SAMPLING AND ANALYSIS PROCEDURES FOR SCREENING OF INDUSTRIAL EFFLUENTS FOR PRIORITY POLLUTANTS

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FOREWORD

These guidelines for sampling and analysis of industrial wastes have been prepared by the staff of the Environmental Monitoring and Support Laboratory, at the request of the Effluent Guidelines Division, Office of Water and Hazardous Wastes, and with the cooperation of the Environmental Research Laboratory, Athens, Georgia. The procedures represent the current state-of-the-art but improvements are anticipated as more experience with a wide variety of industrial wastes is obtained. Users of these methods are encouraged to identify problems encountered and assist in updating the test procedures by contacting the Environmental Monitoring and Support Laboratory, EPA, Cincinnati, Ohio 45268.

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Organics by Purge and Trap - Gas Chromatography

1. Scope

This method is designed to determine those "unambiguous priority pollutants," associated with the Consent Decree, that are amenable to the purge and trap method[1]. These compounds are listed in Table I of this section. It is a gas chromatographic-mass spectrometric (GC-MS) method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study..

Certain compounds, acrolein and acrylonitrile, are not efficiently recovered by this method and should be determined by direct aqueous injection GC-MS. Direct aqueous injection GC-MS is recommended for all compounds that exceed 1000 µg/l.

The purge and trap and the liquid-liquid extraction methods are complementary to one another. There is an area of overlap between the two and some compounds may be recovered by either method. However, the efficiency of recovery depends on the vapor pressure and water solubility of the compounds involved. Generally, the area of overlap may be identified by compounds boiling between 130°C and 150°C with a water solubility of approximately two percent. When compounds are efficiently recovered by both methods, the chromatography determined the method of choice. The gas chromatographic conditions selected

for the purge and trap method are, generally, not suitable for the determination of compounds eluting later than chlorobenzene.

2. Special Apparatus and Materials

Sample extraction apparatus (minimum requirements):

5-ml glass syringes with Luer-Lok - 3 each

2-way syringe valves (Teflon or Kel-F) - 3 each

8-inch, 20 gauge syringe needle - 2 each

5-ml glass, gas-tight syringe, pressure-lok[a] or equivalent - 1 each

Tekmar Liquid Sample Concentrator, model LSC-1[b] or equivalent. Includes a sorbent trap consisting of 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long stainless steel tube packed with 4 inches of Tenax-GC (60/80 mesh and 2 inches of Davison Type-15 silica gel (35/60 mesh).

3. Gas Chromatographic Column Materials

Stainless steel tubing 1/8 in. O.D. (0.09 to 0.105 in. I.D.) by 8 ft. long. Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500[c]. Chromosorb-W (60-80 mesh) coated with 3% Carbowax 1500.

(a) Available from Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA 70815.

(b) Available from Tekmar Company, P.O. Box 37202, Cincinnati, OH 45222.

(c) Available from Supelco, Supelco Park, Bellefonte, PA 16823. Stock No. 1-1826.

4. Procedure

Preparation of Standards - Prepare standard stock solutions (approximately 2 µg/µl) by adding, from a 100 µl syringe, 1 to 2 drops of the 99+% pure reference standard to methanol (9.8 ml) contained in a tared 10 ml volumetric flask (weighed to nearest 0.1 mg). Add the compound so that the two drops fall into the alcohol and do not contact the neck of the flask. Use the weight gain to calculate the concentration of the standard. Prepare gaseous standards, i.e., vinyl chloride, in a similar manner using a 5 ml valved gas-tight syringe with a 2 in. needle. Fill the syringe (5.0 ml) with the gaseous compound. Weigh the 10 ml volumetric flask containing 9.8 ml of methyl alcohol to 0.1 mg. Lower the syringe needle to about 5 mm above the methyl alcohol meniscus. Slowly inject the standard into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask, dilute to volume, mix, tightly stopper, and store in a freezer. Such standards are generally stable for at least one week when maintained at less than 0°C. Stock standards of compounds which boil above room temperature are generally stable for at least four weeks when stored at 4°C.

[Safety Caution: Because of the toxicity of most organohalides, primary dilutions must be prepared in a hood. Further, it is advisable to use an approved respirator when handling high concentration of such materials.]

From the primary dilution prepare a secondary dilution mixture in methyl alcohol so that 20.0 µl of the standard, diluted to 100.0 ml in organic free water, will give a standard which produces a response close to that of the unknown. Also prepare a complex test mixture at a concentration of 100 ng/µl containing each of the compounds to be determined. Prepare a 20 µg/l quality check sample from the 100 ng/µl standard by dosing 20.0 µl into 100.0 ml of organic free water.

Internal Standard Dosing Solution - From stock standard solutions prepared as above, add a volume to give 1000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic free (blank water) contained in a 50 ml volumetric flask, mix and dilute to volume. Prepare a fresh internal standard on a weekly basis. Dose the internal standard mixture into every sample and reference standard analyzed.

Preliminary Treatment of Sample - Remove samples from cold storage (approximately an hour prior to analysis) and bring to room temperature by placing in a warm water bath at 20-25°C.

Purging and Trapping Procedure - Adjust the helium purge gas flow to 40 ml/min. Set the Tekmar 2-way valve to the purge position and open the purging device inlet. Remove the plungers from two 5-ml syringes and attach a closed 2-way syringe valve to each. Open the sample bottle and carefully

pour the sample into one of the syringes until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while carefully adjusting the volume to 5.0 ml. Then close the valve. Fill the second syringe in an identical manner from the same sample bottle. Use the second syringe for a duplicate analysis as needed. Open the syringe valve and introduce 5.0 µl of the internal standard mixture through the valve bore, then close the valve. Attach the 8-inch needle to the syringe valve and inject the sample into the purging device. Seal the purging device and purge the sample for 12 minutes. The purged organics are sorbed on the Tenax-silica gel trap at room temperature (20-25°C).

While the sample is being purged, cool the gas chromatographic column oven to near room temperature (20-30°C). To do this, turn heater off and open column oven door.

At the completion of the 12-minute purge time, inject the sample into the gas chromatograph by turning the valve to the desorb position. Hold in this position for four minutes while rapidly heating the trap oven to 180°C, then return the valve to the purge position, close the GC column oven door, and rapidly heat the GC oven to 60°C. Consider this time zero and begin to collect retention data. Hold at 60°C for four minutes, then program at 8°/minute to 170°C and hold until all compounds have eluted. Begin collecting GC-MS

GC-MS data as soon as the GC-MS vacuum system has stabilized ($<10^{-5}$ torr).

While the sample is being chromatographed, flush the purging device with two 5-ml volumes of organic free water. Then bake out the trap (vent to atmosphere) to minimize the amount of water desorbed into the GC-MS system during the succeeding injection step. [Note: If this bake out step is omitted, the amount of water entering the GC-MS system will progressively increase causing deterioration of and potential shut down of the system.]

GC-MS Determination - Suggested analytical conditions for determination of the priority pollutants amenable to purge and trap, using the Tekmar LSC-1 and the computerized Finnigan 1015 GC-MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for his equipment.

Purge Parameters

Purge gas - Helium, high purity grade

Purge time - 12 minutes

Purge flow - 40 ml/min.

Trap dimensions - 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long

Trap sorbent - Tenax-GC, 60/80 mesh (4 in.) plus Type 15 silica gel, 35/60 mesh (2 in.)

Desorption flow - 20 ml/min.

Desorption time - 4 min.

Desorption temperature - 180°C

Gas Chromatographic Parameters

Column - Stainless steel, 8 ft. long x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500, preceded by a 1 ft. x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Chromosorb-W coated with 3% Carbowax 1500.

Carrier gas - Helium at 33 ml/min.

Oven temperature - Room temperature during trap desorption, then rapidly heat to 60°C, hold at 60°C for four minutes, then program to 170°C at 8°/minute. Hold at 170°C for 12 minutes or until all compounds have eluted.

Mass Spectrometer Parameters

Data system - System Industries System 150

Separator - glass jet

Electron energy - 70 ev

Emission current - 500 ua

Ion energy - 6 volts

Lens voltage - (-)100 volts

Extractor voltage - 8 volts

Mass range - 20-27, 33-260 amu

Integration time/amu - 17 milliseconds

Samples/amu - 1

Gas Chromatographic Column Conditioning Procedure - Attach the Carbowax 1500-Chromosorb end of the column to the inlet system of the gas chromatograph. Do not, at this time,

attach the column exit to the detector. Adjust the helium flow rate through the column to 33 ml/minute. Allow the column to flush with helium for ten minutes at room temperature, then program the oven from room temperature to 190°C at 4°C/minute. Maintain the oven at 190°C overnight (16 hours).

Handle the column with extreme care once it has been conditioned because the Carbopack is fragile and easily fractured. Once fractured, active sites are exposed resulting in poor peak geometry (loss of theoretical plates). Reconditioning, generally, revitalizes the analytical column. Once properly conditioned, the precolumn may be removed. The retention data listed in Table I was collected with the precolumn in the system.

Quality Assurance - The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with low-organic water (blank water) that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

After each sample analysis, thoroughly, flush the purging device with blank water and bake out the system. Subsequently, analyze a sample blank (one that has been transported

to and from the sampling site). If positive interferences are noted, analyze a fresh laboratory sample of blank water. If positive interference still occurs, repeat the laboratory blank analysis. If interference persists, dismantle the system, thoroughly, clean all parts that the sample, purge gas and carrier gas come into contact with and replace or repack the sorbent trap and change purge and carrier gas.

