PART A

PROTOCOL FOR THE ANALYSIS OF PURGEABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

1. Scope and Application

1.1 This method is used for the determination of purgeable (volatile) organics. The complete list of compounds is provided in Table 1.

1.2 The method is for qualitative and quantitative analysis of these compounds in municipal and industrial wastewater treatment sludges. The procedure requires the use of a gas chromatography/mass spectrometer (GC/MS) as the final detector.

1.3 The method detection limit for each compound is very dependent on the compound characteristics and the particular sludge analyzed. However, typical detection limits are 2 to 5 µg/liter for publicly owned treatment works (POTW) sludges with 1 to 5% total solids.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of purge and trap systems and GC/MS and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. Summary of Method

2.1 An inert gas is bubbled through a 10-ml sludge aliquot contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.[1,2]

3. Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the

purge gas and organic compounds outgassing from the plumbing upstream of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from the interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with reagent water and analyzing it in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organic materials (particularly dichloromethane) through the septum seal into the sample during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. To reduce cross-contamination, it is recommended that the purging device and sample syringe be rinsed twice between samples with reagent water to check for cross-contamination. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds or high organohalide levels, it may be necessary to wash the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. Safety

4.1 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[3-5] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. 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.

5. Apparatus and Materials

5.1 Sampling

5.1.1 Vial - 25-ml capacity or larger, equipped with a screw cap with hole in center (Pierce No. 13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum - Teflon-faced (Pierce No. 12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for 1 hr before use.

5.2 Sample Preparation

5.2.1 Purge and Trap System. Assemble the system as depicted in Figures 1 and 2. A commercial version, such as the Tekmar Liquid Sample Concentrator Model LSC-1, or its equivalent, may be modified for use by replacing the standard purge tube with the purge tube shown in Figure 3. The trap is packed according to Figure 4. In order to function properly, the trap must be packed in the following order: Place the glass wool plug in the inlet end of the trap and follow with the OV-1, Tenax®, silica gel, charcoal, and finally, a second glass wool plug. Reversing the packing order, i.e., placing the charcoal in the trap first, will cause the silica gel and Tenax® layers to become contaminated with charcoal dust causing poor desorption efficiencies. Install the trap so that the effluent from the purging device enters the Tenax® end of the trap.

5.2.2 Glassware

5.2.2.1 Screw-cap vials, 40 ml with TFE-lined caps.

5.2.2.2 Graduated cylinder. 10 ml.

5.2.2.3 Volumetric flasks, 10 ml and 50 ml.

5.2.2.4 Round-bottom flask (optional), 250 ml for sample compositing.

5.2.3 Analytical balance, for standards preparation.

5.2.4 Roller mill and 1/8-in. stainless steel ball bearings.

5.2.5 Catalytic gas purifier.

5.2.6 Purging gas, He or N_2, water compressed, high-purity grade.

5.2.7 Syringes, 10 µl, 25 µl, 100 µl, 1 ml, and 10 ml gas tight.

5.2.8 Magnetic stirring motor with 2- to 2.5 cm TFE-coated spin bar.

5.3 For Quantitation and Identification

Gas chromatograph/mass spectrometer/data system, Finnigan 4000 or equivalent. The GC/MS interface should be a glass jet separator. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICP) and integration of the peaks. The GC/MS should be fitted with a stainless steel or glass column packed with 0.2% Carbowax 1500 on Carbopack C. Typical column dimensions are 1/8-in. OD stainless steel or 2-mm ID glass and 2.4 to 2.8 m in length.

6. Reagents

6.1 Trap Packing Materials

6.1.1 3% OV-1 on Chromosorb-W 60/80 mesh.

6.1.2 Tenax-GC®, 60/80 mesh.

6.1.3 Silica gel, Davison Grade 15, 35/60 mesh or equivalent.

6.1.4 Coconut charcoal, 26 mesh Barnaby Chaney No. CA-580-26, Lot No. M-2649 or equivalent.

6.2 Reagent Water (purgeable organic-free). Generate organic-free water by passing tap water through a carbon filter bed containing about 1 lb of activated carbon and purging overnight with prepurified nitrogen. A Millipore Super-Q Water System or its equivalent may be used to generate organic-free deionized water. Organic-free water can also be prepared by boiling distilled water for 15 min. While still hot, transfer to a glass-stoppered bottle. Cool to room temperature. Continuously purge the water during storage. Test organic-free water daily by analyzing according to the method described in Section 10.

6.3 Methanol. "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.4 Analytical Standards

6.4.1 Primary Standards. Prepare standard stock solutions (at 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 component so that the two drops fall into the alcohol and do not come in contact with the neck of the flask. Prepare gaseous standards, e.g., vinyl chloride, in a similar manner using a 10.0 ml valved gas-tight syringe with a 2-in. needle. Fill the syringe (10.0 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 and slowly inject the standard into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask and use the weight gain to calculate the concentration of the standard. Dilute to volume, mix, and transfer to a 10-ml screw-cap vial with a silicone rubber/TFE cap liner. Gas stock standards are generally stable for at least 1 week when maintained at less than 0°C. With the exception of 2-chloroethylvinyl ether, stock standards of compounds that boil above room temperature are generally stable for at least 4 weeks when stored at 4°C. (Safety Caution: Because of the toxicity of most organohalides, dilutions should be made in a glove box suitable for handling carcinogens. It is advisable to use an approved respirator when high concentrations of such materials must be handled in a fume hood.)

6.4.2 Working Standards. From the primary dilutions, prepare 10 ml of a multicomponent secondary dilution mixture in methyl alcohol at a concentration of 50 ng/µl containing each of the compounds to be determined. Prepare 50 ml of a 50-ng/ml standard from the 50 ng/µl standard by dosing 50.0 µl into 50.0 ml of organic-free water. Additional working standards should be prepared as required to bracket concentrations of compounds for referee analyses.

6.5 Internal Standard Spiking Solution. From stock standard solutions prepared as above, add a volume to give 1,000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic-free water (blank water) contained in a 50-ml volumetric flask, mix, and dilute to volume. Dose 9.0 µl of this internal standard spiking solution into every sample and reference standard analyzed. Prepare a fresh method recovery spiking solution on a weekly basis.

6.6 Surrogate Standard Spiking Solution. Select a minimum of three surrogate compounds from Table 2. Prepare and store stock standard and spiking solutions as described in Section 6.5

7. Calibration

7.1 Establish GC/MS operating parameters equivalent to those indicated in Section 11. The purge-trap GC/MS system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External Standard Calibration Procedure

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to 10.0-ml aliquots of reagent water. Analyze immediately. One of the external standards should be at a concentration near, but above, the

method detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Analyze each calibration standard with the purge-trap GC/MS system described in Section 11. Tabulate peak heights or area responses against the concentration of the analyte in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration analyzed (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 Verify the working calibration curve or calibration factor on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal Standard Calibration Procedure. To use this approach, select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The internal standards used for this procedure should include bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Because of the limitations, no additional internal standards can be suggested that are applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a 10.0-ml aliquot of reagent water, add 9.0 µl of the internal standard spiking solution, and analyze immediately. One of the standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Analyze each calibration standard with the purge-trap GC/MS system described in Section 11. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = (A_s B_{is})/(A_{is} B_s) \qquad \text{(Eq. 1)}$$

where: A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

B_{is} = Mass of the internal standard (ng).

B_s = Mass of the parameter to be measured (ng).

If the RRF value over the working range is a constant (< 10% RSD), the RRF can be assumed to be nonvariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RRF.

7.3.3 Verify the working calibration curve or RRF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Daily Calibration of the Gas Chromatography-Mass Spectrometry (GC/MS) System

7.4.1 Evaluate the system performance each day that it is used for the analysis of samples or blanks by injecting 20 ng of p-bromofluorobenzene (BFB) into the GC inlet. Check to be sure that the performance criteria listed in Table 2 are met. If the criteria are not met, the instrument must be retuned to satisfy those criteria before continuing.

To perform the calibration test, the following instrumental parameters are required.

Electron energy, 70 eV (nominal)
Mass range, m/e 20-275
Scan time, 5 sec or less.

7.4.2 At the beginning of each working day, verify the calibration of the system by analyzing a standard (Section 7.3.3).

8. Quality Control

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. After January 1, 1982, ongoing performance checks must be compared with established performance criteria to determine if the results of anayses are within accuracy and precision limits expected

of the method. 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 8.1. In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted 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 8.1. The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1 Demonstrate Acceptable Performance. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure.

8.1.1 For each compound to be measured, select a spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check standard in methanol 1,000 times more concentrated than the selected concentrations.

8.1.2 Syringe 10.0 µl of the check standard to each of a minimum of four 10.0-ml aliquots of reagent water. A representative sludge can be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.1.3 Calculate average recovery (R) and standard deviation (s), in percentage recovery, for the results. Sludge background corrections must be made before R and s calculations are performed.

8.1.4 Using the appropriate data from Table 7, determine the recovery and single operator precision expected for the method for each parameter, and compare these results to the values calculated in Section 8.1.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.1.5 After January 1, 1982, the values for R and s must meet rigid method performance criteria provided by the U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, before any samples may be analyzed.

8.2 Precision and Accuracy Statement. The analyst must calculate method performance criteria for each of the surrogate standards.

8.2.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.1.3:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

The UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance. After January 1, 1982, the control limits above must be replaced by method performance criteria provided by the U.S. Environmental Protection Agency.

8.2.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of sludge as described in Section 8.1.2, followed by the calculation of R and s. Alternately, the analyst may use four sludge data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.3 Surrogate Spikes. The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 13.3. The laboratory should monitor the frequency of suspect data to ensure that it remains at or below 5%.

8.4 System Blanks. Analyze daily an organic-free water blank spiked with 75 ng of BFB prior to the analysis of samples. The intensities of EICPs for the internal standards gives an overall check of the system sensitivity. Check the spectrum obtained for BFB and adjust the mass spectrometer tuning parameters as required to meet the ion abundance criteria specified in Table 3.

8.5 Fortified and Duplicate Samples

8.5.1 Sample Selection. Analyze all samples in duplicate. Using the procedures described in Section 8.5.2, spike and analyze two additional aliquots. Analyze a third unspiked aliquot on the same day that the spiked aliquots are analyzed.

8.5.2 Spiking Procedures. Determine the volume of an empty vial to within 0.5 ml by filling the vial with volatile organics-free water and then measuring the volume of water with a graduated cylinder. Mark the volume on the vial and allow it to air-dry. Add 3 to 5 precleaned ball bearings to the vial. Transfer the sample to the vial and spike with all of the compounds identified and the representative purgeable compounds listed in Table 4 at two times the concentration found in the unspiked sample or at 10 times the lower limit of detection, whichever

is greater. Seal the vial and place on a roller mill in a 4°C cold room; tumble the sample for 16 hr before analysis.

8.6 Field Blanks. Analyze a field blank for each day of sampling at each plant if available.

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

9. Sampling and Preservation

9.1 Sampling. Samples must be collected in 40-ml screw-cap vials with zero headspace and sealed with TFE-lined septa. Before using, wash all sample bottles and TFE seals in detergent and rinse with tap water and finally distilled water. Allow the bottles and seals to air-dry at room temperature, heat in a 105°C oven for 1 hr, then allow to cool in an area known to be free of organics.

NOTE: Do not heat the TFE seals for extended periods of time (more than 1 hr) because the silicone layer slowly degrades at 105°C.

9.2 Preservation. As a general guideline, ice samples immediately after collection, refrigerate at 4°C, and purge within 10 days. Desorb and complete the analyses immediately after purging.

9.3 Special Preservation for Aromatics. Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions.[2] Refrigeration alone may not be adequate to preserve these compounds in sludges for more than 7 days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 ml of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.1. If chlorine residual is present, add sodium thiosulfate to another sample container and fill as in Section 9.1 and mix thoroughly.

10. Sample Preparation and Purging

10.1 Sample Compositing. Sludge samples for the analysis of purgeable compounds are typically collected as grab samples. Several samples may be composited with minimal analyte losses. Chill the appropriate sample vials and a clean 250-ml round-bottom flask by immersing them in an ice bath. Gently pour the entire contents of each vial into the flask and swirl gently. Vigorous mixing must be avoided

to prevent analyte losses. Prepare a number of composite aliquots sufficient for subsequent analysis by gently pouring the composited sludge into precleaned 40-ml vials. Seal the vials with zero headspace using TFE-lined septa and screw-caps. Store the composited samples at 4°C.

10.2 Sample Purging. Condition the adsorbent trap at 200°C with nitrogen or helium flow. Allow the trap to cool to ambient room temperature and turn off the gas flow through the trap and purge tube before sample purging. Remove an aliqout of the sludge sample by gently pouring the sludge into a 10-ml graduated cylinder. Fill the cylinder just to the 10.0-ml mark. Dose the aliquot with 9 µl of the internal standard spiking solution by slowly injecting the solution (with a 10-µl syringe) 3 to 4 cm under the surface of the sludge. Gently pour the spiked sludge aliquot into the purge tube. If solids adhere to the inner walls of the graduated cylinder, rinse the cylinder with a small amount of organics-free water and add the rinsings to the purge tube. Seal the purge tube and turn on the purge gas flow (40 ml/min). Purge the sample for 12 min while maintaining the sample and trap at ambient room temperature.

