samples with the addition of 0.02 ml of 2,2,6-trichlorophenol solvent injected directly into the measured sample volume.

4.2.2 Analysis

Sample Analysis: detection limit = 0.008 mg/l. This is accomplished as follows:

a. Open the chamber and place the carbon from the upper carbon column into the quartz boat for analysis by pushing the carbon out with the push rod.

b. Close the chamber and check for a stable baseline below 1.00 on the digital readout.

c. Set the switch from detector mode to integrate mode and press start button.

d. The entire cycle will take 10 minutes.

e. Record this digital readout at the end of this period.

f. Repeat the above process for the lower carbon column, removing carbon ash from the previous sample in the quartz boat with a vacuum line.

g. Rinse titration cell occasionally with 70% acetic acid and anytime a sample has a readout of greater than 25 grams.

4.3 Oil Extraction and Analysis Procedure

a. Weigh out one gram of each sample on an analytical balance (into a glass vial with a teflon lined cap. Record the weight.

b. Add 10 ml of methanol to the sample, shake manually for 30 seconds, then sonicate for 15 minutes.

c. Duplicates and spikes are prepared in at a frequency of one duplicate and one spike per ten samples. In addition to methanol, 0.05 mls of 10,000 ppm 2,4,6-trichlorophenol standard is added to the sample as a spike.

d. Centrifuge for 10 minutes if the solution is spiked.

e. Prepare glass columns with granular activated carbon as previously described in section 4.2.

f. Inject a glass column packed with carbon (0.2 ml of the methanol extract with a syringe).

g. Place the carbon containing the sample into the quartz boat by pushing out the carbon with a push rod after KNO_3 rinse.

h. Follow the sample analysis routine as described in sample analysis for H_2O.

i. The method detection limit for oil samples is 40 mg/kg.

4.4 Soil Extraction and Analysis Procedure

a. Weigh out 5 grams of sample on an analytical balance (into a glass vial with a teflon lined cap). Record the weight.

b. Add 5 mls of ethyl acetate and 2 mls of H_2O.

c. Shake for 30 seconds, then place in sonicator and sonicate for 15 minutes.

d. If extract appears turbid, centrifuge for 10 minutes.

e. Duplicates and spikes should be extracted at this time. Spike with 0.5 ml of 10,000 2,4,6-trichlorophenol standard.

f. Follow steps "4.3.e" through "4.3.h" above.

g. The method detection limit for soils is 5 mg/kg.

5.0 QUALITY ASSURANCE/QUALITY CONTROL

5.1 Quality Control Monitoring shall be as follows:

10% per batch matrix (one QC for every ten samples)

Spike water: 20 µl of 500 ppm 2,4,6-trichlorophenol standard.

Spike soils: 50 µl of 10,000 ppm 2,4,6-trichlorophenol standard.

Spike oils: 0.05 ml of 10,000 ppm 2,4,6-trichlorophenol standard.

5.2 Calibration Procedure

Solutions shall be checked for initial makeup date. Solutions must be less than six months old.

Absorption module system blanks are run to check for adequate cleaning of the system after last run.

6.0 CALCULATIONS

6.1 Calculations for waters

Digital readout in micrograms minus two times the carbon blank readout in micrograms. Divide this number by the mls sample. This gives a final value in micrograms per ml or ppm for the sample.

6.2 Calculation for soils and oils

$$\frac{\text{(Sample Reading in micrograms - Blank)}}{\text{(Amount of sample injected (0.2 ml)}} \times \frac{\text{Sample volume (mls)}}{\text{Sample weight (gms)}}$$

7.0 SAFETY, HAZARDS, WASTE DISPOSAL

7.1 Safety and Hazards

Material Data Safety Sheets (MSDS's) for every chemical used are available for reference. The analyst must be aware of all hazardous warnings pertaining to each chemical used.

Safety glasses shall be worn at all times. A respirator is available for use when handling materials whose MSDS's contain respiratory hazardous warnings.

Vinyl or latex gloves shall be worn when handling samples. Samples contain unknown contaminants which may be extremely toxic. All sampling scoops and devices must be thoroughly cleaned after use. All weighing shall be done in a well ventilated area and/or a respirator shall be worn.

7.2 Sample Disposal

Sample disposal shall be per ATI SOP 002.

8.0 REFERENCES

8.1 Total Organic Halide Analysis Handbook, Dohrmann DX-20

8.2 Standard Methods Sixteenth Edition, pages 516-525

8.3 EPA Method 9020 Total Organic Halides