Precision - Determine the precision of the method by dosing blank water with the compounds selected as internal standards - bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane - and running replicate analyses. These compounds represent early, middle, and late eluters over the range of the Consent Decree compounds and are not, themselves, included on the list. Construct Quality Control charts from the data obtained according to directions in Reference 9.

The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the internal standards and analyzed in a manner identical to the internal standards in blank water. When the results of the dosed sample analyses show a deviation greater than two sigma, repeat the dosed sample analyses. If the deviation is again greater than two sigma, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.*

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*See Reporting of Data Section, p. 11.

Calibration of the gas chromatography-mass spectrometry (GC-MS) system - Evaluate the system performance each day that it is to be used for the analysis of samples or blanks. Inject a sample of 20 nanograms of decalfuorotriphenylphosphine[d] and plot the mass spectrum. The criteria in Reference 2 must be met and all plots from the performance evaluation, documented and retained as proof of valid performance.

Analyze the 20 µg/l standard to demonstrate instrument performance for these compounds.

Qualitative and Quantitative Determination - The characteristic masses or mass ranges listed in Table II of this section are used for qualitative and quantitative determination of volatile priority pollutants. They are used to obtain an extracted ion current profile (EICP)[e] for each compound. For very low concentrations, the same masses may be used for selected ion monitoring (SIM)[f]. The primary ions to be used to quantify each compound are also listed. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

(d) Available from PCR, Inc., Gainesville, FL.

(e) EICP is the reduction of mass spectrometric data acquired by continuous, repetitive measurement of spectra by plotting the change in relative abundance of one or several ions as a function of time.

(f) SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

Quantify samples by comparing the area of a single mass (see Table II) of the unknown in a sample to that of a standard. When positive responses are observed, prepare and analyze a reference standard so that the standard response closely approximates the sample response. Calculate the concentration in the sample as follows:

$$\frac{\text{(Area for unknown)}}{\text{(Area for standard)}} \; \text{Concentration of standard } (\mu g/l) = \mu g/l \text{ of unknown}$$

5. Reporting of Data

Report all results to two significant figures or to the nearest 10 µg/l. Report internal standard data to two significant figures.

As the analyses are completed, transfer GC-MS data to magnetic tape as described under reporting of data in method for "Organics by Liquid-Liquid Extraction - Gas Chromatography."

Report all quality control (QC) data along with the analytical results for the samples. In addition, forward all QC data to EMSL, Cincinnati.

6. Direct Aqueous Injection Gas Chromatography

As noted in the Scope, Acrolein and acrylonitrile should be analyzed by direct aqueous injection gas chromatography-mass spectrometry. See references (3), (4), and (5) for these methods. The detection level for these methods is 0.1 mg/l and above.

Table I

Elution Order of Volatile Priority Pollutants[a]

Compound	RRT[b]	Purging Efficiency (percent)	Purging Efficiency Modified Method (percent)
chloromethane	0.152	91	
dichlorodifluoromethane	0.172	0	100[c]
bromomethane	0.181	85	
vinyl chloride	0.186	101	
chloroethane	0.204	90	
methylene chloride	0.292	76	
trichlorofluoromethane	0.372	96	
1,1-dichloroethylene	0.380	97	
bromochloromethane(IS)	0.457	88	
1,1-dichloroethane	0.469	89	
trans-1,2-dichloroethylene	0.493	92	
chloroform	0.557	95	
1,2-dichloroethane	0.600	98	
1,1,1-trichloroethane	0.672	94	
carbon tetrachloride	0.684	87	
bromodichloromethane	0.750	92	
bis-chloromethyl ether[d]	0.760	0	
1,2-dichloropropane	0.818	92	
trans-1,3-dichloropropene	0.847	90	
trichloroethylene	0.867	89	
dibromochloromethane	0.931	87	
cis-1,3-dichloropropene	0.913	85	
1,1,2-trichloroethane	0.913	88	
benzene	0.937	no data	
2-chloroethylvinyl ether	0.992	no data	
2-bromo-1-chloropropane(IS)	1.000	92	
bromoform	1.115	71	
1,1,2,2-tetrachloroethene	1.262	88	
1,1,2,2-tetrachloroethane	1.281	58	

Table I (cont'd)

Compound	RRT[b]	Purging Efficiency (percent)	Purging Efficiency Modified Method (percent)
1,4-dichlorobutane(IS)	1.312	74	
toluene	1.341	no data	
chlorobenzene	1.489	89	
ethylbenzene	1.814	no data	
acrolein	unknown	12	74[e]
acrylonitrile	unknown	no data	

(a) These data were obtained under the following conditions: GC column - stainless steel, 8 ft. long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; preceeded by a 1 ft. long x 0.1 in. I.D. column packed with Chromosorb W coated with 3% Carbowax 1500; carrier flow - 40 ml/min.; oven temperature - initial 60°C held for 3 min., programmed 8°C/min. to 160°C and held until all compounds eluted. The purge and trap system used was constructed by EPA. Under optimized conditions, commercial systems will provide equivalent results.

(b) Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 829 seconds.

(c) No measurable recovery using standard purging and trapping conditions. Under modified conditions, i.e., purging at 10 ml/min. for 12 min., recovery is 100%.

(d) Bis-chloromethyl ether has a very short half-life in water and is not likely to be detected in water.

(e) Recovery 12% under standard purging conditions, i.e., room temperature, 30% at 55°C, and 74% at 95°C.

Table II

Characteristic Ions of Volatile Organics

Compound	EI Ions (Relative intensity)	Ion used to quantify
chloromethane	50(100); 52(33)	50
dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
bromomethane	94(100); 96(94)	94
vinyl chloride	62(100); 64(33)	62
chloroethane	64(100); 66(33)	64
methylene chloride	49(100);51(33); 84(86); 86(55)	84
trichlorofluoromethane	101(100); 103(66)	101
1,1-dichloroethylene	61(100); 96(80); 98(53)	96
bromochloromethane(IS)	49(100); 130(88); 128(70); 51(33)	128
1,1-dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
trans-1,2-dichloroethylene	61(100); 96(90); 98(57)	96
chloroform	83(100); 85(66)	83
1,2-dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1-trichloroethane	98(100); 99(66); 117(17); 119(16)	97
carbon tetrachloride	117(100); 119(96); 121(30)	117
bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
bis-chloromethyl ether	79(100); 81(33)	79
1,2-dichloropropane	63(100); 65(33); 112(4); 114(3)	112
trans-1,3-dichloropropene	75(100): 77(33)	75
trichloroethylene	95(100); 97(66); 130(90); 132(85)	130
dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-dichloropropene	75(100); 77(33)	75

Table (cont'd)

Compound	EI Ions (Relative intensity)	Ion used to quantify
1,1,2-trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
benzene	78(100)	78
2-chloroethylvinyl ether	63(95); 65(32); 106(18)	106
2-bromo-1-chloropropane(IS)	77(100); 79(33);156(5)	77
bromoform	171(50);173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,1,2,2-tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
1,4-dichlorobutane(IS)	55(100); 90(30); 92(10)	55
toluene	91(100); 92(78)	92
chlorobenzene	112(100); 114(33)	112
ethylbenzene	91(100); 106(33)	106
acrolein	26(49); 27(100); 55(64); 56(83)	56
acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

Organics by Liquid-Liquid Extraction - Gas Chromatography

1. Scope

This method is designed to determine those "unambiguous priority pollutants" associated with the Consent Decree, that are solvent extractable and amenable to gas chromatography. These compounds are listed in Tables III to V of this section. Except for the pesticides, it is a gas chromatographic-mass spectrometric method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study. Pesticides are initially determined by electron capture-gas chromatography and, qualitatively, confirmed by mass spectrometry.

2. Special Apparatus and Materials

Separatory funnels - 2 and 4-liter with Teflon stopcock

Continuous liquid-liquid extractors - any such apparatus designed for use with solvents heavier than water and having a capacity of 2 to 5-liters[a]. Connecting joints and stopcocks must be of Teflon or glass with no lubrication.

3. Procedure

Sample Preparation for GC-MS Survey - Blend the composite sample to provide a homogeneous mixture including

(a) Available from Aldrich Chemical Co., Milwaukee, WI, Catalog No. Z10, 157-5.

a representative portion of the suspended solids that are present. No specific method is required but a motor driven mechanical stirrer with a propeller type blade is suggested. Stirring with metal devices is acceptable for organic sampling.

Transfer the sample from the composite container through a glass funnel into a 2-liter graduated cylinder and measure the volume. Then transfer to a 4-liter separatory funnel or a continuous extractor as described below. Rinse the cylinder with several portions of the first volume of extracting solvent. Note: [Either separatory funnel or continuous extraction is acceptable for isolation of the organics. Continuous extraction must be used when emulsions cannot be broken. See discussion under Emulsions.]

Base-Neutral Extraction

Separatory Funnel Extraction - Adjust the pH of the sample with 6 N NaOH to 11 or greater. Use multirange pH paper for the measurement. Serially extract with 250 x 100 x 100 ml portions of distilled-in-glass methylene chloride. (About 40 ml of the first 250 ml portion will dissolve in the sample and not be recovered.) Shake each extract for at least 2 min by the clock.

Dry and filter the solvent extract by passing it through a short column of sodium sulfate. Concentrate the solvent by Kuderna-Danish (K-D) evaporation (distillation). The sodium sulfate should be prewashed in the column with methylene

chloride. [Note: Check sodium sulfate blank and, if necessary, heat in an oven at 500°C for 2 hours to remove interfering organics.] After drying the extract, rinse the sodium sulfate with solvent and add to the extract.