11. Analysis of the Sample Purge

Analyze the sample purge by GC/MS using the Carbowax 1500/Carbopack C column described in Section 5.2 operated with a helium carrier gas flow of 30 ml/min. Heat the trap to 180 to 200°C. Backflush it for 3 min into the gas chromatograph, with the oven at 40°C. At the end of the 3-min period, program the column at 10°C/min to 170°C. Hold at this temperature until all compounds have eluted. An example of the separation achieved by this column is shown in Figure 5. Relative retention times for the purgeable compounds are listed in Table 5. The purging device must be removed from the instrument and thoroughly rinsed with volatile organic-free water between each sample. The trap must be conditioned at 200°C with flow for 10 min between each sample.

12. Qualitative Identification

12.1 Obtain EICPs for the primary ion (Table 5) and, if available, at least two secondary ions for each parameter of interest. The following criteria must be met to make a qualitative identification.

12.1.1 The characteristic ion of each parameter of interest must maximize in the same or within one scan of each other.

12.1.2 The retention time must fall within ± 30 sec of the retention time of the authentic compound.

12.1.3 The relative peak heights of the three characteristic ions in the EICPs must fall within ± 20% of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

12.2 Structural isomers that have very similar mass spectra and less than 30 sec difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When a parameter has been identified, the quantitation of that parameter should be based on the integrated abundance from the EICP of the first listed characteristic ion given in Table 5. If the sample produces an interference for the primary ion, use a secondary characteristic ion to quantitate. Quantitation may be performed using the external or internal standard techniques.

13.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the area of the characteristic ion using the calibration curve or calibration factor in Section 7.2.

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the relative response factor (RRF) determined in Section 7.3 and Equation 2.

$$\text{Concentration } \mu g/\ell = \frac{(A_s)(B_{is})}{(A_{is})(RRF)(V)} \qquad \text{(Eq. 2)}$$

where: A_s = Area of the characteristic ion for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

B_{is} = Mass of the internal standard (ng).

V = Volume of sample purged (ml).

13.2 Report results in micrograms per liter. The results for cis- and trans-1,3-dichloropropene should be reported as total 1,3-dichloropropene (Storet No. 34561, CAS No. 542-75-6). When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 If any of the surrogate standard recoveries fall outside the control limits which were established as directed in Section 8.3, data for all parameters in that sample must be labeled as suspect.

14. Method Performance

Performance data for the application of this method to both POTW and industrial sludges are shown in Table 7. These data were generated by analyzing duplicate aliquots of unspiked sludge and triplicate aliquots of sludge spiked at 2, 20, and 200 times the typical detection limits for representative purgeable compounds. The method was evaluated using three POTW sludges and two industrial sludges. The recoveries and standard deviations represent the results from all determinations from each sludge type. The mean RSD for triplicates illustrate the precision for triplicate analyses. Although the recoveries observed were generally good, many recovery determinations were influenced by relatively high concentrations of the spiking compounds in the unspiked sludges. In most cases, the results of recovery determinations for compounds present in the unspiked aliquots at concentrations in excess of the spiking level were not included in Table 7. The small mean RSD for triplicates observed for most compounds indicate that the largest component of the method variance can be attributed to differences in the characteristics of the test sludges. These data represent the results from one laboratory.

15. References

1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, 66, p. 739 (1964).

2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Measurement of Organic Pollutants in Water and Wastewater, C. E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publication 686, 1978.

3. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publication No. 77-206, August 1977.

4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

16. Additional Sources

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, March 1977, Revised April 1977. Effluent Guidelines Division, Washington, DC 20460.

2. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, OH 45268. In preparation.

3. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. In preparation.

4. Budde, W. L., and J. W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

5. Kleopfer, R. D., "Priority Pollutant Methodology Quality Assurance Review," U.S. Environmental Protection Agency, Region VII, Kansas City, KS. Seminar for Analytical Methods for Priority Pollutants, Norfolk, VA, January 17-18, 1980, U.S. Environmental Protection Agency, Office of Water Programs, Effluent Guidelines Division, Washington, D.C. 20460.

TABLE 1. PURGEABLE ORGANIC PRIORITY POLLUTANTS

Compound	STORET No.	CAS No.
Acrolein	34210	107-02-8
Acrylonitrile	34215	107-13-1
Chloromethane	34418	74-87-3
Dichlorodifluoromethane	32105	75-71-8
Bromomethane	34413	74-83-9
Vinyl chloride	39175	75-01-4
Chloroethane	34311	75-00-3
Dichloromethane	34423	75-09-2
Trichlorofluoromethane	34488	75-69-4
1,1-Dichloroethene	34501	75-35-4
1,1-Dichloroethane	34496	75-34-3
trans-1,2-Dichloroethene	34546	540-59-0
Chloroform	32106	67-66-3
1,2-Dichloroethane	34531	107-06-2
1,1,1-Trichloroethane	34506	71-55-6
Carbon tetrachloride	32102	56-23-5
Bromodichloromethane	32101	75-27-4
1,2-Dichloropropane	34541	78-87-5
Benzene	34030	71-43-2
trans-1,3-Dichloropropene	34561	542-75-6
Trichloroethene	39180	79-01-6
cis-1,3-Dichloropropene	34561	542-75-6
Dibromochloromethane	34306	124-48-1
1,1,2-Trichloroethane	34511	79-00-5
2-Chloroethylvinyl ether	34576	110-75-8
Bromoform	32104	75-25-2
Tetrachloroethane	34516	127-18-4
Toluene	34010	108-88-3
1,1,2,2-Tetrachloroethane	34475	79-34-5
Chlorobenzene	34301	108-90-7
Ethylbenzene	34371	100-41-4

TABLE 2

SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	Retention Time (minutes)[a]	Primary Ion	Secondary Ions
Surrogate Standards			
Benzene d-6	17.0	84	-
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane d-4	12.1	-	-
1,4-Difluorobenzene	19.6	114	63,88
Ethylbenzene d-5	26.4	-	-
Ethylbenzene d-10	26.4	98	-
Fluorobenzene	18.4	96	70
Pentafluorobenzene	23.5	-	-
Internal Standards			
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	ND	77	79, 156
1,4-Dichlorobutane	ND	55	90, 92

a For chromatographic conditions, see Table 5.

TABLE 3. p-BROMOFLUOROBENZENE[a] IONS AND ION ABUNDANCE CRITERIA

m/e	Ion abundance criteria
50	25-40% of m/e 95
75	30-60% of m/e 95
95	base peak, 100% relative abundance
96	5-9% of m/e 95
173	< 2% of m/e 95
174	> 50% of m/e 95
175	5-9% of m/e 174
176	> 95% but < 101% of m/e 95
177	5-9% of m/e 176

a Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000 (1979).

TABLE 4. REPRESENTATIVE PURGEABLE COMPOUNDS FOR RECOVERY STUDIES

Benzene
Carbon tetrachloride
Chlorobenzene
Chloroform
1,2-Dichloroethane
1,1-Dichloroethene
Ethyl benzene
Tetrachloroethene
1,1,1-Trichloroethane
Trichloroethene
Vinyl chloride

TABLE 5. RELATIVE RETENTION TIMES OF PURGEABLE PRIORITY POLLUTANTS[a]

Compound	RRT[b]
Chloromethane	0.116
Bromomethane	0.146
Dichlorodifluoromethane	0.169
Vinyl chloride	0.179
Chloroethane	0.209
Dichloromethane	0.312
Trichlorofluoromethane	0.435
1,1-Dichloroethene	0.475
Bromochloromethane (IS)	0.502
1,1-Dichloroethane	0.545
trans-1,2-Dichloroethene	0.585
Chloroform	0.621
1,2-Dichloroethane	0.661
1,1,1-Trichloroethane	0.728
Carbon tetrachloride	0.751
Bromodichloromethane	0.784
Bis-chloromethyl ether	Unknown[c]
1,2-Dichloropropane	0.854
trans-1,3-Dichloropropene	0.870
Trichloroethene	0.900
Benzene	0.917
Dibromochloromethane	0.934
cis-1,3-Dichloropropene	0.937
1,1,2-Trichloroethane	0.937
2-Chloroethylvinyl ether	Unknown[d]
2-Bromo-1-chloropropane (IS)	1.000
Bromoform	1.073
1,1,2,2-Tetrachloroethane	1.206
Tetrachloroethene	1.213
1,4-Dichlorobutane (IS)	1.236
Toluene	1.292
Chlorobenzene	1.412
Ethylbenzene	1.641
Acrolein	Unknown[e]
Acrylonitrile	Unknown[e]

a These data were obtained under the following conditions: GC column - glass, 8-ft long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; carrier flow - 30 ml/min; oven temperature - initial 40°C held for 3 min, programmed 10°C/min to 170°C and held until all compounds eluted.

b Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 903 sec.

c Bis-Chloromethyl ether has a half-life of about 10 sec in aqueous mixtures.

d 2-Chloroethylvinyl ether may be unstable in aqueous mixtures. Retention time is unknown.

e Acrolein and acrylonitrile do not purge efficiently from aqueous mixtures. Retention times under these conditions are not known.

TABLE 6. CHARACTERISTIC IONS OF PURGEABLE ORGANICS

Compound	EI ions (relative intensity)	Ion used to quantify
Chloromethane	50(100); 52(33)	50
Bromomethane	94(100); 96(94)	94
Dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
Vinyl chloride	62(100); 64(33)	62
Chloroethane	64(100); 66(33)	64
Dichloromethane	49(100); 51(33); 84(86); 86(55)	84
Trichlorofluoromethane	101(100); 103(66)	101
1,1-Dichloroethene	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-Dichloroethene	64(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
Trichloroethene	95(100); 97(66); 130(90); 132(85)	130
Benzene	78(100); 52(15)	78
Dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-Dichloropropene	75(100); 77(33)	75
1,1,2-Trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
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-Tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
Tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
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

TABLE 7. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Compound	Three POTW Sludges						Two Industrial Sludges					
	Spike Recovery						Spike Recovery					
	Determinations	Spike Level (µg/ℓ) Min	Max	Mean (%)	Standard deviation	Mean RSD for tripl. (%)	Determinations	Spike Level (µg/ℓ) Min	Max	Mean (%)	Standard deviation	Mean RSD for tripl. (%)
Benzene	17	1	100	160	55	16	15	1	100	98	25	16
Carbon tetrachloride	12	100	1,000	0	-	-	12	100	1,000	43	50	8
Chloroform	23	2	200	100	58	20	17	2	200	76	22	20
1,1-Dichloroethane	27	5	500	170	53	15	15	5	500	110	51	28
Tetrachloroethane	15	3	300	150	33	16	12	3	300	150	70	24
Vinyl chloride	18	50	500	130	38	14	16	5	500	110	47	13
1,2-Dichloroethane	27	5	500	140	51	14	12	5	500	100	28	16
Trichloroethene	18	20	200	160	69	24	12	2	200	140	44	21
1,1,1-Trichloroethane	21	16	1,600	130	47	23	15	16	1,600	110	40	11
Chlorobenzene	21	2	200	120	36	16	15	2	200	160	62	14
Ethyl benzene	18	5	500	120	26	15	12	5	500	150	55	14

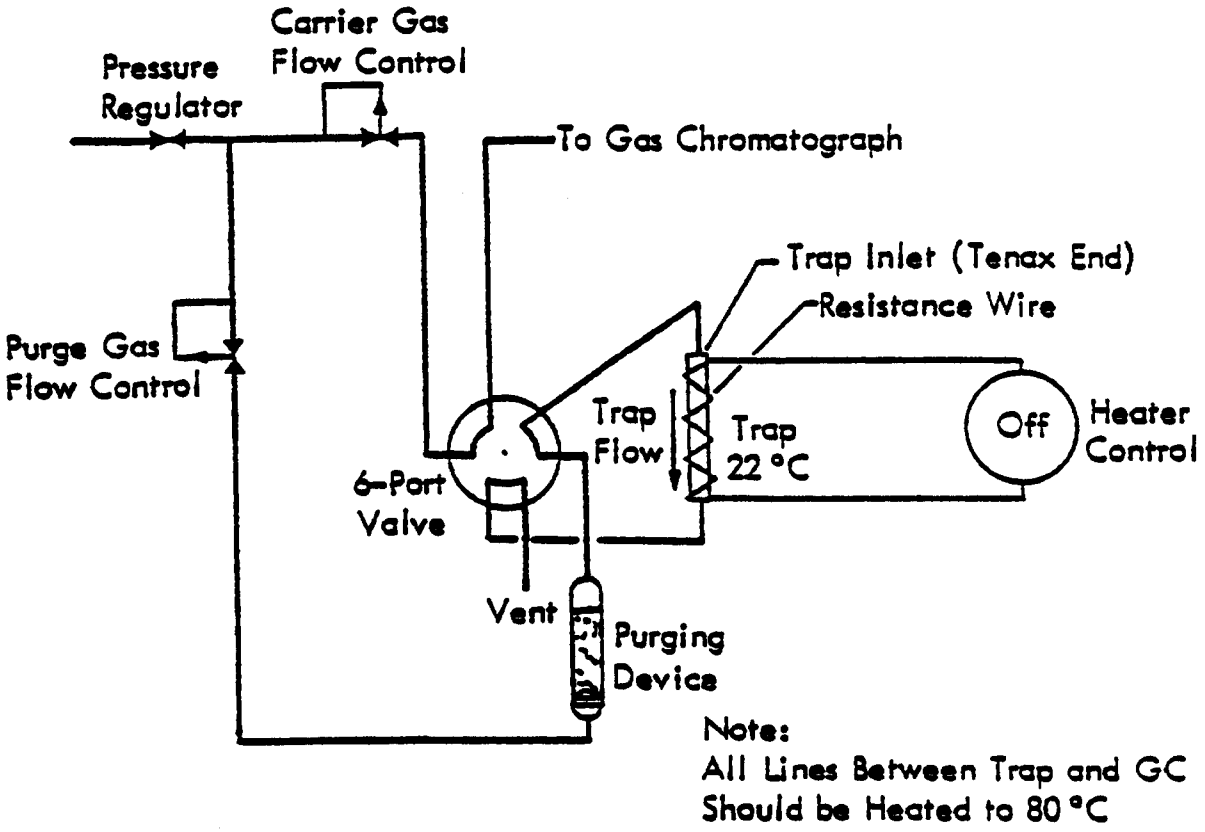

Figure 1. Schematic of the purge-trap system in the purge mode.