Evaporate the extract to 5-10 ml in a 500 ml K-D apparatus fitted with a 3-ball macro-Snyder column and a 10 ml calibrated receiver tube. Allow the K-D to cool to room temperature. Remove the receiver, add fresh boiling chips, attach a two-chamber micro-Snyder column and carefully evaporate to 1.0 ml or when active distillation ceases. Remove the micro-Snyder column and carefully evaporate to 1.0 ml or when active distillation ceases. Remove the micro-Snyder column and add the internal standard: 10 µl of 2 µg/µl d_{10}-anthracene (per each ml of extract). Mix thoroughly.

If it is to be overnight or longer before the extract is run by GC-MS, transfer it from the K-D ampul with a disposable pipet to a solvent tight container. The recommended container is a standard 2 ml serum vial with a crimp cap lined with Teflon coated rubber. These are inert and methylene chloride can be held without evaporation loss for months if caps are unpierced. When the extracts are not being used for analysis, store them with unpierced caps in the dark and at refrigerator or freezer temperatures.

Acid (Phenols) Extraction - Adjust the pH of the base-neutral extracted water with 6 N HCl to 2 or less. Serially

extract with 200 x 100 x 100 ml portions of distilled-in-glass methylene chloride. (Note that only 200 ml is used for the first extraction). Proceed as described for the base-neutral extract, including the addition of the internal standard.

Emulsions - The recovery of 85% of the added solvent will constitute a working definition of a broken emulsion. (You may correct the recovery of the first portion for water solubility of methylene chloride.) Any technique that meets this criteria is acceptable. Among techniques that have been tried on these samples with fair success are:

1. Centrifugation of the emulsion layer after removel of any separated solvent.
2. Passage of the emulsion through a column plugged with a ball of methylene chloride-wet glass wool. The solvent used to wet the wool and to wash it after the emulsion goes through must be measured and subtracted from the total volume to determine 85% recovery.
3. Relative to labor, solvent is cheap. The addition of excess solvent sometimes breaks weak emulsions. You must remember to use excess solvent in the blanks also.
4. Let the emulsion stand for up to 24 hrs.
5. Draw off the small amount of free solvent that separates and slowly drip it back in the top of the

separatory funnel and through the sample and emulsion.

Other ideas include stirring with a glass rod, heating on a steam bath, addition of concentrated sodium sulfate solution, and sonication. See discussion in Appendix I.

Continuous Extraction - If you cannot achieve 85% solvent recovery, start with a fresh aliquot of sample and extract by continuous extraction.

Adjust the pH of the sample as appropriate, pour into the extractor, and extract for 24 hours. When extracting a 2-liter sample, using the suggested equipment, two liters of blank water must be added to provide proper solvent recycle.

For operation, place 200-300 ml of solvent in the extractor before the sample is added and charge the distilling flask with 500 ml of solvent. At the end of the extraction remove the solvent from the distilling flask only and evaporate and treat as described in the base-neutral extract section.

Blank Extraction: It is not entirely certain that 2 liters of blank will always be available. When it is, proceed to process it as the corresponding sample was done. Include any emulsion breaking steps that used glass wool, excess solvent or additional chemicals. If less than 2 liters is available, measure the blank and bring it to volume with distilled water. On analysis make the necessary quantitative corrections.

Pesticides: These compounds are to be analyzed by EC-GC using the EPA method published in the Federal Register, Vol. 38, Number 125, Part II, pp. 17318-17323. (Friday, June 29, 1973). One-liter rather than 100 ml is to be extracted. The solvent amounts given in the method and other parameters remain unchanged. If pesticides are found by EC, the extract is to be carefully evaporated (clean airstream) to 0.5 ml and sent for GC-MS confirmation.

The compounds to be analyzed by EC-GC are listed in Table III.

If the pesticide sample has been received in a 1-gal. bottle, hand shake the bottle for 1 min. by the clock to evenly suspend sediment. Pour the sample into a 1-liter graduated cylinder and measure the volume. Then transfer the sample to a 2-liter separatory funnel and rinse the cylinder with the first volume of extracting solvent. Use additional small volumes of solvent if necessary to transfer all of the sample. Proceed with the extraction using the solvents and amounts prescribed in the published method.

If the sample is to be taken from the original composite bottle, homogeneously mix as described earlier and transfer a 1-liter aliquot to a graduated cylinder, then transfer to the separatory funnel with the aid of a glass funnel and rinse the cylinder as above.

If intractable emulsions are encountered that cannot be broken as described in the GC-MS survey section, then a fresh 1-liter sample should be processed in a continuous extractor using methylene chloride as the solvent as described earlier. The methylene chloride will have to be evaporated to a small volume and exchanged into hexane for clean-up or EC-GC analysis. To do this, evaporate the methylene chloride to 6 to 8 ml, cool, add 20 ml of hexane and a fresh boiling stone and re-evaporate to the desired analytical volume (5 ml or less).

Final storage and transport of sample extracts: After analysis, the extracts of the base-neutrals, acids, blanks and pesticides are to be sent to ERL, Athens, GA 30601, ATTN: Dr. Walter Shackelford.

Each extract is to be washed out of its container into a 10 ml glass ampul and brought to 5 ml ± 1 ml. Methylene chloride is the solvent for the base-neutrals and acids, hexane for pesticides. The ampuls are to be sealed in a rounded-off, fire polished manner, i.e., no thin sharp peaks of glass that are easily broken on handling and shipping. After sealing the ampuls, put an indelible mark at the solvent level. Securely attach a label or tag that gives:

Type of fraction (base-neutral, etc.)

Industrial category

Name (of plant, city and state)

Specific source or stage of treatment

Date sampled

Date sealed

Name of contractor and analytical laboratory

Wrap the ampuls in packing material to prevent breakage and mail or ship them postpaid at ambient temperature. When the samples are safely in ampuls, the remainder of the composite sample may be discarded.

4. GC-MS Analysis

Compounds to be analyzed by GC-MS alone fall into two categories--those in the base-neutral extract (Table IV) and those in the acid extract (Table V). Pesticides (Table III that were tentatively identified in the pesticide analysis will be confirmed by GC-MS.

The base-neutral extractables may be separated and eluted into the MS under the following chromatographic conditions:

Column - 6 foot, 2.0 mm inside diameter, glass

Packing - 1% SP2250 on 100/120 mesh Supelcoport

Program - hold 4 minutes @ 50°, program 50°-260° @ 8°/min., hold 20 minutes @260°

Injector - 275°

Separator - 275°

Carrier gas - He @ 30 ml/min

Injection size - $\geq$2 µl

Table IV lists the 49 base-neutral extractable compounds in order of relative retention times (compared to hexachlorobenzene) for the above GC conditions. Detection limits were determined by MS response. The seven compounds without retention times or limits of detection were not available for this report. It is not recommended that 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) be acquired due to its extreme toxicity. Based on their similarity to compounds that were available all seven are expected to be chromatographable using these standard conditions. In addition the characteristic masses recommended for MS identification are listed in Table IV.

The limits of detection given in Tables III and IV refer to the quantity necessary to inject to get confirmation by the MS methods described below.

At the beginning of each GC-MS run of a base-neutral extract, the operator should demonstrate the ability to chromatograph benzidine at the 40 ng level. Only after this is accomplished should the run be started. If benzidine can be chromatographed, the other nitrogen-containing compounds of Table IV can be chromatographed as well.

If desired, capillary or SCOT columns may be used instead of the packed column of SP-2250. Coatings of OV-17 or SP-2250 may be used. The elution order of OV-17 and SP-2250 are very similar. Some specific data for OV-17 is given in Table VII. The performance criteria for benzidine must still be met

and in addition, the system must be shown to elute the late running polynuclear aromatic compounds.

The acid extractables may be chromatographed as follows:

Column, 6 foot, 2.0 mm inside diameter, glass

Packing - Tenax GC, 60/80 mesh

Program - 180° - 300° @ 8°/min

Injector - 290°

Separator - 290°

Carrier Gas - He @ 30 ml/min

Injection size - $\geq$2 µl

Table V lists the 11 acid extractables in order of relative retention times (compared to 2-nitrophenol). Chromatography of nitrophenols is poor. The limits of detection given refer to the amounts required to get MS confirmation by the methods described below. See Appendix I.

Before an acid extract is run on the GC-MS the operator should demonstrate the ability to detect 100 ng of pentachlorophenol.

Mass Spectrometry should be conducted with a system utilizing a jet separator for the GC effluent since membrane separators lose sensitivity for light molecules and glass frit separators inhibit the elution of polynuclear aromatics. A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system

should also be equipped with mass storage devices for saving all data from GC-MS runs. There should be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

To indicate the presence of a compound by GC-MS, three conditions must be met. First, the characteristic ions for the compound (Tables III-V) must be found to maximize in the same spectrum. Second, the time at which the peak occurs must be within a window of ± 1 minute for the retention time of this compound. Finally, the ratios of the three peak heights must agree with the relative intensities given in Tables III-V within ± 20%.

An example of identifying a component is as follows:

It is known that hexachlorobenzene elutes from the SP2250 column at 19.4 minutes. Hexachlorobenzene has characteristic mass ions at 284(100%), 142(30%), and 249(24%). The computer is asked to display a plot of the intensities of these ions versus time (or MS scan number) and the window from 18.4-20.4 minutes is examined for the simultaneous peaking of the intensities of these ions. If all three ions are present, the ratio of the peak heights is checked to verify that it is 100:30:24 ± 20%. If the three tests are successful, hexachlorobenzene has been identified in the sample.

Table III lists the 18 pesticides and PCB's that will be confirmed by GC-MS using the SP2250 column. Chlordane, toxaphene and the PCB's have retention ranges rather than specific times due to their being multicomponent mixtures. It is suggested that the first 14 materials be confirmed exactly as the other base-neutral compounds.

The last four materials require special treatments. Chlordane is expected to produce two main peaks within the retention range given in which all three masses listed will maximize. Toxaphene will produce several (5-15) peaks in which the masses given will maximize within the retention time range. For the PCB's each mass given corresponds to the molecular ion of PCB isomers, e.g., 294 is tetrachlorobiphenyl. A specific mass plot will show multiple peaks for each of these ions within the retention time listed, but in general they will not maximize in the same TIC peak. For these four materials in particular it is necessary to also run a standard. Because GC-MS is only being used for confirmation--and at its limit of detection--all quantification will be done by EC-GC for the pesticides. The methods for these four are not final and feedback from the field to Dr. Shackelford is welcome.

When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables IV and V. Quantification will be done by the internal standard method using deuterated anthracene. Response

factors, therefore, must be calculated to compare the MS response for known quantities of each priority pollutant with that of the internal standard. The response ratio (R) may be calculated as:

$$R = \frac{Ac}{Aa} \times \frac{Ca}{Cc}$$

where Ac is the integrated area of the characteristic ion from the specific ion plot for a known concentration, Cc. Aa and Ca are the corresponding values for deuterated anthracene. The relative response ratio for the priority pollutants should be known for at least two concentration values--40 ng to approximate 10 ppb and 400 ng to approximate the 100 ppb level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. For guidance in MS limits of detection refer to the values given in Tables III-V.

The concentration of a compound in the extract may now be calculated using:

$$C = \frac{Ac \times Ca}{Aa \times R}$$

where C is the concentration of a component, Ac is the integrated area of the characteristic ion from the specific ion plot, R is the response ratio for this component, Aa is the integrated area of the characteristic ion in the specific ion plot for deuterated anthracene, and Ca is the concentration of deuterated anthracene in the injected extract.

In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables IV and V characteristic CI ions for most compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

5. Quality Assurance

GC-MS system performance evaluation is required each day the system is used for samples or reagent blanks. A sample of 20 ng of decafluorotriphenylphosphine[b] is injected into the system and the mass spectrum is acquired and plotted. Criteria established in Reference 2 must be met. The analyst must also demonstrate that the analytical conditions employed result in sharp total ion current peaks for 40 ng of benzidine on the SP2250 column when this column is used and 100 ng of pentachlorophenol on the Tenax GC column when it is used with the MS as a detector. All plots from the performance evaluation must be retained as proof of valid performance.

As performance evaluation samples become available from EMSL-Cincinnati, they are to be analyzed by solvent extraction once each 20 working days and the results reported with other analytical data.

The 1% SP2250 and Tenax GC column packings are available by request to EPA contractors from Dr. Walter Shackelford, EPA, Athens, GA.

(b) Available from PCR, Gainesville, FL

Standards for the priority pollutants may be obtained from the sources listed in Appendix II. Those compounds marked with an asterisk have not yet been received by the Athens laboratory.

In order to minimize unnecessary GC-MS analysis of blanks, the extract may be run on a FID-GC equipped with appropriate SP2250 and Tenax GC columns. If no peaks are seen of intensities equal to or greater than the deuterated anthracene internal standard, then it is not necessary to do a GC-MS analysis. If such peaks are seen, then the blank must be sent for full priority pollutant analysis.

The contractor will look for all priority pollutants to the limit of 10 μg/l except in those cases listed in Tables IV-V in which limits of detection are too high for analysis at this level.

6. Reporting of Data

All concentrations should be reported in ranges--10 ppb, 100 ppb, and greater than 100 ppb. Report concentrations for pesticides as prescribed in the Federal Register Method. The relative response ratios from MS analysis should be included when reporting data.

All GC-MS data is to be saved on 9-track magnetic tape and sent to the Athens Environmental Research Laboratory for storage and later evaluation. The tape format is:

Type - 9 track, 800 BPI, 2400 foot reels

Record length - 80

Block Size - $\leq$4000 (specify)

Code - EBCDIC

An acceptable data format would have the first two records containing the sample identification. Subsequent records contain eight mass-intensity pairs, each of which is 10 characters long. Each mass and each intensity is 5 characters long and left justified. At the end of each spectrum in a sample run, the last mass-intensity pair is blank to denote the end of the spectrum. When all data for the run is on the tape, an end-of-file mark should be written. The next sample run can then be entered. One example is:

2 Records:Sample 1 identification

N Records:Spectrum 1 of sample, last mass-intensity pair is blank to denote end of spectrum

M Records:Spectrum 2 of sample, last mass-intensity pair is blank to denote end of spectrum

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L Records:Spectrum N of sample, last mass-intensity pair is blank to denote end of spectrum

END OF FILE

2 Records:Sample 2 identification

etc.

Other data formats are possible, but <u>any</u> format that is used <u>must</u> be accompanied by a full explanation of all record formats.

All magnetic tapes, documentation and a table of MS response ratios should be sent to:

Dr. W. M. Shackelford
Athens Environmental Research Laboratory
College Station Road
Athens, GA 30601

Table III. Pesticides

Compound Name	RRT[1] (hexachlorobenzene)	Detection Limit (ng)	Characteristic EI ions (Rel. Int.)
β-endosulfan	0.51	40	201(100), 283(48), 278(30)
α-BHC	1.02	40	183(100), 109(86), 181(91)
γ-BHC	1.09	40	183(100), 109(86), 181(91)
β-BHC	1.12	40	181(100), 183(93), 109(62)
aldrin	1.14	40	66(100), 220(11), 263(73)
heptachlor	1.15	40	100(100), 272(60), 274(46)
heptachlor epoxide	1.23	40	355(100), 353(79), 351(60)
α-endosulfan	1.24	40	201(100), 283(48), 278(30)
dieldrin	1.28	40	79(100), 263(28), 279(22)
4,4'-DDE	1.30	40	246(100), 248(64), 176(65)
4,4'-DDD	1.33	40	235(100), 237(76), 165(93)
4,4'-DDT	1.38	40	235(100), 237(72), 165(59)
endrin	1.41	40	81(100), 82(61), 263(70)
endosulfan sulfate	1.41	20	272(100), 387(75), 422(25)
δ-BHC			183(100), 109(86), 181(90)
chlordane	1.14-1.37		373(19), 375(17), 377(10)**
toxaphene	1.22-1.47		(231, 233, 235)*
PCB-1242	0.93-1.24		(224, 260, 294)*
PCB-1254	1.18-1.41		(294, 330, 362)*

* These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

** These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

1 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

Table IV. Base-neutral Extractables

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
1,3-dichlorobenzene	0.35	40	146(100), 148(64), 113(12)	146, 148, 150
1,4-dichlorobenzene	0.36	40	146(100), 148(64), 113(11)	146, 148, 150
hexachloroethane	0.38	40	117(100), 199(61), 201(99)	199, 201, 203
1,2-dichlorobenzene	0.39	40	146(100), 148(64), 113(11)	146, 148, 150
bis(2-chloroisopropyl) ether	0.47	40	45(100), 77(19), 79(12)	77, 135, 137
hexachlorobutadiene	0.55	40	225(100, 223(63), 227(65)	223, 225, 227
1,2,4-trichlorobenzene	0.55	40	74(100), 109(80), 145(52)	181, 183, 209
naphthalene	0.57	40	128(100), 127(10), 129(11)	129, 157, 169
bis(2-chloroethyl)ether	0.61	40	93(100), 63(99), 95(31)	63, 107, 109
hexachlorocyclopentadiene	0.64	40	237(100), 235(63), 272(12)	235, 237, 239
nitrobenzene	0.64	40	77(100), 123(50), 65(15)	124, 152, 164
bis(2-chloroethoxy)methane	0.68	40	93(100), 95(32), 123(21)	65, 107, 137
2-chloronaphthalene	0.76	40	162(100), 164(32), 127(31)	163, 191, 203
acenaphthylene	0.83	40	152(100), 153(16), 151(17)	152, 153, 181
acenaphthene	0.86	40	154(100), 153(95), 152(53)	154, 155, 183
isophorone	0.87	40	82(100), 95(14), 138(18)	139, 167, 178
fluorene	0.91	40	166(100), 165(80), 167(14)	166, 167, 195
2,6-dinitrotoluene	0.93	40	165(100), 63(72), 121(23)	183, 211, 223
1,2-diphenylhydrazine	0.96	40*	77(100), 93(58), 105(28)	185, 213, 225
2,4-dinitrotoluene	0.98	40	165(100), 63(72), 121(23)	183, 211, 223
N-nitrosodiphenylamine	0.99	40*	169(100), 168(71), 167(50)	169, 170, 198
hexachlorobenzene	1.00	40	284(100), 142(30), 249(24)	284, 286, 288
4-bromophenyl phenyl ether	1.01	40	248(100), 250(99), 141(45)	249, 251, 277
phenanthrene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
anthracene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
dimethylphthalate	1.10	40	163(100), 164(10), 194(11)	151, 163, 164
diethylphthalate	1.15	40	149(100), 178(25), 150(10)	177, 223, 251
fluoranthene	1.23	40	202(100), 101(23), 100(14)	203, 231, 243
pyrene	1.30	40	202(100), 101(26), 100(17)	203, 231, 243
di-n-butylphthalate	1.31	40	149(100), 150(27), 104(10)	149, 205, 279
benzidine	1.38	40*	184(100),92(24), 185(13)	185, 213, 225
butyl benzylphthalate	1.46	40	149(100), 91)50)	149, 299, 327

Table IV. Base-neutral Extractables (Cont'd.)