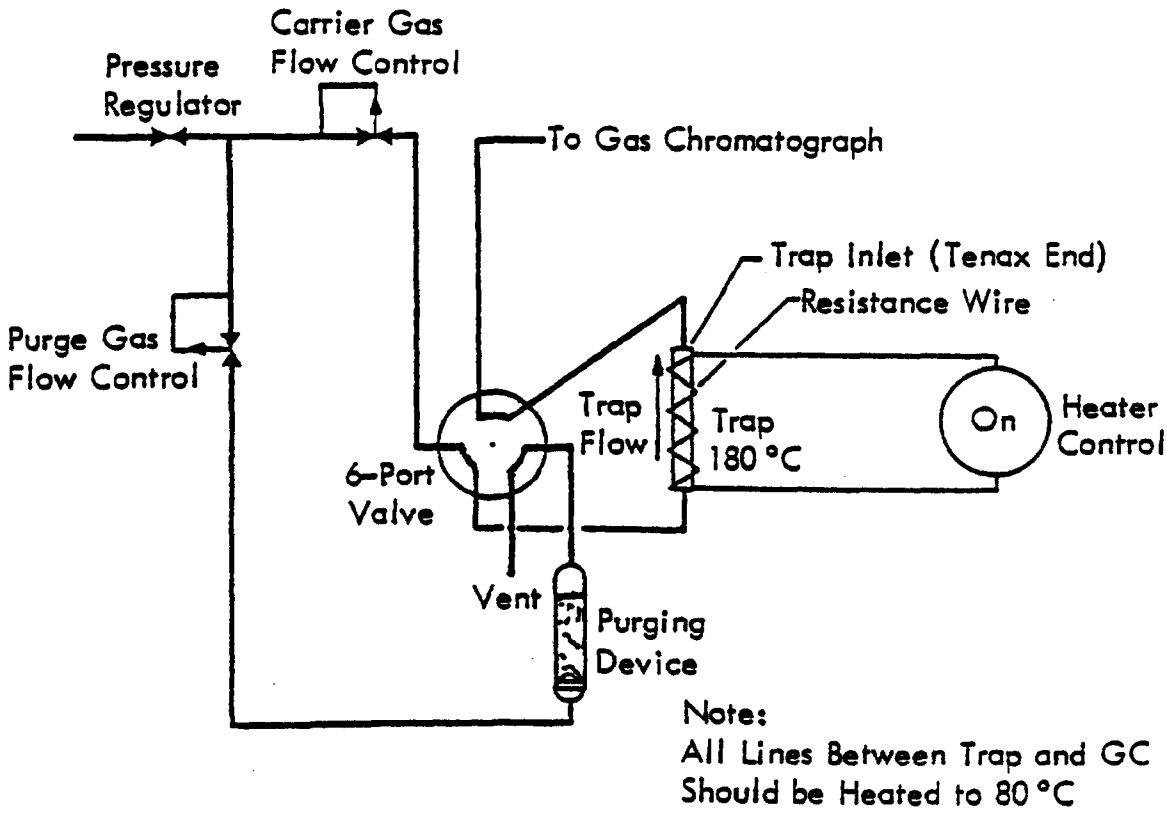

Figure 2. Schematic of the purge-trap system in the desorb mode.

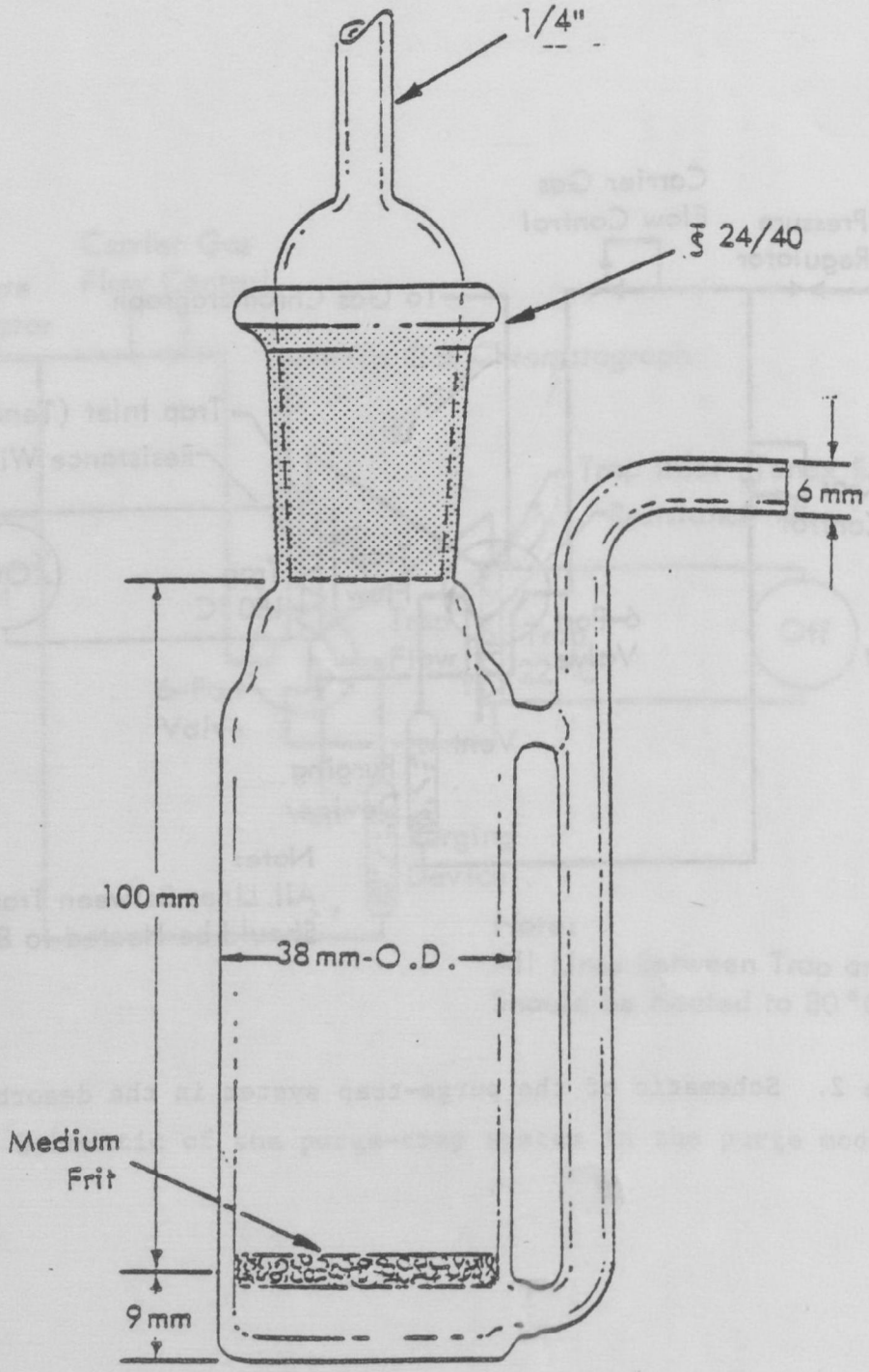

Figure 3. Bottom frit purge tube.

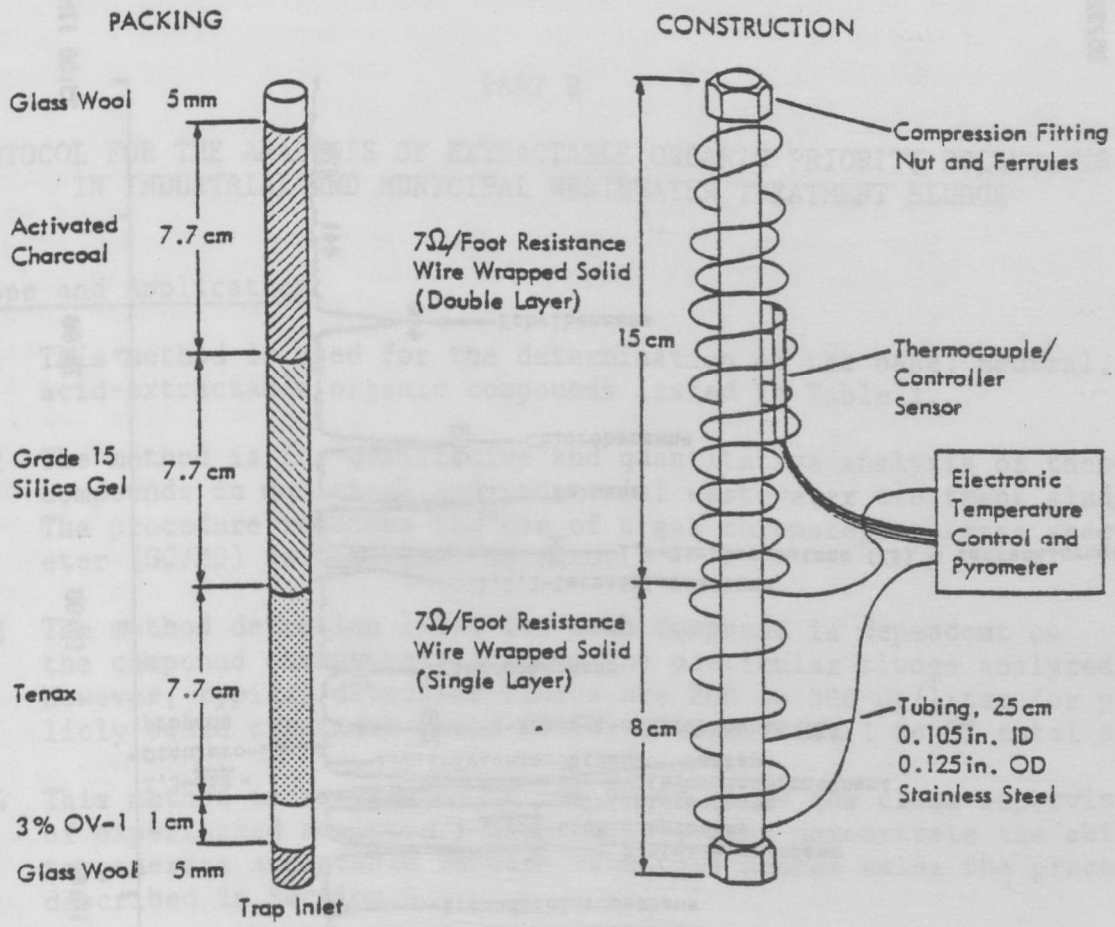

Figure 4. Trap packings and construction.