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
chrysene	1.46	40	228(100), 229(19), 226(23)	228, 229, 257
bis(2-ethylhexyl)phthalate	1.50	40	149(100), 167(31), 279(26)	149
benzo(a)anthracene	1.54	40	228(100), 229(19), 226(19)	228, 229, 257
benzo(b)fluoranthene	1.66	40	252(100), 253(23), 125(15)	252, 253, 281
benzo(k)fluoranthene	1.66	40	252(100), 253(23), 125(16)	252, 253, 281
benzo(a)pyrene	1.73	40	252(100), 253(23), 125(21)	252, 253, 281
indeno(1,2,3-cd)pyrene	2.07	100	276(100), 138(28), 277(27)	276, 277, 305
dibenzo(a,h)anthracene	2.12	100	278(100), 139(24), 279(24)	278, 279, 307
benzo(g h i)perylene	2.18	100	276(100), 138(37), 277(25)	276, 277, 305
N-nitrosodimethylamine			42(100), 74(88), 44(21)	
N-nitrosodi-n-propylamine			130(22), 42(64), 101(12)	
4-chloro-phenyl phenyl ether			204(100), 206(34), 141(29)	
endrin aldehyde				
3,3'-dichlorobenzidine			252(100), 254(66), 126(16)	
2,3,7,8-tetrachlorodibenzo-p-dioxin			322(100), 320(90), 59(95)	
bis(chloromethyl)ether			45(100), 49(14), 51(5)	
deuterated anthracene (d10)	1.09	40	188(100), 94(19), 80(18)	189, 217

1 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

* Conditioning of column with base is required.

Table V. Acid Extractables

Compound Name	RRT[1] (2-nitrophenol)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
2-chlorophenol	0.63	100	128(100), 64(54), 130(31)	129, 131, 157
phenol	0.66	100	94(100), 65(17), 66(19)	95, 123, 135
2,4-dichlorophenol	0.96	100	162(100), 164(58), 98(61)	163, 165, 167
2-nitrophenol	1.00	100	139(100), 65(35), 109(8)	140, 168, 122
p-chloro-m-cresol	1.05	100	142(100), 107(80), 144(32)	143, 171, 183
2,4,6-trichlorophenol	1.14	100	196(100), 198(92), 200(26)	197, 199, 201
2,4-dimethylphenol	1.32	100	122(100), 107(90), 121(55)	123, 151, 163
2,4-dinitrophenol	1.34	2 μg	184(100), 63(59), 154(53)	185, 213, 225
4,6-dinitro-o-cresol	1.42	2 μg	198(100), 182(35), 77(28)	199, 227, 239
4-nitrophenol	1.43	100	65(100), 139(45), 109(72)	140, 168, 122
pentachlorophenol	1.64	100	266(100), 264(62), 268(63)	267, 265, 269
deuterated anthracene (d10)	1.68	40	188(100), 94(19), 80(18)	189, 217

[1] Column: 6' glass, 2 mm i.d.
Tenax GC - 60/80 mesh
180° - 300° @ 8°/min.
He @ 30 ml/min

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a]

Compound	RRT[b,c]
1,3-dichlorobenzene	0.35[d]
2-chlorophenol	0.35[e]
1,4-dichlorobenzene	0.36[d]
hexachloroethane	0.38
1,2-dichlorobenzene	0.39
bis(2-chloroisopropyl)ether	0.47
β-endosulfan	0.51
2,4-dimethyl phenol	0.52[e]
2-nitrophenol	0.53[e]
2,4-dichlorophenol	0.53[e]
hexachlorobutadiene	0.55
1,2,4-trichlorobenzene	0.55
naphthalene	0.57
bis(2-chloroethyl)ether	0.61
hexachlorocyclopentadiene	0.64
nitrobenzene	0.64
phenol	0.67
bis(2-chloroethoxy)methane	0.68
2,4,6-trichlorophenol	0.71[e]
p-chloro-m-cresol	0.73[f]
2-chloronaphthalene	0.76
acenaphthylene	0.83
acenaphthene	0.86
isophorone	0.87
fluorene	0.91

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
2,6-dinitrotoluene	0.93
1,2-diphenylhydrazine	0.96
2,4-dinitrotoluene	0.98
N-nitrosodiphenylamine	0.99
hexachlorobenzene	1.00
4-bromophenyl phenyl ether	1.01
α-BHC	1.02
γ-BHC	1.09[f]
phenanthrene	1.09[f]
anthracene	1.09
dimethyl phthalate	1.10
pentachlorophenol	1.11[f]
β-BHC	1.12
aldrin	1.14
diethyl phthalate	1.15
heptachlor	1.15
heptachlor epoxide	1.23
fluoranthene	1.23
α-endosulfan	1.24
dieldrin	1.28
4,4'-DDE	1.30
pyrene	1.30
di-n-butyl phthalate	1.31
4,4'-DDD (p,p'-TDE)	1.33
4,4'--DDT	1.38[d]
endosulfan sulfate	1.41[f]
endrin	1.41
benzidine	1.38
butyl benzyl phthalate	1.46
chrysene	1.46

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
bis(2-ethylhexyl)phthalate	1.50
benzo(a)anthracene	1.54
benzo(b)fluoranthene	1.66
benzo(k)fluoranthene	1.66
benzo(a)pyrene	1.73
indeno(1,2,3-cd)pyrene	2.07
dibenzo(a,h)anthracene	2.12[d]
benzo(ghi)perylene	2.12[f]

[a] 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2mm id glass column; He @ 30ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

[b] Relative to hexachlorobenzene at 19.4 min.

[c] 40ng gives 5-90% response on FID unless otherwise noted.

[d] 200ng required to obtain 5-90% response on FID.

[e] 2 µg required.

[f] 40 µg required.

Table VI

(continued)

Standards not available: as of 2/8/77

N-nitrosodi-n-propylamine
4-chlorophenyl phenyl ether
TCDD
endrin aldehyde
N-nitrosodimethylamine
3,3'-dichlorobenzidine
bis(chloromethyl)ether (unstable in water)

Standards that would not chromatograph:

4,6-dinitro-o-cresol
4-nitrophenol
2,4-dinitrophenol

Standards yielding a range of peaks:

	RRT[b]
PCB-1242	0.93-1.24
PCB-1254	1.18-1.41
toxaphene	1.22-1.47
chlordane	1.14-1.37

Table VII. Order of Elution for OV-17 SCOT Column[1]

Compound	Spectrum Number[2]
1,3-dichlorobenzene	134
1,4-dichlorobenzene	137
2-chlorophenol	141
1,2-dichlorobenzene	153
bis(2-chloroethyl)ether	163
phenol	165
bis(2-chloroisopropyl)ether	173
hexachloroethane	178
nitrobenzene	194
2-nitrophenol	219
1,2,4-trichlorobenzene	234
2,4-dimethylphenol	240
naphthalene	240
2,4-dichlorophenol	244
hexachlorobutadiene	262
isophorone	272
p-chloro-m-cresol	317
hexachlorocyclopentadiene	325
2,4,6-trichlorophenol	332
chloronaphthalene	339
2,4-dinitrotoluene	372
acenaphthylene	374
acenaphthene	390
dimethylphthalate	397
fluorene	434
diethylphthalate	447
N-nitrosodiphenylamine	447
2,6-dinitrotoluene	454
α-BHC	476
4-bromophenyl phenyl ether	478
γ-BHC	487
hexachlorobenzene	490
β-BHC	506
phenanthrene	518
anthracene	518
di-n-butylphthalate	583
aldrin	592
fluoranthene	617
pyrene	634
DDE	659
DDD	664
endrin	688
dieldrin	688
DDT	713
butyl benzyl phthalate	713
benzo(a)anthracene	748
chrysene	748

Table VII. Continued

Compound	Spectrum Number[2]
bis(2-ethylhexyl)phthalate	804
benzo(a)pyrene	906
benzo(b)fluoranthene	970
benzo(k)fluoranthene	970

1 33 meter glass OV-17 SCOT column,
Program: 60° - 260° @ 6°/minute

2 Number of 2.5 second scans up to point of elution.

Metals

1. Sample Preparation

With the exception of mercury, the metals to be determined may be divided into two groups as follow:

a) those metals which are to be first analyzed by flame atomic absorption (AA), and, if not detected, then analyzed by flameless AA--Be, Cd, Cr, Cu, Ni, Pb and Zn,

b) those metals which are to be analyzed by flameless AA only--Ag, As, Sb, Se, and Tl.

For flame AA analysis the sample should be prepared using the procedure as given in "Methods for Chemical Analyses of Water and Wastes (1974)", 4.1.4, page 83 (Reference 7).

With the exception of antimony and beryllium, samples to be analyzed by flameless AA should be prepared as an industrial effluent as described in "Atomic Absorption Newsletter," 14, page 111 (1975) (Reference 8). Note: Nickel nitrate should be added only to those aliquots on which the analysis of selenium and arsenic are to be accomplished. The sample preparation procedure for antimony and beryllium analysis by flameless AA is the same procedure used for flame AA.

The sample preparation procedure to be used for mercury analysis is that given in "Methods for Chemical Analysis of Water and Wastes (1974)", 8.1, page 124 (Reference 7).

2. Apparatus

All samples are to be analyzed using an atomic absorption spectrophotometer equipped with simultaneous background capability. For arsenic, cadmium, antimony, selenium, thallium, and zinc, either electrodeless discharge lamps or high intensity hollow cathode lamps may be utilized. A heated graphite atomizer is to be used for all flameless AA work. A strip chart recorder must be used as part of the readout system to detect and avoid the inclusion of extraneous data.

3. Procedure

a) Flame AA - The procedures to be used are those described in "Methods for Chemical Analysis of Water and Wastes (1974)"(Reference 7) as referenced in Table I below. Instructions as to when flameless AA is to be used are also included. For those defined in the recommended procedures, the instrument manufacturers recommendations are to be followed. Background correction is to be used on all analyses.

Table VIII

Element	Methods for Chemical Analysis of Water and Wastes, 1974*	Comments
Be	p. 99	Analyze by flameless AA if conc. <20 μg/l
Cd	p. 101	Analyze by flameless AA if conc. <20 μg/l
Cr	p. 105	Use nitrous oxide-acetylene flame for all analyses--analyze by flameless AA if conc. <200 μg/l
Cu	p. 108	Analyze by flameless AA if conc. <50 μg/l
Ni	p. 141	Analyze by flameless AA if conc. <100 μg/l
Pb	p. 112	Analyze by flameless AA if conc. <300 μg/l
Zn	p. 155	Analyze by flameless AA if conc. <20 μg/l

*In those instances where more vigorous digestion for sample preparation is desired (or necessary) the procedure on page 82 (4.1.3) should be followed.

b) Standard solutions to be used for the flameless work should also be prepared as described in "Methods for Chemical Analysis of Water and Wastes (1974)" (Reference 7). The working standards should be diluted to contain the same acid concentration as the prepared samples. The instrumental settings and conditions recommended by the manufacturers are to be considered the procedural guidelines. In addition, the following requirements should also be incorporated into the procedures:

1) Argon should be used as the purge gas in all analyses.

2) Background correction and method of standard addition must be used on all analyses.

3) A blank maximum temperature atomization, without gas interrupt, should be accomplished before each analytical determination.

4) The graphite tube or cuvette should be replaced as suggested by the instrument manufacturer or when contamination or lack of precision indicates that replacement is necessary.

5) All disposable pipet tips should be cleaned before use by soaking overnight in 5% redistilled nitric acid, rinsed with tap and deionized water, and dried.

6) The accuracy of the temperature indicator on the heated graphite atomizer should be verified before beginning any analytical work. This should be done by plotting charring temperature for a standard solution of a compound where the volatilization temperature is known. The compound used should have a volatilization temperature between 800 and 1200°C.

7) To insure that there is no loss from the acid matrix prior to atomization, the optimum charring temperature for each metal should be established in the same manner (i.e., by plotting charring temperature versus atomization signal of standard solution of each metal).

For the determination of selenium the procedure given for industrial effluents ("Atomic Absorption Newsletter," Vol. 14, page 109 [1975]) (Reference 8) should be followed. Arsenic should be determined in the same manner (using the nickel nitrate matrix) with an optimum charring temperature of approximately 1300°C.

The analysis of zinc by flameless AA is difficult because of environmental contamination. The analyst must take precaution to provide a clean work area to minimize this problem.

c) Mercury analyses - The cold vapor technique as described in "Methods for Chemical Analysis of Water and Wastes, (1974)", page 118 (Reference 7) is to be followed.

4. Quality Assurance

a) To verify that the instrument is operating correctly within the expected performance limits, an appropriate standard should be included between every ten samples.

b) Spiked aliquots shall be analyzed with a frequency of 15% of the sample load for each metal determined by flame AA. If the recovery is not within ±10% of the expected value the sample should be analyzed by method of standard addition. (The spike should be added to the aliquot prior to sample preparation.) The amount added should increase the absorbance by not less than 0.01 units where the absorbance in the unspiked aliquot was less than 0.1, and not more than 0.1 when the absorbance in the unspiked aliquot was 0.1 or greater.

c) For mercury, the spike added should be an amount equal to five times the detection level.

d) Reagent blanks shall be run for each metal being determined with the sample values being corrected accordingly.

e) When using the method of standard addition, a linear curve over the entire range of addition is necessary for the results to be considered valid.

5. Data Reporting

Report all metal concentrations as follows: Less than 10 µg/l, nearest µg; 10 µg/l and above, two significant figures.

Cyanides

1. Sample Preparation

All samples are to be distilled prior to determination for total cyanides. The distillation procedure given on page 43 of "Methods for Chemical Analysis of Water and Wastes, (1974)" (Reference 7) is to be followed.

2. Sample Procedure

The procedure for total cyanides as given on pages 43-48 of "Methods for Chemical Analysis of Water and Wastes, (1974)" (Reference 7) is to be followed.

3. Quality Assurance

a) Initially, demonstrate quantitative recovery with each distillation-digestion apparatus by comparing distilled standards to non-distilled standards. Each day, distill at least one standard to confirm distillation efficiency and purity of reagents.

b) At least 15% of the cyanide analysis will consist of duplicate and spiked samples. Quality control limits are to be established and confirmed as described in Chapter 6 of the "Analytical Quality Control Handbook" (Reference 9).

4. Reporting of Data

Report cyanide concentrations as follows: Less than 1.0 mg/l, nearest 0.01 mg; 1.0 mg/l and above, two significant figures.

Phenols

1. Sample Preparation

Distill all samples prior to determination of phenols. Use the procedure in "Standard Methods for the Examination of Water and Wastewater," 14th edition, 1975, p. 576 (Reference 10).

2. Procedure

Use method 510 for phenols in Appendix X, pages 577-580 and 580-581. Use method 510B for samples that contain less than 1 mg/l of phenol. Use method 510C for samples that contain more than 1 mg/l of phenol.

3. Quality Assurance

Demonstrate quantitative recovery with each distillation apparatus by comparing distilled standards to non-distilled standards. Each day distill, at least, one standard to confirm the distillation efficiency and purity of reagents.

Run duplicate and dosed sample analyses on at least 15% of the samples analyzed for phenol. Establish and confirm quality control limits as described in Reference 9.

4. Reporting of Data

Report phenol concentrations as follows:

Method 510B to the nearest µg/l.

Method 510C - when less than 1.0 µg/l to the nearest 0.01 mg; 1.0 mg/l and above to two significent figures.

Report all quality control data when reporting results of sample analysis.

REFERENCES

1. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," T. A. Bellar and J. J. Lichtenberg, Jour. AWWA, 66 ,739-744, Dec. 1974.

2. "Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography--Mass Spectrometry Systems," J. W. Eichelberger, L. E. Harris and W. L. Budde, Anal. Chem. 47, 995-1000 (1975).

3. ASTM Annual Standards - Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

4. ASTM Annual Standards - Water, part 31, Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution by Gas Liquid Chromatograph."

5. "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry," Harris. L. E., Budde, W. L., and Eichelberger, J. W. Anal. Chem., 46, 1912 (1974).

6. Federal Register, Volume 38, number 125, part II, Appendix II, p. 17319, Friday, June 29, 1975, "Determination of Organo-chlorine Pesticides in Industrial Effluents,"

7. "Methods for Chemical Analysis of Water and Wastes (1974)", U.S. Environmental Protection Agency, Technology Transfer.

8. "Determining Selenium in Water, Wastewater, Sediment and Sludge by Flameless Atomic Absorption Spectroscopy", T. D. Martin and J. F. Kopp, Atomic Absorption Newsletter, 14, 109-116 (1975).

9. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories (1972)," U.S. Environmental Protection Agency, Technology Transfer.

10. "Standard Methods for the Examination of Water and Wastewater," 14th edition, 1975.

APPENDIX I

General Information

Emulsions

Limited work with several categories of industrial effluents covered by this study (tanneries, petroleum, soap and detergent, steam electric, pesticide) show that emulsions of widely differing frustration factors are often encountered in the extraction procedure. Samples that emulsify at basic pH usually also emulsify at acid pH. There are two equally acceptable alternatives available for the purposes of this protocol: break the emulsion or start over with fresh sample and use a continuous extractor, to prevent the formation of emulsions.

By the 85% solvent recovery criteria, no way was found to break the emulsion formed on extraction of untreated tannery wastes. A soap and detergent sample was also very difficult. The use of a continuous heavier-than-water liquid extractor allowed the extraction to take place with no difficulties and very little labor. However, two days time is required. Comparison of samples from four industries--petroleum, tannery, pesticide, and soap and detergent--by both shake-out and continuous extraction using wastes spiked with priority pollutants indicate that the two techniques are comparable. For some individual cases one technique is better than the other but no clear pattern emerges. Therefore, if desired, a continuous extraction technique may be used in place of separatory funnel extraction for all samples as well as those for which it is absolutely necessary because of intractable emulsions.

APPENDIX I

(continued)

There is a justifiable concern that the extraction efficiency for these compounds may differ widely depending on the nature of the effluents. This is true but no better approach is apparent. For example, recoveries of most of the base-neutrals were judged to be about 75% from the tannery and petroleum samples but less than 25% from soap and detergent.

Acid (Phenol) Analysis

Although the 11 phenols of interest here do chromatograph on the Tenax column cited, the chromatography is poor, particularly for the nitrophenols. Two other columns have shown good response for the acid extractables. SP2250 can be used for this purpose. Phenol responses on SP2250 are shown in Table IV. It should be noted, however, that 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-o-cresol, and pentachlorophenol failed to give MS response at the 100 ng level using this column.

SP1000 (4% load) has also been evaluated for use with the acid fraction. All but 2,4-dinitrophenol and 4,6-dinitro-o-cresol elute from this column. Pentachlorophenol and 4-nitrophenol are eluted from SP1000, but they produce broad peaks which are difficult to quantify.