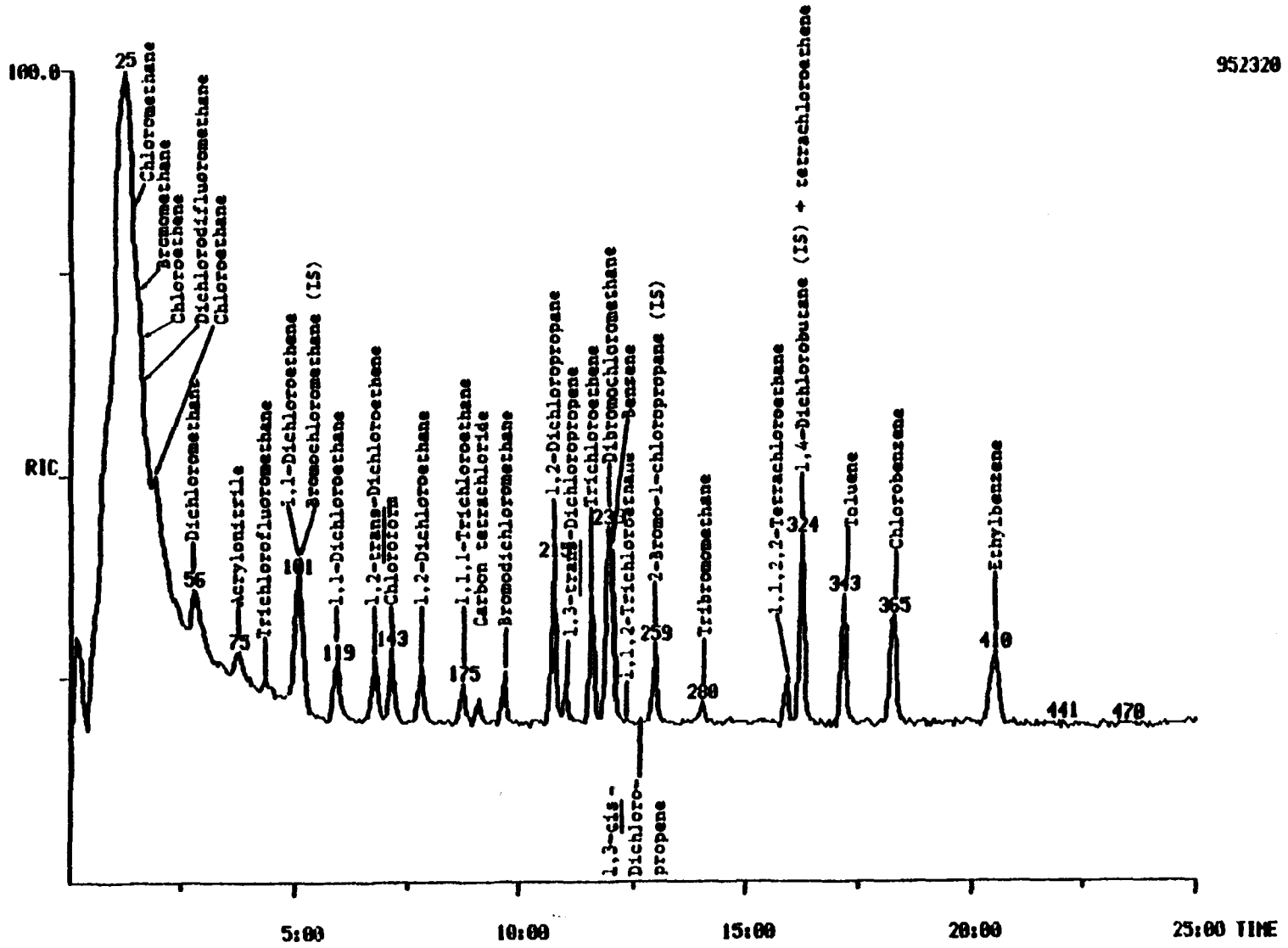

Figure 5. GC/MS chromatogram for the purgeable compounds.

PART B

PROTOCOL FOR THE ANALYSIS OF EXTRACTABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

1. Scope and Application

1.1 This method is used for the determination of the base, neutral, and acid-extractable organic compounds listed in Table 1.

1.2 The method is for qualitative and quantitative analysis of these compounds in municipal and industrial wastewater treatment sludges. The procedure requires the use of a gas chromatograph/mass spectrometer (GC/MS) as the final detector.

1.3 The method detection limit for each compound is dependent on the compound characteristics and the particular sludge analyzed. However, typical detection limits are 200 to 300 µg/liter for publicly owned treatment works (POTW) sludges with 1 to 5% total solids.

1.4 This method is restricted to use by or under the close supervision of experienced analysts. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. Summary of Method

This method (Figure 1) uses repetitive solvent extraction aided by a high-speed homogenizer. The extract is separated by centrifugation and removed with a pipette or syringe. Sludges are extracted at pH $\geq$ 11 to isolate base/neutral compounds and at pH $\leq$ 2 to isolate acidic compounds. Extracts containing base/neutral compounds are cleaned by silica gel or florisil chromatography or by gel permeation chromatography (GPC). Extracts containing the acidic compounds are cleaned by GPC. The organic priority pollutants are determined in the cleaned extracts by capillary column or packed column GC/MS. Option A is preferred since capillary GC/MS (HRGC/MS) allows easier data interpretation. Qualitative identification of compounds is performed using the retention time and the relative abundance of three characteristic ions. Quantitative analysis is performed using external or internal standard techniques with a single characteristic ion.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in GC/MS chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and reagent water. It should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality dichloromethane may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It should be stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the wastewater treatment system being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve acceptable detection limits.

4. Safety

4.1 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.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mamalian carcinogens; benzo[a]anthracene, benzidine, 3,3'-dichlorobenzidine, benzo[a]pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo[a,h]anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls.

5. Apparatus and Materials

5.1 Sampling, Extraction, and Extract Cleanup

5.1.1 Emulsifier-Tekmar Tissumizer® or equivalent, high capacity.

5.1.2 Centrifuge, capable of handling 200 ml bottles.

5.1.3 Centrifuge bottles with TFE lined screw caps, 200 ml.

5.1.4 Kuderna-Danish (K-D) glassware.

5.1.4.1 Snyder columns, 3 bulb, macro.

5.1.4.2 Snyder columns modified micro.

5.1.4.3 Evaporating flasks, 500 ml, 250 ml.

5.1.4.4 Receiver ampuls 5 and 10 ml, graduated, with spring attachment.

5.1.4.5 Beakers, 100 ml.

5.1.5 Water or steam bath for Kuderna-Danish concentrations.

5.1.6 Chromatographic (drying) Column - Pyrex (400 mm x 20 mm ID) without a fritted plate.

5.1.7 Separatory funnels, 500 ml with TFE stopcock.

5.1.8 Syringe, 100 ml, Pyrex, with long needle.

5.1.9 Graduated cylinder, 100 or 250 ml.

5.1.10 Vials, 2 ml, 4 ml, and 8 ml with TFE lined screw caps.

5.1.11 Sample bottles, 1,000 ml or 4,000 ml glass with TFE lined screw caps.

5.1.12 Disposable pipettes, for transferring extracts.

5.1.13 Gel Permeation Chromatograph (GPC), Analytical Biochemical Labs, Inc., GPC Autoprep 1002 or equivalent including:

5.1.13.1 Glass column 25 mm ID x 60-70 mm packed with 70 g of Bio-Beads SX-3.

5.1.13.2 Chromatographic pump, operated at 5 ml/min with 350-700 millibars (5-10 psi).

5.1.13.3 Injector with loop.

5.1.13.4 Syringe filter holder, stainless steel and TFE, Gelman 4310 or equivalent.

5.1.13.5 Spectrophotometric chromatographic detector, 254 nm, with strip chart recorder (optional, for GPC calibration).

5.1.14 Chromatographic column, 200 mm x 20 mm ID, with solvent reservoir (250 ml) and TFE stopcock.

5.1.15 Roller mill.

5.1.16 Bottles, 500 ml, brown glass.

5.2 For Identification and Quantitation

5.2.1 Gas chromatograph/mass spectrometer with data system, Finnigan 4000 or equivalent. The GC/MS interface should include a glass jet separator and a direct capillary line. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICPs) and integration of the peaks. The GC should have injectors for both packed columns and a splitless Grob-type capillary injector. GC columns required are:

5.2.1.1 0.9 to 1.8 m x 2 mm ID glass packed with 1% SP-1240-DA on 100/120 mesh Supelcoport.

5.2.1.2 15-30 m x 0.2 mm ID wall coated open tubular capillary column coated with SE-54 providing at least 25,000 effective theoretical plates, measured at C_{13}, or a 1.8 m x 2 mm ID glass packed with 3% SP-2250 on 100/120 mesh Supelcoport.

5.2.2 Gas chromatograph/flame ionization detector with the same GC columns as for the GC/MS system.

6. Reagents

6.1 For Extraction and Extract Cleanup

6.1.1 Dichloromethane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.2 Hexane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.3 Acetone, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.4 Hydrochloric acid solution (6N). Slowly add 100 ml of HCl (12N) to 100 ml of reagent water.

6.1.5 Sodium hydroxide solution (6N). Dissolve 24 g NaOH in reagent water and dilute to 100 ml.

6.1.6 Sodium sulfate (Na_2SO_4), Anhydrous, granular. Clean by overnight Soxhlet extraction with dichloromethane, drying in an oven at 110 to 160°C oven, and then heating to 650°C for 2 hr. Store in a glass jar tightly sealed with TFE-lined screw cap.

6.1.7 Silica gel, 75/150 mesh. Clean silica gel for 16 hr by Soxhlet extraction with dichloromethane. Dry and activate for 16 hr at 160°C. Deactivate by adding 3% water (by weight) and mixing for at least 4 hr on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.8 Florisil 60/100 mesh, Floridan. Clean florisil for 16 hr by Soxhlet extraction with dichloromethane. Dry and activate for 16 hr at 160°C. Deactivate by adding 1% water by weight and mixing for at least 4 hr on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.9 Glass wool. Clean glass wool by thorough rinsing with hexane, dried in a 100°C oven, and stored in a hexane rinsed glass jar with TFE lined screw cap.

6.1.10 Boiling chips - silica or carborundum.

6.1.11 GPC Calibration Solutions

6.1.11.1 Corn oil, 200 mg/ml in dichloromethane.

6.1.11.2 Pentachlorophenol and di-n-octylphthalate, 4 mg/ml each in dichloromethane.

6.2 For Identification and Quantitation

6.2.1 Analytical Standards

6.2.1.1 Prepare stock solutions from the pure compounds by dissolving 10 mg quantities into 10 ml of dichloromethane. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.2.1.2 Transfer the stock standard solutions into TFE sealed screw cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, that can be used to determine the accuracy of calibration standards.

6.2.1.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicate a problem.

6.2.1.4 Prepare mixed analytical standards by diluting aliquots of the stock solutions. Analytical standards for all semivolatile compounds should be prepared in three solutions. The acids standard should contain each of the phenolic compounds at concentrations in the range of 50 to 200 ng/µl. Base, neutral, and pesticide (B/N/P) compounds should be split between two solutions, both at concentrations in the range of 20 to 100 ng/µl. One standard should contain the more unstable B/N compounds listed in Table 2, and the second should contain the remaining B/N/P compounds. All working standards must include d_{10}-anthracene at 20 ng/µl.

6.2.1.5 Prepare mixed spiking solutions by serial dilution from the individual stock solutions prepared above. The specifications for spiking solutions for individual samples are described in Section 8.3.2.

7. Method Calibration

7.1 Establish GC/MS operating parameters equivalent to those indicated in Section 12. The GC/MS system can be calibrated using the external standard technique or the internal standard technique.

7.2 External Standard Calibration Procedure

7.2.1 Prepare calibration tandards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with dichloromethane. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 1 to 2 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected in the calibration factor is a constant over the working range (< 10% relative standard deviation RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 Verify the working calibration curve or calibration factor on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal Standard Calibration Procedure. To use this approach, select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The internal standards used for this procedure must include d_{10}-anthracene. Because of limitations listed above, no additional internal standards can be suggested that are applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with dichloromethane. One of the standards should be at a concentration near, but above, the method detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = (A_s B_{is})/(A_{is} B_s) \qquad \text{(Eq. 1)}$$

where A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

B_{is} = Mass of the internal standard (ng).

B_s = Mass of the parameter to be measured (ng).

If the RRF value over the working range is a constant (< 10% RSD), the RRF can be assumed to be nonvariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} vs. RRF.

7.3.3 Verify the working calibration curve or RRF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Daily Calibration of the GC/MS System

7.4.1 At the beginning of each day, check the calibration of the GC/MS system and adjust if necessary to meet DFTPP specifications (Section 7.4.3). Each day base/neutrals are measured, the column performance specification (Section 12) with benzidine must be met. Each day the acids are measured, the column performance specification (Section 12) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

7.4.2 To perform the calibration test of the GC/MS system, the following instrumental parameters are required.

Electron energy, 70 eV (nominal)

Mass range, m/e 40-475

Scan time, 3 sec or less for acids or base/neutrals with the packed column, 1 sec or less for base/neutrals with the capillary column.

7.4.3 Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ng DFTPP and check to ensure that performance criteria listed in Table 3 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

7.4.4 At the beginning of each working day, verify the calibration of the GC/MS system by injecting a standard mixture (Section 7.3.3).

7.4.5 For instrument performance verification, to each acid and base/neutral extract and each standard analyzed, add an amount of d_{10}-anthracene immediately prior to injection such that 40 ± 4 ng will be injected.

8. Quality Control

8.1 Demonstrate Acceptable Performance

Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure.

8.1.1 For each compound to be measured, select a spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check standard in acetone 1,000 times more concentrated than the selected concentrations.

8.1.2 Add 80 µl of the check standard to each of a minimum of four 80 ml aliquots of reagent water with a syringe. A representative sludge can be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.1.3 Calculate average recovery (R) and standard deviation (s), in percentage recovery, for the results. Sludge background corrections must be made before R and s calculations are performed.

8.1.4 Using the appropriate data from Tables 13-15, determine the recovery and single operator precision expected for the method for each parameter, and compare these results to the values calculated in Section 8.1.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.1.5 After January 1, 1982, the values for R and s must be rigid method performance criteria provided by the U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, before any samples may be analyzed.

8.2 Precision and Accuracy Statement. The analyst must calculate method performance criteria for each of the surrogate standards.

8.2.1 Calculate upper and lower control limits for method performane for each surrogate standard, using the values for R and s calculated in Section 8.1.3:

$$\text{Upper Control Limit (UCL)} = R + 3s$$
$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts[4] that are useful in observing trends in performance. After January 1, 1982, the control limits above must be replaced by method performance criteria provided by the U.S. Environmental Protection Agency.

8.2.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of sludge as described in Section 8.1.2, followed by the calculation of R and s. Alternately, the analyst must use four sludge data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.3 Surrogate Spikes. The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. Suggested surrogate compounds are listed in Table 5. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 14.3. The laboratory should monitor the frequency of suspect data to ensure that it remains at or below 5%.

8.4 Method Blank. Before processing any samples, the analyst should demonstrate through the analysis of an 80 ml aliquot of reagent water, that all glassware and reagents are interference free. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.5 Replicate and Spiked Samples

8.5.1 Analyze all samples in duplicate. Using the procedures described in Section 8.3-2, spike and analyze two additional aliquots. Analyze a third unspiked aliquot on the same day that the spiked aliquots are analyzed.

8.5.2 Spike an 80 ml aliquot of sludge with all of the compounds identified in the sample and the representative semivolatile compounds listed in Table 4 at two times the observed concentration or at 10 times the lower limit of detection, whichever is greater. Prepare the spike as two acetone solutions with the acidic and neutral compounds in the first solution and the basic compounds in the second solution. The concentrations of the spiking solutions should be such that 1 to 5 ml of each solution are added to the sludge sample to attain the required spike concentration. Homogenize the spiked sample for 45 to 60 sec and store overnight at 4°C with tumbling before extraction and analysis.

9. Sampling and Preservation

9.1 Sampling. Collect samples in glass containers (1,000 to 4,000 ml) with a TFE lined screw cap. The container should be prewashed with acetone and dried before use. Containers should be filled no more than two-thirds full with sample to minimize breakage during freezing.

9.2 Preservation. Preferably, samples should be iced or refrigerated at 4°C for not more than 24 hr before extraction. Where extraction cannot be performed within 24 hr, samples should be frozen. Samples may be stored for up to 30 days at -20°C or indefinitely at -75°C. In order to prevent breakage during storage, the containers should not be slightly warmed and then recooled. The iced or defrosted sample should be homogenized by mixing for 1 min with a Tissumizer® before analysis.

10. Sample Extraction

10.1 Preparation of Drying Column. Immediately prior to extracting a sample, prepare a drying tube for the extract. Place a small glass wool plug in the bottom of the column and add anhydrous sodium sulfate to a depth of 10 to 15 cm.

10.2 pH Adjustment. Thoroughly mix the sludge sample by homogenizing in the sample bottle for 1 min, then quickly remove a 80 ml aliquot into a 250 ml graduated cylinder. Transfer the aliquot into a 250 ml centrifuge bottle. Basify to pH $\geq$ 11 with a 6 N sodium hydroxide solution. Mix briefly with the homogenizer to ensure uniform sample pH. (Note: If copious precipitation of carbonates is observed when sodium hydroxide is added, make the sample slightly acidic with 6 N hydrochloric acid and allow the carbon dioxide evolution to cease before basifying the sample.)

10.3 Basic Extraction. Add 80 ml of dichloromethane to the centrifuge bottle and homogenize for 45 to 60 sec. Do not homogenize more than 60 sec to avoid heating the sample. Cap the centrifuge bottles with TFE-lined screw caps and centrifuge at 2,500 to 3,000 rpm for 30 min. Stir and repeat centrifugation if satisfactory phase separation is not achieved. The mixture will separate into an aqueous layer over the dichloromethane extract with a solids cake at the water-dichloromethane interface. Withdraw the extract from each centrifuge bottle with a 100 ml syringe. Discharge the extracts into a 500 ml separatory funnel. Drain the dichloromethane through the drying column into a Kuderna-Danish evaporator. Retain any aqueous layer and return it to the centrifuge bottle. Extract the sample two more times to achieve three-fold extraction. Wash the drying column with an additional 100 ml of dichloromethane and combine the eluent with the dried extracts.

10.4 Extract Concentration. Add a boiling chip to the extract in the Kuderna-Danish evaporator and concentrate the extract to 8 ml using an 85°C bath or a steam bath. If the extract is only slightly colored and not notably viscous, fit a modified Snyder column onto

the Kuderna-Danish receiving tube and immerse the tube halfway in a 35°C water bath. Direct a gentle stream of nitrogen directly on the surface of the extract until the volume is ≥ 4 ml. Transfer the extract to a clean vial, seal it with TFE lined screw cap, and store the extract at 4°C. If the extract is highly colored, viscous or solidifies when concentrating to 4 ml, dilute the extract to 12 ml with dichloromethane, transfer to a clean vial, and store as described above.

10.5 Acidic Extraction. Acidifiy the sludge sample portions to pH ≤ 2 with 6 N hydrochloric acid and extract the sample again by procedures described in Sections 10.3 to 10.4. Discard the extracted sludge aliquots.

11. Extract Cleanup

11.1 Base/Neutral Extracts. Clean the base/neutral sludge extracts by adsorption chromatography on either florisil or silica gel. Although there does not appear to be any significant difference in the performance of these adsorbents, the adsorbent selected for analyses of all quality assurance blanks, spiked blanks, and spiked sludges associated with a specific sludge sample must be the same as was selected for the original sample analysis. In cases where the base/neutral extracts are to be analyzed by packed column GC/MS, the GPC procedure (Section 11.2) may be used as an alternative cleanup method.

11.1.1 Column Preparation. Prepare a 200 mm x 20 mm ID silica gel or florisil column by pouring 20 g fresh 3% deactivated silica gel or 1% deactivated florisil, no more than 5 days old, into a chromatographic column containing 60 to 70 ml hexane. Tap the side of the clamped column with a stirring rod to aid packing and air bubble escape. If clumping should occur at the bottom of the solvent reservoir, a stirring rod can be used to break the clumps. Add hexane as needed. After most packing has settled, rinse down the florisil or silica gel adhering to the column walls with additional hexane. Wash the column with an additional 20 ml hexane until the solvent level is within 1 to 2 mm of the top of the silica gel or florisil.

11.1.2 Column Calibration. Check the elution pattern for each new batch of adsorbent prepared by chromatographing a spiked blank. Mix 1 ml of a dichloromethane solution containing 100 µg of each of the specific analytes of interest and the representative B/N/P compounds included in quality assurance method spikes (described in Section 8.3) with 2 g of adsorbant. Evaporate the solvent with a gentle stream of dry nitrogen and add the adsorbant to the column. Elute the column with 20 ml of hexane (Fraction I), 50 ml of 10% dichloromethane in hexane (Fraction II), 50 ml of 50% dichloromethane in hexane (Fraction III), and then 150 ml

of 5% acetone in dichloromethane (Fraction V). Maintain the elution flow at 2 to 4 ml/min. Collect each fraction in separate Kuderna-Danish evaporators and concentrate the fractions according to the procedures described in Section 7.4. Analyze each fraction by GC/FID or GC/MS with the SE-54 capillary or packed SP-2250 column. Determine the recovery of each compound in each fraction by comparing the detector responses with those from a duplicate aliquot of the original spiked blank. Elution patterns and recoveries observed for selected compounds chromatographed on silica gel and florisil are shown in Tables 6 and 7. Increasing the volume of Fraction I may be required to provide acceptable cleanup for sludge extracts containing high concentrations of aliphatic hydrocarbons or other non-polar compounds. However, additional hexane may elute significant portions of the chlorinated benzenes, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, 2-chloronaphthalene, aldrin, and p,p'-DDE. The elution patterns and recoveries observed for many B/N/P compounds chromatographed on silica gel using 100 ml of hexane for Fraction I are shown in Table 8. In cases where the volume of Fraction I must be increased to achieve acceptable cleanup and the analytes of interest include the compounds listed in this section, Fraction I must be analyzed separately from Fraction II-IV.

11.1.3 Column Operation. Place 2 g of fresh 1% deactivated florisil or 3% deactivated silica gel into a small beaker and add the concentrated base/neutral extract. Dry the sample with a gentle nitrogen stream with stirring to ensure fast and uniform drying. Load dried florisil or silica gel containing the sludge components into the column. Elute the column as described in Section 11.1.2. Discard Fraction I. Collect and composite in Kuderna-Danish evaporators all fractions containing the compounds of interest such as Fractions II through IV for all B/N/P compounds. Fraction II frequently contains much higher levels of interfering materials than to Fractions III or IV. As a result, it should not be composited with Fractions III and IV if it contains no compounds of interest. Fractions may be analyzed separately if desired. Concentrate all fractions collected to 1 ml according to procedures described in Section 10.4.

11.2 Acidic Fraction. Use gel permeation chromatography is used to remove triglycerides and fatty acids.

11.2.1 GPC Column Preparation. Place 70 g of Bio-Beads SX-3 in a 400 ml beaker. Cover the beads with dichloromethane and allow the beads to swell overnight before packing the columns. Transfer the swelled beads to the column and start pumping solvent in this case, dichloromethane, through the

column, with upward flow at 5.0 ml/min. After ~ 1 hr, adjust the pressure on the column to 350 to 700 millibars (5 to 10 psi) and pump an additional 4 hr to remove air from the column. Adjust the column pressure periodically as required to maintain 350 to 700 millibars.

11.2.2 Column Calibration. Calibrate the GPC column elution at least once a week according to the following procedure. Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fractions, for 36 min, changing the fraction at 2 min intervals. Inject the phenols solution and collect 10-ml fractions for 1 hr. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the SP-2250 and SP-1240-DA columns. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≥ 85% removal of the corn oil and ≥ 85% recovery of the di-n-octylphthalate. Choose the "collect time" to extend at least 10 min after the elution of pentachlorophenol. "Wash" the column 20 min between samples. Typical parameters selected are: dump time, 20 min (100 ml); collect time, 30 min (150 ml); and wash time, 20 min (100 ml). The column can also be calibrated using a 254-nm UV detector to monitor the elution of the corn oil and the phenols. Measure the peak areas at various elution times to determine appropriate fractions.

11.2.3 Column Operation. Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load the ≤ 4-ml extracts into the 5-ml loops with a clean solvent on both sides of the extract. Load the ~ 12-ml extracts in three consecutive loops. Use sufficient clean solvent after the extract to transfer the entire aliquot into the loop. Between extracts, purge the sample loading tubing thoroughly with clean solvent. After especially dirty extracts, run a GPC blank using dichloromethane to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 250 ml brown bottles. Concentrate the cleaned extracts, combining collected fractions from multiple injections, to ~ 8 ml using Kuderna-Danish evaporators and then to ≤ 4 ml using modified Snyder columns and nitrogen blowdown. Transfer the cleaned extracts to 8 ml graduated tubes and dilute to 4 ml with dichloromethane. Store at 4°C for GC/MS analysis. Intensely colored extracts may require a second GPC cleanup.

Note: Sample extracts must be in the same solvent used for column elution. Injection of solutions in other solvents can cause a significant change in the bead swell. In extreme cases a traumatic pressure increase may damage the column and cap, or even break the glass column.

12. Sample Extract Analysis

12.1 Base/Neutral/Pesticide Extracts. Analyze the B/N/P extracts by GC/MS using the capillary column or packed column systems described in Section 5.2.1 under the conditions shown below. The capillary column GC/MS procedure is preferred because this procedure provides more unambiguous interpretation of the resulting data. However, if satisfactory performance of the column cannot be demonstrated or if the required Grob-type injection system with direct capillary GC/MS interface is not available, the packed column GC/MS procedure may be used.

12.1.1 Capillary GC/MS with a SE-54 WCOT Column

12.1.1.1 Column Temperature: 50°C for 4 min, 50 to 320°C at 4°C/min, and 320°C until after the elution time for benzo[g,h,i]perylene.

GC/MS interface, 300°C

Carrier gas helium at 10 psi

Splitless injection for 30 sec

Injection size, 2 µl

Examples of the separations achieved by this column are shown in Figure 2. Relative retention times for the base/neutral compounds on this column are listed in Table 9.

12.1.1.2 Capillary Column GC/MS Performance Checks

12.1.1.2.a Column Performance Screening. Fully evaluate the performance of each new column by GC/FID prior to installation in the GC/MS system.[5] In addition, recheck columns that show a marked decrease in performance on the GC/MS (as described in Section 12.2.1.3) or that have not been used the previous 2 weeks for GC/MS analyses under this protocol. Install the capillary column in a gas chromatograph equipped with a Grob-type split/splitless injector and flame ionization detector. Adjust carrier gas at about 15 to 20 cm/sec for N_2 or 30 to 40 cm/sec when He or hydrogen are used as the

carrier gas. Set the splitter flow at 30 to 50 ml/min, makeup gas at 30 ml/min, and column oven temperature at 85°C. Using splitless injection, inject 2 µl of a column performance test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, 2-octanone, n-tridecane, and n-tetradecane or an equivalent commercial test mixture. Table 10 shows the contents of three appropriate commercial mixtures. Measure the pH of the column as the ratio of the peak height of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A value of 0.5 to 1.5 is acceptable. Determine the activity of the column toward polar compounds by determining both the asymmetry for the 1-octanol peak and the ratio of the peak height of 1-octanol to that of C_{13} alkane. The peak asymmetry is evaluated by drawing a perpendicular from the apex of the peak to the baseline and measuring the width from the front of the peak to the perpendicular line (W_F) and from the back of the peak to the perpendicular line (W_B).

$$AS = \frac{W_B}{W_F} \times 100$$

Peak asymmetries between 75 and 200 are acceptable. The ratio of peak height of the 1-octanol to that of C_{13} alkane should be higher than 0.5. Determine the number of effective theoretical plates (N_{eff}) from the tridecane peak using the equation

$$N_{eff} = 5.545 \left(\frac{tr'}{W_{0.5}}\right)^2$$

where tr' is the adjusted retention time of tridecane and $W_{0.5}$ is the peak width at half height. The number of effective plates of acceptable columns must be at least 25,000.