Appendix II

Possible Sources for Some Priority Pollutant Standards

Compound	Source of Standard[2]
acenaphthene	AN p. 118
acrolein	AL p. 18
acrylonitrile	AL p. 19
aldrin	HERL #80
dieldrin	HERL #2380
benzene	B p. 154
benzidine[1]	RFR
carbon tetrachloride (tetrachloromethane)	B p. 88
chlordane (technical mixture & metabolites)	HERL #1200
<u>Chlorinated benzenes</u> (other than dichlorobenzenes)	
chlorobenzene	AL p. 165
1,2,4-trichlorobenzene	AL p. 710
hexachlorobenzene	AL p. 416
<u>Chlorinated ethanes</u> (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)	
1,2-dichloroethane	AL p. 261
1,1,1-trichloroethane	B p. 309
hexachloroethane	AL p. 416
1,1-dichloroethane	PB p. 142
1,1,2-trichloroethane	PB p. 388
1,1,2,2-tetrachloroethane	PB p. 372
chloroethane	EA p. 53
<u>Chloroalkyl ethers</u> (chloromethyl, chloroethyl and mixed ethers)	
bis(chloromethyl) ether[1]	RFR
bis(2-chloroethyl) ether	AL p. 173
2-chloroethyl vinyl ether	AL p. 174
<u>Chlorinated naphthalene</u>	
2-chloronaphthalene	ICN p. 50

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	
2,4,6-trichlorophenol	AL p. 712
p-chloro-m-cresol	TCI p. 102
chloroform (trichloromethane)	B p. 92
2-chlorophenol	AL p. 187
DDT and metabolites	
4,4'-DDT	HERL #1920
4,4'-DDE	HERL #1860
4,4'-DDD (p,p'-TDE)	HERL #1780
Dichlorobenzenes (1,2-;1,3-; and 1,4-dichlorobenzenes)	
1,2-dichlorobenzene	AL p. 258
1,3-dichlorobenzene	AL p. 258
1,4-dichlorobenzene	AL p. 258
Dichlorobenzidine	
3,3'-dichlorobenzidine[1]	CPL p. 81
Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)	
1,1-dichloroethylene	AL p. 746
1,2-trans-dichloroethylene	AL p. 262
2,4-dichlorophenol	AL p. 265
Dichloropropane and dichloropropene	
1,2-dichloropropane	AL p. 267
1,3-dichloropropylene (1,3-dichloropropene)	AL p. 267
2,4-dimethylphenol	AL p. 323
Dinitrotoluene	
2,4-dinitrotoluene	PB p. 180
2,6-dinitrotoluene	PB p. 180
1,2-diphenylhydrazine	AL p. 338

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
Endosulfan and metabolites	
α-endosulfan	HERL #3220
β-endosulfan	HERL #3200
endosulfan sulfate	NI p. 45
Endrin and metabolites	
endrin	HERL #3260
endrin aldehyde	NI p. 147
ethylbenzene	B p. 161
fluoranthene	AN p. 118
Haloethers (other than those listed elsewhere)	
4-chlorophenyl phenyl ether (p-chloro-diphenyl ether)	RFR p. 6*
4-bromophenyl phenyl ether	ICN p. 37
bis(2-chloroisopropyl) ether	PB
bis(2-chloroethoxy) methane	PB p. 62
Halomethanes (other than those listed elsewhere)	
methylene chloride (dichloromethane)	PB p. 276
methyl chloride (chloromethane)	PB p. 277
methyl bormide (bromomethane)	PB p. 276
bromoform (tribromomethane)	PB p. 73
dichlorobromomethane	CO p. 16
trichlorofluoromethane	PB p. 358
dichlorodifluoromethane	PB p. 142
chlorodibromomethane	CO p. 27
Heptachlor and metabolites	
heptachlor	HERL #3860
heptachlor epoxide	HERL #3880
hexachlorobutadiene	AL p. 416
Hexachlorobyclohexane (all isomers)	
α-BHC	HERL #620
β-BHC	HERL #640
γ-BHC (lindane)	HERL #680
δ-BHC	HERL #660

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
hexachlorocyclopentadiene	AL p. 416
isophorone	AL p. 464
naphthalene	AN p. 118
nitrobenzene	AL p. 557
Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)	
2-nitrophenol	AL p. 564
4-nitrophenol	AL p. 564
2,4-dinitrophenol	AL p. 332
4,6-dinitro-o-cresol	TCI p. 188
Nitrosamines	
N-nitrosodimethylamine[1]	NI p. 173
N-nitrosodi-n-propylamine	PB p. 310
N-nitrosodiphenylamine	EA p. 159
pentachlorophenol	AL p. 587
phenol	AL p. 595
Phthalate esters	
bis(2-ethylhexyl) phthalate	CS p. 8
butyl benzyl phthalate	CS p. 8
di-n-butyl phthalate	CS p. 8
diethyl phthalate	CS p. 8
dimethyl phthalate	CS p. 8
Polychlorinated biphenyls (PCB's)	
PCB-1242 (Aroc lor 1242)	HERL #5703
PCB-1254 (Aroc lor 1254)	HERL #5705
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)	
1,2-benzanthracene	AN p. 118
benzo[a]pyrene (3,4-benzopyrene)	AN p. 118
3,4-benzofluoranthene	NI
11,12-benzofluoranthene	NI
chrysene	AN p. 118

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
acenaphthylene	AN p. 1
anthracene	AN p. 118
1,12-benzoperylene	AN p. 118
fluorene	AN p. 118
phenanthrene	AN p. 118
1,2:5,6-dibenzanthracene	AN p. 118
indeno (1,2,3-C,D)pyrene	AN p. 118
pyrene	AN p. 118
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	NI p. 174
tetrachloroethylene	AL p. 680
toluene	AL p. 701
toxaphene	HERL #6740
trichloroethylene	AL p. 711
vinyl chloride (chloroethylene)	PB p. 406
1-bromodecane (possible internal standard)	
1-bromododecane (possible internal standard)	

Footnotes:

1 These compounds or any mixture containing 1% or more by weight of these compounds are defined as carcinogens in the Federal Register, Vol. 38, No. 144, pp. 20074-20076, 27 July 1973. Prescribed safety regulations for handling are in the Federal Register, Vol. 39, No. 20, pp. 3756-3797, 29 January 1974.

2 Only one source is listed even though several may be available These sources are not to be interpreted as being endorsed by the EPA; they serve to show at least one vendor where each standard can be obtained. When several sources were available and compound purity was listed, the source having the highest purity material was selected.

* These compounds have been ordered but have not been received at Athens ERL as yet.

Sources of Standards and Abbreviations

AL	Aldrich Chemical Co., Milwaukee, Wisc.; Catalog 1977-1978.
AN	Analabs, Inc., North Haven, Conn.; Catalog 18 (June 1976).
B	J. T. Baker Chemical Co., Phillipsburgh, N.J.; Catalog 750 (July 1975).
CS	Chem-Service, West Chester, Pa.; Bulletin CS-100-8 (1975).
CPL	Chemical Procurement Laboratories, College Point, N.Y.; 1975 catalog.
EA	Eastman Kodak Co., Rochester, N.Y.; Catalog 48 (1976).
ICN	K&K Rare & Fine Chemicals, Plainview, N.Y.; Catalog No. 10 (1975).
NI	Nanogens International, P.O. Box 487, Freedom, CA 95019 "Nanogen Index" (1975).
PB	Pfaltz & Bauer Chemical Co., STamford, Conn.; Catalog 1976.
RFR	RFR Corp., Hope, R.I.; "Chemical Standards for Air-Water-Industry-Foods" (1975).
HERL	"Analytical Reference Standards and Supplemental Data for Pesticides and Other Selected Organic Compounds", EPA-660/9-76-012 (May 1976), Health Effects Research Laboratory, Environmental Toxicology Division, Research Triangle Park, NC. A sample order blank for standards and the above publication are attached.
CO	Columbia Organics Catalog A-7, Columbia, S.C. (1975).
TCI	Tridom Chemical Inc., Hauttauge, N.Y., Catalog No. 1 (1976).

ENVIRONMENTAL TOXICOLOGY DIVISION
HEALTH EFFECTS RESEARCH LABORATORY
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711

SUBJECT: Index of Pesticides Analytical Reference Standards - Update of Mailing List

DATE: June, 1976

FROM: Health Effects Research Laboratory, ETD, ACB, Research Triangle Park, NC, U.S.A. 27711 (MD-69) J. F. Thompson

TO: All Laboratory Facilities on our Mailing List

This copy of the 1976 revision of our pesticides reference standards index was mailed to the address appearing on our mailing list. As this list is several years old, we are sure that a number of addresses have changed and that some are probably no longer existent.

If you wish to remain on our mailing list to receive future updates of this publication, would you be good enough to complete the mail-back below, snip it off, and return it to us. Do not tear off the back cover to return to the address shown. If you have no use for this publication but know of some other individual within your organization who is concerned with pesticides analysis, would you convey this index, along with the mailback, to that person.

To: U. S. Environmental Protection Agency
Health Effects Research Laboratory
Environmental Toxicology Division
Research Triangle Park, NC, U.S.A. 27711 (MD-69)

_____
Date

☐ We wish to be retained on your mailing list to receive future updates of the Pesticides Standards Index. The address shown on the envelope is entirely correct and requires no changes.