12.1.1.2.b System Performance. Evaluate the performance of the capillary column in the GC/MS system each time the column is installed and each working day prior to its use. Using splitless injection, inject 2 µl of a test mixture containing 20 ng each of 2,6-dimethylaniline, 2,6-dimethylphenol, DFTPP, methylstearate, octadecene, and octadecane. Measure the pH of the column by taking the ratio of peak

heights of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A pH of 0.5 to 1.5 is acceptable. Determine the resolution of the peaks corresponding to octadecane and octadecane. The peaks should be resolved with no more than a 50% valley. Determine the asymmetry of the methylstearate peak according to the formula given in Section 12.1.1.2.a. If the methylstearate peak tails, the GC/MS transfer line is not adequately heated.

12.1.1.3 At the beginning of each day that base/neutral analyses are to be performed, inject 100 ng of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. Acceptable performance is achieved when the benzidine is identified according to Section 13.

12.1.2 Packed Column GC/MS with a SP-2250 Column

12.1.2.1 Chromatographic Conditions

Column temperature, 60°C for 2 min, 60 to 260°C at 80°C/min, and 260°C until after the elution time for benz[g,h,i]perylene.

Injector temperature, 225°C

GC/MS interface temperature, 275°C

Carrier gas, helium at 30 ml/min

Injection size, 2 µl

An example of the separation achieved by the column is shown in Figure 3. Relative retention times for the base/neutral and pesticide compounds on this column are listed in Table 11.

12.1.2.2 At the beginning of each day that base/neutral analyses are to be performed, inject 100 ng of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. Acceptable performance is achieved when the benzidine is identified according to Section 13.

12.2 Acid Extracts

12.2.1 Analyze acid extracts by GC/MS using the SP-1240-DA column described in Section 5.2.1, operated under the following conditions.

Column temperature, 85°C for 2 min, 85 to 185°C at 10°C/min and 185°C until after the elution time for 4-nitrophenol.

Injector temperature, 185°C.

GC/MS surface temperature, 275°C.

Carrier gas, helium at 30 ml/min.

Injection size, 2 µl.

An example of the separation achieved by the column is shown in Figure 4. Relative retention times for the acid compounds are listed in Table 11.

12.2.2 At the beginning of each day that acid fraction analyses are to be performed, inject 50 ng of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. Acceptable performance is achieved when pentachlorophenol is identified according to Section 13.

13. Qualitative and Quantitative Determination

13.1 Using the characteristic mass spectral ions listed in Tables 8 or 10 for the base/neutral and pesticide compounds and in Table 11 for the acid compounds, plot at least three extracted ion current plots (EICPs) for each analyte.

13.2 Identify the presence of analytes by the coincidence of peaks in the characteristic EICPs at the appropriate retention times and with intensities in the characteristic ratios (Tables 8 or 10 and 11).

13.3 Record the area (intensity) of the peak in the EICP for the most intense ion for each compound identified.

14. Calculations

14.1 Determine the concentration of individual compounds in the sample.

14.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from Equation 2:

$$\text{Concentration, } \mu g/\text{liter} = \frac{(M)(V_E)}{(V_I)(V_s)} \qquad \text{(Eq. 2)}$$

where: M = Mass of material injected (ng).

V_I = Volume of extract injected (µl).

V_E = Volume of total extract (ml).

V_s = Volume of wet sludge extracted (liter)

14.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using Equation 3.

$$\text{Concentration, } \mu g/\text{liter} = \frac{(A)(I_s)(V_E)}{(A_{IS})(RRF)(V_I)(V_s)} \qquad \text{(Eq. 3)}$$

where: A = Area of peak in sample extract.

A_{IS} = Area of internal standard peak in sample extract.

I_S = Areas of internal standard injected (ng).

V_E = Total volume of extract (ml).

V_I = Volume of extract injected (µl).

V_s = Volume of sludge extracted (liter).

RRF = Relative response factor.

14.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

14.3 If the surrogate standard recoverues fall outside the limits in Section 8.2, data for all parameters in that sample must be labeled as suspect.

15. Method Performance

Performance data for the application of this method to both POTW and industrial sludges are shown in Tables 13 to 15. Table 13 shows data for B/N compounds analyzed in POTW and industrial sludges via Option A. Table 14 shows data for B/N compounds analyzed via Option B and acidic compounds in aliquots of the same sludges. Data for B/N compound were analyzed via Option B and acidic compounds in sludges from 40 POTWs. Most of these data represent results from one laboratory. Approximately 25% of the data in Table 15 was contributed by a second laboratory.

16. References

1. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry" (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1979).

3. "Safety in Academic Chemistry Laboratories," American Chemical Society Committee on Chemical Safety, 3rd Edition Publication (1979).

4. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

5. Grob, K., Jr., G. Grob, and K. Grob, "Comprehensive Standardized Quality Test for Glass Capillary Columns," J. Chrom., 156, 1-20 (1978).

17. Additional Sources

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, March 1977, Revised April 1977. Effluent Guidelines Division, Washington, DC 20460.

2. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, OH 45268. In preparation.

3. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. In preparation.

4. Budde, W. L., and J. W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

5. Kleopfer, R. D., "Priority Pollutant Methodology Quality Assurance Review," U.S. Environmental Protection Agency, Region VII, Kansas City, KS. Seminar for Analytical Methods for Priority Pollutants, Norfolk, VA, January 17-18, 1980, U.S. Environmental Protection Agency, Office of Water Programs, Effluent Guidelines Division, Washington, DC 20460.

TABLE 1. EXTRACTABLE ORGANIC PRIORITY POLLUTANTS

Compound	STORET No.	CAS No.
Acids		
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	32730	108-95-2
2,4,5-Trichlorophenol	34621	88-06-2
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
4,6-Dinitro-2-methylphenol	34657	534-32-1
Bases		
Benzidine	39210	93-87-5
3,3'-Dichlorobenzidine	34631	92-94-1
Polycyclic Aromatic Hydrocarbons		
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34461	120-12-7
Benz[a]anthracene	34562	56-55-3
Benzo[b]fluoranthene	34242	205-99-2
Benzo[k]fluoranthene	34242	207-08-9
Benzo[g,h,i]perylene	34521	191-24-2
Benzo[a]pyrene	34247	50-32-8
Chrysene	34562	218-01-9
Dibenz[a,h]anthracene	34556	53-70-3
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Indeno[1,2,3-cd]pyrene	34403	193-39-5
Naphthalene	39250	91-20-3
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Phthalates		
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Butylbenzylphthalate	34292	85-68-7
Diethylphthalate	34336	84-66-2
Dimethylphthalate	34341	131-11-3
Di-n-butylphthalate	39110	84-74-2
Di-n-octylphthalate	34596	117-84-0

(continued)

TABLE 1 (continued)

Compound	STORET No.	CAS No.
Chlorinated Hydrocarbons		
2-Chloronaphthalene	34581	91-58-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Hexachlorobenzene	39700	118-74-1
Hexachloro-1,3-butadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Hexachlorocyclopentadiene	34386	77-47-4
1,2,4-Trichlorobenzene	34551	129-82-1
Chloroalkyl Ethers		
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-chloroisopropyl)ether	34283	39638-32-9
Miscellaneous Neutrals		
4-Bromophenyl phenyl ether	34636	101-55-3
4-Chlorophenyl phenyl ether	34641	7005-72-3
2,4-Dinitrotoluene	34611	121-14-2
N-Nitrosodi-n-propylamine	34428	621-64-7
N-Nitrosodimethylamine	34438	62-75-9
2,6-Dinitrotoluene	34626	606-20-2
Isophorone	34408	78-59-1
Nitrobenzene	34447	98-95-3
N-Nitrosodiphenylamine	34433	86-30-6
1,2-Diphenylhydrazine	34346	122-66-7
Pesticides		
β-Endosulfan	34356	33213-65-9
α-BHC	39337	319-84-6
γ-BHC	34264	58-89-9
β-BHC	39338	319-85-7
Aldrin	39330	309-00-2
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
α-Endosulfan	34361	959-98-8
Dieldrin	39380	60-57-1
4,4'-DDE	39320	72-55-9
4,4'-DDD	39310	72-54-8
4,4'-DDT	39300	50-29-3

(continued)

TABLE 1 (concluded)

Compound	STORET No.	CAS No.
Endrin	39390	72-20-8
Endosulfan sulfate	34351	1031-07-8
δ-BHC	34259	319-86-8
Chlordane	39350	57-74-9
Toxaphene	39400	8001-35-2
PCB-1242	39496	53469-21-9
PCB-1221	39504	11104-28-2
PCB-1254	39488	11097-69-1
PCB-1232	39492	11141-16-5
PCB-1248	39500	12672-29-6
PCB-1260	39508	11096-82-5
PCB-1016	34671	12674-11-2

TABLE 2. UNSTABLE B/N COMPOUNDS

Bis(2-chloroisopropyl)ether
Nitrobenzene
N-Nitroso-di-n-propylamine
Bis(2-chloroethoxy)methane
Isophorone
2,6-Dinitrotoluene
2,4-Dinitrotoluene
1,2-Diphenylhydrazine
Benzidine
3,3'-Dichlorobenzidine
N-Nitrosodimethylamine

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

m/e	Ion abundance criteria
51	30-60% of m/e 198
68	< 2% of m/e 69
70	< 2% of m/e 69
127	40-60% of 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of m/e 198
275	10-30% of m/e 198
365	1% of m/e 198
441	Present and < m/e 443
442	40% of m/e 198
443	17-23% of m/e 442

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

TABLE 4. REPRESENTATIVE EXTRACTABLE COMPOUNDS FOR RECOVERY STUDIES

Acenaphthylene
Benzidine
Benzo[a]pyrene
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)phthalate
Butylbenzyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,4-Dimethylphenol
2,6-Dinitrotoluene
Fluoranthene
Hexachloroethane
N-Nitrosodimethylamine
1;4-Dichlorobenzene
Pentachlorophenol
Phenol
Dieldrin
α-BHC
p,p'-DDE
Heptachlor

TABLE 5. SUGGESTED SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo[a]anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
2-Fluoraniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
1,2,3,4,5-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

TABLE 6. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON SILICA GEL[a]

Compound	Spike level (µg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	46.8		+[c]	+		78
Hexachloroethane	31.2		+			83
Bis(2-chloroisopropyl)ether)	49.6				+	85
Bis(2-chloroethyl)ether	31.6				+	93
Acenaphthylene	28.5			+		79
2,6-Dinitrotoluene	35.1				+	96
Fluoranthene	27.0			+		90
Benzidine	31.0					0
3,3'-Dichlorobenzidine	36.4				+	50
n-Butylbenzylphthalate	45.2				+	97
Bis(2-ethylhexyl)phthalate	39.6				+	93
Benzo[a]pyrene	30.0			+		78

a 3% deactivated silica gel.

b Analyses done by packed column GC/MS.

c + indicates more than 1% recovery in that fraction.

TABLE 7. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON FLORISIL.[a]

Compound	Spike level (µg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	93.6		+[c]	+	+	48
Hexachloroethane	62.4		+	+	+	67
Bis(2-chloroisopropyl)ether	42.2			+	+	152
Bis(2-chloroethyl)ether	66.2			+	+	48
Acenaphthylene	57.0		+	+	+	92
2,6-Dinitrotoluene	70.2				+	125
Fluoranthene	54.0		+	+	+	121
Benzidine	62.0					0
3,3'-Dichlorobenzidine	72.8				+	65
n-Butylbenzylphthalate	90.4				+	106
Bis(2-ethylhexyl)phthalate	79.2				+	92
Benzo[a]pyrene	60.8			+	+	87

a 1% deactivated florisil.

b Analyses done by packed column GC/MS.

c + indicates more than 1% recovery in that fraction.

TABLE 8. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRAL/PESTICIDES CHROMATOGRAPHED ON SILICA GEL WITH AN ALTERNATE ELUTION[a,b] SCHEME

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Bis(2-chloroethyl)ether				+[d]	95 ± 22
1,3-Dichlorobenzene	+				64 ± 6
1,2-Dichlorobenzene	+				67 ± 9
Hexachloroethane	+				73 ± 14
N-nitrosodi-n-propylamine				+	94 ± 12
Nitrobenzene			+	+	67 ± 3
Bis(2-chloroethoxy)methane				+	66 ± 5
1,2,4-Trichlorobenzene	+				70 ± 17
Naphthalene	+	+	+		58 ± 7
Hexachlorobutadiene	+				142 ± 51
Hexachlorocyclopentadiene	+				300 ± 55
2-Chloronaphthalene	+	+			94 ± 5
Acenaphthylene		+	+		77 ± 21
2,6-Dinitrotoluene				+	93 ± 19
Acenaphthalene		+	+		88 ± 12
2,4-Dinitrotoluene				+	95 ± 14
Fluorene			+		87 ± 22
4-Chlorophenylphenylether			+		109 ± 12
Diethylphthalate				+	90 ± 41
4-Bromophenylphenylether			+		116 ± 15
Hexachlorobenzene	+				85 ± 30
Phenanthrene			+		85 ± 30
Anthracene			+		83 ± 28

(continued)

TABLE 8 (continued)

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Di-n-butylphthalate				+	88 ± 51
Fluoranthene			+		51 ± 20
Pyrene			+		63 ± 12
Endosulfan sulfate				+	67 ± 17
n-Butylbenzylphthalate				+	87 ± 35
Chrysene			+		72 ± 5
3,3'-Dichlorobenzidine				+	40 ± 2
Bis(2-ethylhexyl)phthalate				+	95 ± 61
Benzo[a]pyrene			+		70 ± 34
Dibenz[a,h]anthracene			+		84 ± 17
γ-BHC		+	+	+	66 ± 27
Aldrin	+				67 ± 14
Heptachlorepoxide			+	+	88 ± 3
p,p'-DDE	+	+	+		80 ± 6
Endrin				+	77 ± 18
p,p'-DDD			+		78 ± 7
p,p'-DDT			+	+	91 ± 17
α-Endosulfan			+	+	86 ± 17

a Data from Lopez-Avila, Vlorica, Raymond V. Northrett, Jon Onstot, and Margie Wickham. "Analysis of the NBS Sediment by the MRI Sludge Protocol," Final Report prepared for the Environmental Protection Agency under EPA Contract No. 68-03-2711 (1981).

b 3% reactivated silica gel.

c Recoveries determined in duplicate at 8-μg and 80-μg levels for each compound. Analyses done by fused silica capillary GC/MS.

d + indicates more than 1% recovery in that fraction.

TABLE 9. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC EI IONS FOR THE BASE/NEUTRAL COMPOUND ANALYZED BY CAPILLARY COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.04	42(100), 74(88), 44(21)
Bis(2-chloroethyl)ether	0.21	93(100), 63(99), 95(31)
1,3-Dichlorobenzene	0.22	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.22	146(100), 148(64), 113(11)
1,2-Dichlorobenzene	0.25	146(100), 148(64), 113 (11)
Bis(2-chloroisopropyl)ether	0.29	45(100), 77(19), 79(12)
Hexachloroethane	0.29	117(100, 199(61), 201(99)
N-Nitrosodi-n-propylamine	0.31	130(22), 42(64), 101(12)
Nitrobenzene	0.32	77(100), 123(50), 65(15)
Isophorone	0.36	82(100), 95(14), 138(18)
Bis(2-chloroethoxy)methane	0.41	93(100), 95(32), 123(21)
1,2,4-Trichlorobenzene	0.42	74(100), 109(80), 145(52)
Naphthalene	0.43	128(100), 223(63), 227(65)
Hexachlorobutadiene	0.47	225(100), 223(63), 227(65)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.63	162(100), 164(32), 127(31)
Acenaphthylene	0.70	152(100), 153(16), 151(17)
Dimethylphthalate	0.72	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.72	165(100), 63(72), 121(23)
Acenaphthene	0.73	154(100), 155(95), 152(13)
2,4-Dinitrotoluene	0.78	165(100), 63(72), 121(23)
Fluorene	0.82	166(100), 165(80), 167(14)
4-Chlorophenyl phenyl ether	0.84	204(100), 206(34), 141(29)
Diethylphthalate	0.84	149(100), 178(25), 150(10)
N-Nitrosodiphenylamine[c]	0.84	169(100), 168(71), 167(50)
1,2-Diphenylhydrazine[d]	0.86	77(100), 93(58), 105(28)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Hexachlorobenzene	0.93	284(100), 142(30), 249(24)
Phenanthrene	0.98	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
d_{10}-Anthracene	1.00	188(100), 94(19), 80(18)
Di-n-butylphthalate	1.14	149(100), 150(27), 104(10)
Fluoranthene	1.19	202(100), 101(23), 100(14)
Pyrene	1.23	202(100), 101(26), 100(17)
Benzidene	1.24	184(100), 92(24), 185(13)
Butylbenzylphthalate	1.40	149(100), 91(50)
Chrysene	1.45	228(100), 229(19), 226(23)
3,3'-Dichlorobenzidene	1.47	252(100), 254(66), 126(16)
Bis(2-ethylhexyl)phthalate	1.52	149(100), 167(31), 279(26)
Benzo[k]fluoranthene	1.62	252(100), 253(23), 125(16)

(continued)

TABLE 9 (continued)

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Di-n-octylphthalate	1.63	149(100), 167(29), 279(22)
Benzo[a]pyrene	1.67	252(100), 253(23), 125(21)
Dibenz[a,h]anthracene	1.84	278(100), 139(31), 279(12)
Benzo[g,h,i]perylene	1.87	276(100), 138(37), 277(25)

a Relative to d_{10}-anthracene. Retention times data were not determined for the priority pollutant pesticides and a few base/neutral compounds. However, their retention properties should be roughly equivalent to those on SP-2250 (see Table 6).

b SE-54 WCOT glass capillary (15 m x 0.24 mm ID), He at 10 psi, program: 50°C for 4 min, then 4°C/min to 320°C.

c Elutes as diphenylamine.

d Elutes as azobenzene.

TABLE 10. COMPOSITION OF CAPILLARY COLUMN PERFORMANCE TEST MIXTURES

Test mixture	Composition	
Varian		
P/N 82-005049-01	2-octanone	0.2 µg/µl
(nonpolar)	1-octanol	0.2
	naphthalene	0.2
	2,6-dimethylphenol	0.2
	2,4-dimethylaniline	0.2
	C_{12}-alkane	0.2
	C_{13}-alkane	0.2
Alltech		
TP-5 (polar)	C_{13}-alkane	0.1 µg/µl
	C_{14}-alkane	0.1
	C_{15}-alkane	0.1
	C_{16}-alkane	0.1
	1-octanol	0.5
	5-nonanone	0.3
	2,6-dimethylaniline	0.4
	2,6-dimethylphenol	0.4
	naphthalene	0.5
Analabs		
Test probe LPK-013F	C_{12}-acid methyl ester	41 ng/µl
(general purpose)	C_{11}-acid methyl ester	41
	C_{10}-acid methyl ester	42
	C_{10}-alkane	28
	C_{11}-alkane	29
	1-octanol	36
	Nonanal	40
	2,3-butanediol	53
	2,6-dimethylphenol	32
	2,6-dimethylaniline	32
	dicyclohexylamine	31
	2-ethylhexanoic acid	38

TABLE 11. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE BASE/NEUTRAL AND PESTICIDE COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.15	42(100), 74(88), 44(21)
1,3-Dichlorobenzene	0.31	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.33	146(100), 148(64), 113(11)
Hexachloroethane	0.35	117(100), 199(61), 201(99)
1,2-Dichlorobenzene	0.35	146(100), 140(64), 113(11)
Bis(2-chloroisopropyl)ether	0.37	45(100), 77(19), 79(12)
N-Nitrosodi-n-propylamine	0.42	130(22), 42(64), 101(12)
Nitrobenzene	0.45	77(100), 123(50), 65(15)
Isophorone	0.47	82(100), 95(14), 138(18)
Hexachlorobutadiene	0.48	225(100), 223(63), 227(65)
1,2,4-Trichlorobenzene	0.49	74(100), 109(80), 145(52)
Bis(2-chloroethoxy)methane	0.50	93(100), 95(32), 123(21)
Naphthalene	0.51	128(100), 127(10), 129(11)
Bis(2-chloroethyl)ether	0.55	93(100), 63(99), 95(31)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.68	162(100), 164(32), 127(31)
Acenaphthylene	0.75	152(100), 153(16), 151(17)
Acenaphthene	0.77	154(100), 153(95), 152(53)
Dimethyl phthalate	0.78	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.81	165(100), 63(72), 121(23)
Fluorene	0.85	166(100), 165(80), 167(14)
2,4-Dinitrotoluene	0.85	165(100), 63(72), 121(23)
4-Chlorophenyl phenyl ether	0.85	204(100), 206(34), 141(29)
Diethyl phthalate	0.87	149(100), 178(25), 150(10)
1,2-Diphenylhydrazine[b]	0.88	77(100), 93(58), 105(28)
N-Nitrosodiphenylamine[c]	0.89	169(100), 168(71), 167(50)
Hexachlorobenzene	0.92	284(100), 142(30), 249(24)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Phenanthrene	0.99	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
Deuterated anthracene (D-10)	1.00	188(100), 94(19), 80(18)
D-n-butylphthalate	1.09	149(100), 150(27), 104(10)
Fluoranthene	1.18	202(100), 101(23), 100(14)
Pyrene	1.22	202(100), 101(26), 100(17)
Benzidine	1.27	184(100), 92(24), 185(13)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1.33	322(100), 320(90), 59(95)
Butylbenzylphthalate	1.34	149(100), 91(50)
Bis(2-ethylhexyl)phthalate	1.37	149(100), 167(31), 279(26)
Chrysene	1.40	228(100), 229(19), 226(23)

(continued)

TABLE 11 (continued)

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Benz[a]anthracene	1.40	228(100), 229(19), 226(19)
Benzo[b]fluoranthene	1.43	252(100), 253(23), 125(15)
Benzo[k]fluoranthene	1.43	252(100), 253(23), 125(16)
3,3'-Dichlorobenzidine	1.45	252(100), 254(66), 126(16)
Di-n-octylphthalate	1.50	149(100), 167, 279
Benzo[a]pyrene	1.50	252(100), 253(23), 125(21)
Indeno[1,2,3-cd]pyrene	1.86	276(100), 138(28), 277(27)
Benzo[g,h,i]perylene	1.98	276(100), 138(37), 277(25)
Bis(chloromethyl) ether	d	45(100), 49(14), 51(5)
β-Endosulfan	0.47	201(100), 283(48), 278(30)
α-BHC	0.94	183(100), 109(86), 181(91)
γ-BHC	1.00	183(100), 109(86), 181(91)
β-BHC	1.03	181(100), 183(93), 109(62)
δ-BHC	1.04	183(100), 109(86), 181(90)
Aldrin	1.05	181(100), 183(93), 109(62)
Heptachlor	1.06	183(100), 109(86), 181(90)
Heptachlor epoxide	1.13	66(100), 220(11), 263(73)
α-Endosulfan	1.14	100(100), 353(79), 351(60)
Dieldrin	1.18	201(100), 283(48), 278(30)
4,4'-DDE	1.20	79(100), 263(28), 279(22)
4,4'-DDD	1.22	246(100), 248(64), 176(65)
4,4'-DDT	1.27	235(100), 237(76), 165(93)
Endrin	1.30	81(100), 82(61), 263(70)
Endosulfan sulfate	1.30	272(100), 387(75), 422(25)
Chlordane	1.05-1.26	373(19), 375(17), 377(10)[e]
Toxaphene	1.12-1.35	(231, 233, 235)[f]
PCB-1242	0.86-1.14	(224, 260, 294)[f]
PCB-1254	1.09-1.30	(294, 330, 362)[f]

a 3% SP-2250 on 100/120 mesh Supelcoport in a 1.8 m x 2 mm ID glass column; He at 30 ml/min. Program: 60°C for 2 min, then 8°C/min to 260°C and hold for 15 min.

b Elutes as azobenzene.

c Elutes as diphenylamine.

d No data.

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

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

TABLE 12. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE ACID COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Chlorophenol	0.51	128(100), 64(54), 130(31)
2-Nitrophenol	0.55	139(100), 65(35), 109(8)
Phenol	0.61	94(100), 65(17), 66(19)
2,4-Dimethylphenol	0.67	122(100), 107(90), 121(55)
2,4-Dichlorophenol	0.69	162(100), 164(50), 98(61)
2,4,6-Trichlorophenol	0.79	196(100), 198(92), 200(26)
4-Chloro-m-cresol	0.86	142(100), 107(80), 144(32)
2,4-Dinitrophenol	1.04	184(100), 63(59), 154(53)
4,6-Dinitro-o-cresol	1.04	198(100), 182(35), 77(28)
Pentachlorophenol	1.13	266(100), 264(62), 268(63)
4-Nitrophenol	1.63	65(100), 139(45), 109(72)

a Relative to d_{10}-anthracene.

b 1% SP-1240-DA on 100/120 Supelcoport in a 1.2 m x 2 mm ID glass column; He at 30 ml/min. Program: 85°C for 2 min, then 10°C/min to 185°C and hold for 5 min.

TABLE 13. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION A (SILICA GEL CLEANUP, HRGC/MS DETERMINATION) IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
		Spike level (µg/ℓ)		Spike recovery				Spike level (µg/ℓ)		Spike recovery		
Compound	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
1,4-Dichlorobenzene	27	400	40,000	44	25	37	18	400	40,000	65	59	32
Hexachloroethane	25	400	40,000	24	17	33	18	400	40,000	55	65	55
Bis(2-chloroethyl)ether	27	400	40,000	110	77	54	16	400	40,000	80	44	20
Acenaphthylene	27	400	40,000	110	66	26	15	400	40,000	95	27	14
2,6-Dinitrotoluene	25	400	40,000	33	35	72	15	400	40,000	89	63	42
Fluoranthene	24	400	40,000	140	64	25	15	400	40,000	110	42	18
Benzidine	18	7,900	80,000	31	31	49	12	780	80,000	120	96	25
3,3'-Dichlorobenzidine	9	402	4,130	50	78	66	a	-	-	-	-	-
Butylbenzylphthalate	18	4,000	40,000	140	59	18	12	400	40,000	130	92	19
Di-n-octylphthalate	18	400	40,000	130	75	40	15	400	48,800	130	71	30
Benzo[a]pyrene	21	400	40,000	110	43	24	15	400	40,100	82	70	30

a This compound was not spiked into the industrial sludges.