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☐ We wish to be retained on your mailing list, but the address shown on the envelope should be changed to read (print or type)

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REQUEST FOR ANALYTICAL REFERENCE STANDARDS

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Date

Date Request Recd	/ /
Shipment Date	/ /
Lab Code No.	
Order Filled by	
DO NOT WRITE IN THIS SPACE	

TO: Quality Assurance Section
Environmental Toxicology Division,
EPA, HERL, Research Triangle Park, NC 27711
MD-69

The following reference standards are required for our program:

Catalog Code No.	Compound (Catalog Name)	Catalog Code No.	Compound (Catalog Name)

If necessary, use back of sheet to complete list. Covering letter unnecessary if this form is completed in full.

Name and address of laboratory _____

_____

_____

_____

_____
Requestor's Name (Print or type)

IMPORTANT:

1. The amount of each standard is restricted to 100 mg because of the scarcity and expense of refining analytical grade materials.

2. Please return at once the acknowledgement card enclosed with each shipment. This provides the sole evidence of delivery of the shipment.

3. Do not request compounds not listed in the catalog. No others are stocked.

4. If a bottle appears to be empty, remove cap and examine interior of bottle and cap. Certain highly viscous materials tend to collect in cap.

APPENDIX III

COLLECTION OF SAMPLES FOR SCREENING ANALYSES

The initial characterization (screening) of the varied industrial discharges covered by this program will be made on an analysis of a composite effluent sample. Any scheme for collecting a composite sample is, in effect a method for mechanically integrating to obtain average characteristics of a discharge. During the screening phase the sample composite can be used to determine the average characteristics which would be representative of that discharge. Simple composite samples are those that are made up of a series of aliquots of constant volume collected at regular time intervals in a single container. Some situations may require flow or time proportional sampling, this determination will be made by the individual project officer after considering his specific industrial category.

The determination of compositing period 24, 48 or 72 hours will be made on a case by case basis. The duration of compositing will depend on the type of sample being collected, the type of facility being sampled and the time varying characteristics of the discharge. The rate of change of flow and other characteristics of the discharge and the accuracy required will also influence the determination of the compositing period. For example longer compositing periods would be warranted when less stable unit process operations are being sampled.

Collection of Samples

1. Collection of Composite Samples for Liquid-Liquid Extraction

Collect a representative composite sample. The maximum time interval between aliquot samples shall be no longer than 30 minutes. The minimum aliquot size shall be 100 ml. The sample must be collected with an automatic sampler using the equipment and methods outlined below. Minimum composite volume must be 2 1/2 gallons.

Automatic Sample Collection

Sampler - A peristaltic pump automatic sampler with timer and a single glass compositing jug is required. The 2 1/2 - 3 gallon compositing bottle must be glass and cleaned

as outlined below. New unused tubing must be used for the sampling line and for the pump for each individual outfall or sample location. Vacuum type automatic samplers may be used provided that the sample chambers are glass and that they are cleaned after every use as outlined for glass composite containers. Place the sampler or composite container in an insulated chest and ice. Maintain the sample at 4°C during the compositing procedure. At the completion of the compositing period seal the container with a teflon lined cap. Place the container in an insulated shipping container, ice, and seal, then ship to the analytical laboratory. Maintain at 4°C during transport and storage prior to analysis.

When sampling raw untreated industrial discharges which are generally high in suspended solids it is imperative that adequate sample flow rate be maintained throughout the sample train in order to effectively transport the solids. In horizontal runs, the velocity must exceed the scour velocity, while in vertical runs the settling or the fall velocity must be exceeded several times to assure adequate transport of solids in the flow. The equipment used in sampling raw discharges then must have a minimum intake velocity of 2 feet per second. In the sampling of treated effluents just about any commerically available automatic liquid sampler could be used.

When more than one laboratory is involved in the analysis of the various parameters, the sample should if at all possible not be divided in the field but rather at the contractors' laboratory. For purpose of this program the composite will be divided into four parts, one part for metals analysis, one for pesticides and PCB's, one for GC/MS compounds and one for the classic parameters.

Blend the composite sample to provide a homogeneous mixture including a representative suspension of any solids in the container. No specific method is required, hand stirring with clean glass or teflon rods, mechanical paddles or magnetic mixing with teflon coated stirring bars may be used. Metal mixing devices may not be used.

Metals - Withdraw a well blended aliquot of the composite sample. Using a glass funnel, rinse the sample container with a small portion of the sample, then transfer

250 - 500 ml of sample to the bottle. Do not add any preservative to the sample just seal and prepare for shipment. All samples must be carefully identified using labeles supplied by EGD. Indicate on the label whether the sample is a raw discharge or treated effluent as shown. If sample is to be run on the plasma unit only indicate so at base of tag. Ship samples to the Chicago Regional Laboratory at the addressed shown.

U.S. Environmental Protection Agency
Region V, Central Regional Laboratory
1819 W. Pershing Road
Chicago, Illinois 60609

Raw discharge or treated effluent

EPA/EGD № V002200

Location _____

Sampler _____

Sample Point _____

Type Sample _____ Grab _____ Composite

Date _____ to _____

Time _____ to _____

Preservatives _____

Plasma only

Field Blank Procedure for Automatic Samplers

Blank Water - Blank water must be as free from organic interferences as possible. The analytical laboratory should supply this water in bulk glass containers (minimum of five liters) for field use. The supplying laboratory shall analyze the blank water to determine the organic background that may be present.

Procedure - All parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with methylene chloride is required when parts permit, i.e., are not susceptible to dissolution by the solvent. (Note: Tygon plastic tubing is a source of phthalate ester contamination. Where its use is required, i.e., in the peristaltic pump, the length must be kept as short as possible. Teflon is acceptable and may be used in other parts of the sampling system as in intake lines. In the field, pump two liters of blank water through the sampling line and pump tubing and discard. Then pump three liters of blank water through the system and collect as a blank in a 1-gallon sample bottle that has been prepared as described below. Seal the bottle with a Teflon lined cap. Immediately ice the blank (4° C) and maintain at (4°C) during the transport and storage prior to analysis.

Composite Container - Prepare narrow-mouth glass sample bottles for use by washing with hot detergent water and thoroughly rinsing with tap water and blank water. Heat the bottles at 400°C in a muffle-furnace or dry heat sterilizer for 30 minutes or alternatively, rinse with methylene chloride and air dry at room temperature protected from atomspheric or other sources of contamination. Caps for the bottles must be lined with Teflon which has been solvent rinsed as above.

2. Collection of Grab Samples

Collect grab samples (minimum of one per day) for the analysis of phenol, cyanide, and volatile organics (purgable). Collect samples from the raw process discharge, the treated effluent, and the treated effluent after chlorination, when chlorination is practiced. It is recommended that the samples be collected from mid-channel at mid-depth. Samples should be collected at a turbulent, well mixed section of the channel.

Cyanide (Total)

Container - Use new one-liter plastic bottles that will not contaminate the sample. Wash the bottles and caps with hot water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Pretreatment and Preservation - Oxidizing agents such as chlorine decompose many cyanides. Therefore, at time of collection, samples must be treated to eliminate such agents. Test a drop of the sample at the time of collection with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascrobic acid, a few crystals at a time, until a drop of the sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume. Then add 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12).

Seal the sample bottle and place in an insulated chest and ice (4°C). Seal the chest and ship to the analytical laboratory. Maintain at 4°C during transport and storage keep out of direct light prior to analysis.

Phenols

Container - Use new one-liter glass bottles. Wash the bottle and Teflon cap liner with hot water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Preservation - At the time of collection, acidify the sample by addition of phospheric acid or sulfuric to pH 4. Note volume of acid added on sample tag. Seal bottle, place in insulated chest and ice (4°C). Seal chest and ship to analytical laboratory. Maintain at 4°C during transport and storage. Keep out of direct light prior to analysis.

Organics (Purge and Trap Method)

Containers - Use 45 to 125 ml screw cap glass vials with Teflon faced silcone septa:

Vials[a]- Pierce #13074 or equivalent

Septa[a]- Pierce #12722 or equivalent

Wash the bottles, septa, and caps with hot water and thoroughly rinse with tap water and blank water. Heat the bottles and septa at 105°C for one hour, cool to room temperature in an enclosed contaminant free area. When cool, seal bottles with septa (Teflon side down) and screw cap. Maintain the bottles in this condition until just prior to filling with blank water or sample.

[a] Available from Pierce, Inc. Box 117, Rockford, IL 61105.

Collect duplicates 45-125 ml samples each time samples are collected. Two blank water samples, sealed in 45 ml vials, are to accompany the sample bottles during shipment to and from the sampling site. If preservation for residual chlorine is to be used, collect four samples during each sampling period. Two should be preserved and two not preserved. Two preserved and two non-preserved blanks are to be provided.

Filling and Sealing Bottles - Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) on the convex sample meniscus. Seal the sample with the screw cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal. The sample must remain hermetically sealed until it is analyzed.

Preservation - Preservative (sodium thiosulfate or sodium bisulfite) is used to stabilize samples containing residual chlorine. The production of chloroform and other haloforms continues in such samples if they are not stabilized. Waste streams that have been treated with chlorine should be tested on

site to determine whether or not preservative is needed. If preservatation is required, collect both preserved and non-preserved samples. Wrap the samples with water proof packing material, place in an insulated chest and ice at 4°C. Maintain at 4°C during transport and storage prior to analysis.

3. Identification of Samples

All samples and blanks must be carefully identified using water proof labels and water proof ink. Include the following information on the label: sample number, date and hour of sampling, complete information as to source and sampling point, preservative added, if any, and name of person collecting the sample (include address and/or phone number).