TABLE 14. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION 8 (GPC CLEANUP, GC/MS DETERMINATION AND ACIDIC EXTRACTABLE ORGANICS IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
		Spike level (µg/g)		Spike recovery				Spike level (µg/g)		Spike recovery		
Compound	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Minimum	Maximum	Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
1,4-Dichlorobenzene	27	40	41,600	69	28	16	15	400	40,000	75	16	9
Hexachloroethane	23	400	44,100	48	17	10	16	400	40,000	56	31	14
Bis(2-chloroethyl)ether	25	400	40,700	220	190	17	16	400	40,000	120	51	7
Acenaphthylene	21	400	40,000	65	26	9	18	400	40,000	110	47	12
2,6-Dinitrotoluene	14	4,000	40,000	50	31	10	12	4,000	40,000	100	35	10
Fluoranthene	24	400	40,000	51	27	14	15	400	40,000	91	22	8
Benzidine	14	4,870	80,000	79	59	8	16	800	70,000	77	41	10
3,3'-Dichlorobenzidine	13	415	4,130	69	40	11	3	4,000	4,000	110	13	13
Butylbenzylphthalate	18	4,500	40,000	130	120	7	12	400	40,000	69	15	9
Di-n-octylphthalate	28	4,000	40,000	98	77	13	12	400	48,800	81	73	10
Benzo[a]pyrene	16	400	40,600	120	94	13	16	400	40,000	66	47	7
Phenol	24	400	46,300	73	26	27	14	400	40,000	72	34	26
2,4-Dimethylphenol	26	400	41,100	58	62	37	12	400	40,000	110	64	23
2,4-Dichlorophenol	21	399	40,000	89	32	18	15	400	40,000	140	96	15
Pentachlorophenol	26	400	40,000	120	67	37	10	400	40,000	50	16	28

TABLE 15. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION B (GPC CLEANUP, GC/MS DETERMINATIONS) AND ACIDIC EXTRACTABLE ORGANICS IN PRIMARY SLUDGES FROM 40 POTWs[a]

Compound	Determinations	Spike recovery[b] Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
1,3-Dichlorobenzene	27	86	39	11
1,2-Dichlorobenzene	24	68	25	11
Nitrobenzene	13	49	28	17
Hexachlorobutadiene	27	71	22	7
Naphthalene	27	94	37	8
2-Chloronaphthalene	27	89	33	8
Acenaphthalene	24	79	27	8
2,6-Dinitrotoluene	23	59	38	15
Fluorene	27	94	34	10
N-Nitrosodiphenylamine	24	140	84	11
4-Bromophenylphenylether	27	80	27	5
Di-n-butylphthalate	26	79	43	9
Fluoranthene	26	85	40	9
Pyrene	27	90	47	8
Butylbenzylphthalate	26	95	64	11
Bis(2-ethylhexyl)phthalate	22	65	34	8
Benzo[a]pyrene	27	85	49	11
1,4-Dichlorobenzene	27	82	34	11
Hexachloroethane	21	49	25	21
Isophorone	27	51	27	15
1,2,4-Trichlorobenzene	27	83	32	9
Bis(2-chloroethoxy)methane	24	54	27	12
Hexachlorocyclopentadiene	20	0	0	0
Acenaphthylene	19	76	24	9
Dimethylphthalate	27	50	33	20
2,4-Dinitrotoluene	26	65	50	14
Diethylphthalate	27	65	35	12
Hexachlorobenzene	27	63	21	10
Phenanthrene/anthracene	26	71	39	11
Chrysene/Benz[a]anthracene	27	71	27	11
Benzo[g,h,i]perylene	19	31	15	10
N-Nitrosodi-N-propylamine	24	77	54	13
1,2-Diphenylhydrazine	23	64	30	9
Benzidine	21	8	11	15
3,3'-Dichlorobenzidine	27	56	58	14
2-Chlorophenol	27	59	16	14
2-Nitrophenol	27	46	39	17
4-Nitrophenol	25	22	23	15
Phenol	26	66	28	11

(continued)

TABLE 15 (continued)

Compound	Determinations	Spike recovery[b] Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
2,4-Dimethylphenol	27	34	39	20
2,4-Dichlorophenol	27	68	25	11
2,4,6-Trichlorophenol	27	71	25	13
1,3-Dichlorobenzene	27	86	39	11
p-Chloro-m-cresol	22	58	32	9
2,4-Dinitrophenol	24	14	27	11
4,6-Dinitro-o-cresol	26	13	24	15
Pentachlorophenol	27	84	43	15
α-BHC	27	39	32	10
Dieldrin	27	72	30	8
4,4'-DDE	27	57	19	11
Heptachlor	26	76	35	10

a Swanson, Stephen E., T. Murry Williams, Lloyd M. Petrie, and Earl M. Hansen. "Survey of Analysis of POTW Sludges for Priority Pollutants: Part II Quality Assurance Data," Final Report prepared under EPA Contract No. 68-01-5915, Task 35 (1981).

b Minimum spike level 125 µg/ℓ; maximum spike level 1,250 µg/ℓ.

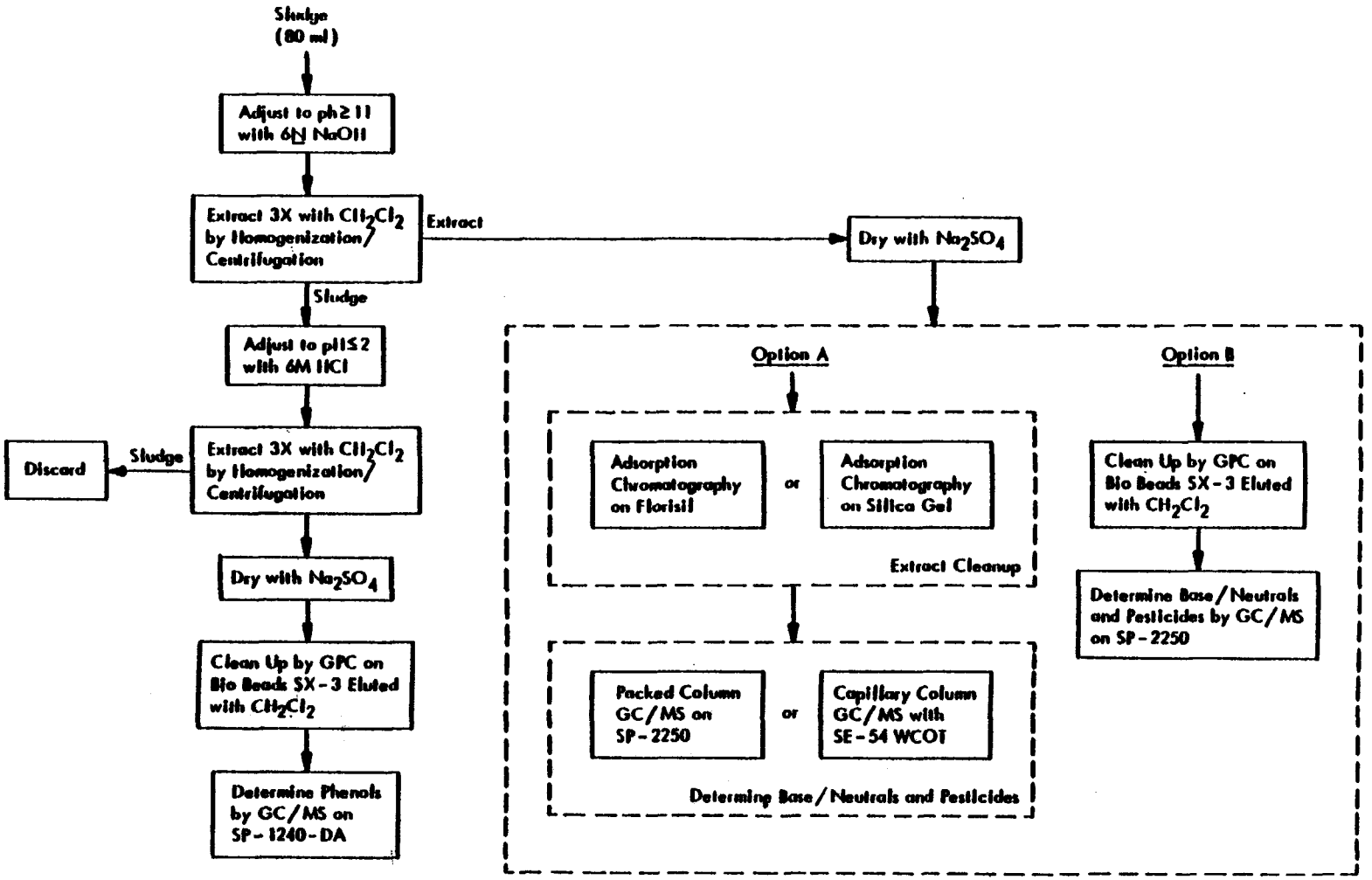

Figure 1. Scheme for analysis of extractable organics in sludge.

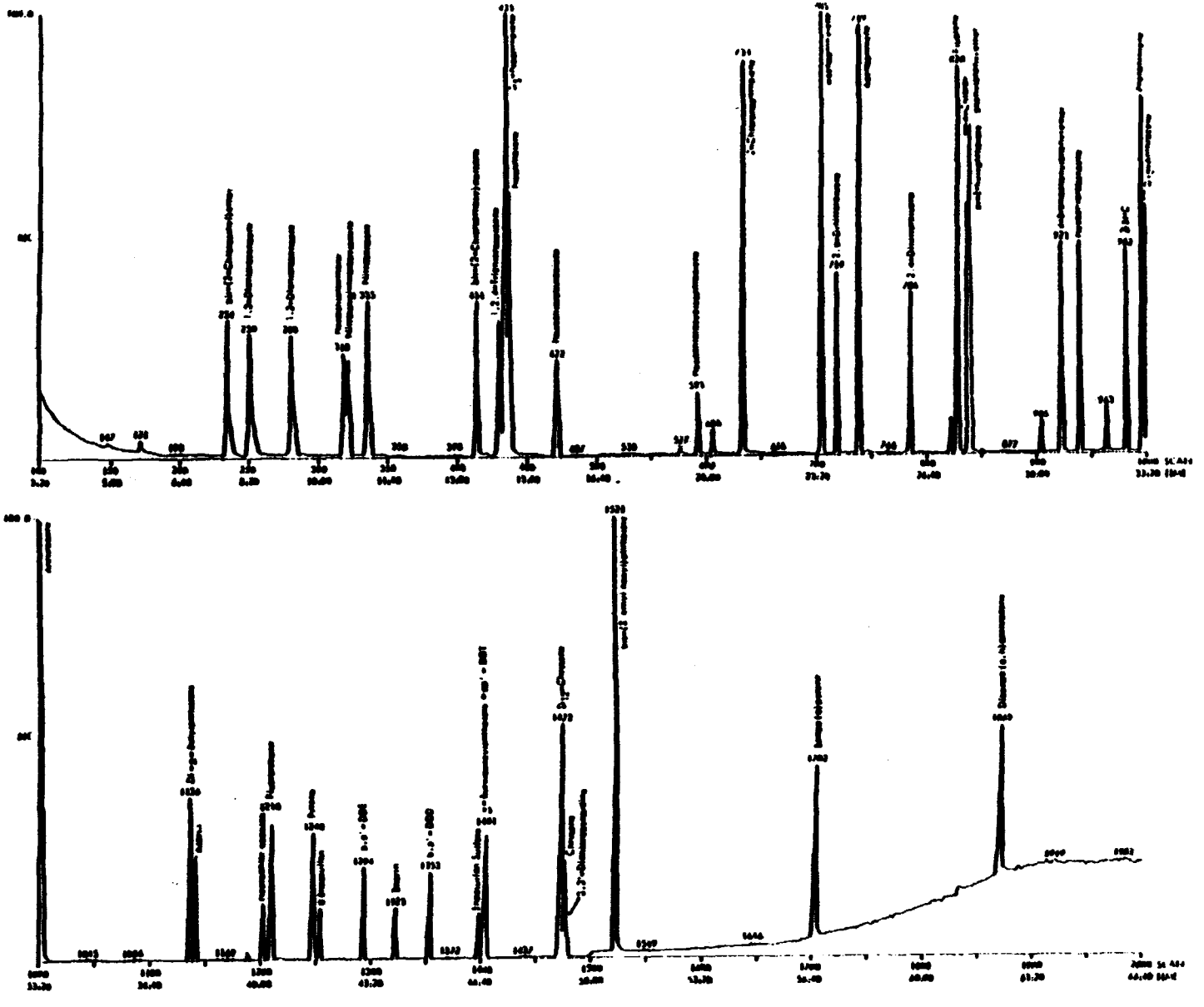

Figure 2. GC/MS chromatogram of base/neutral compounds on a fused silica capillary column.

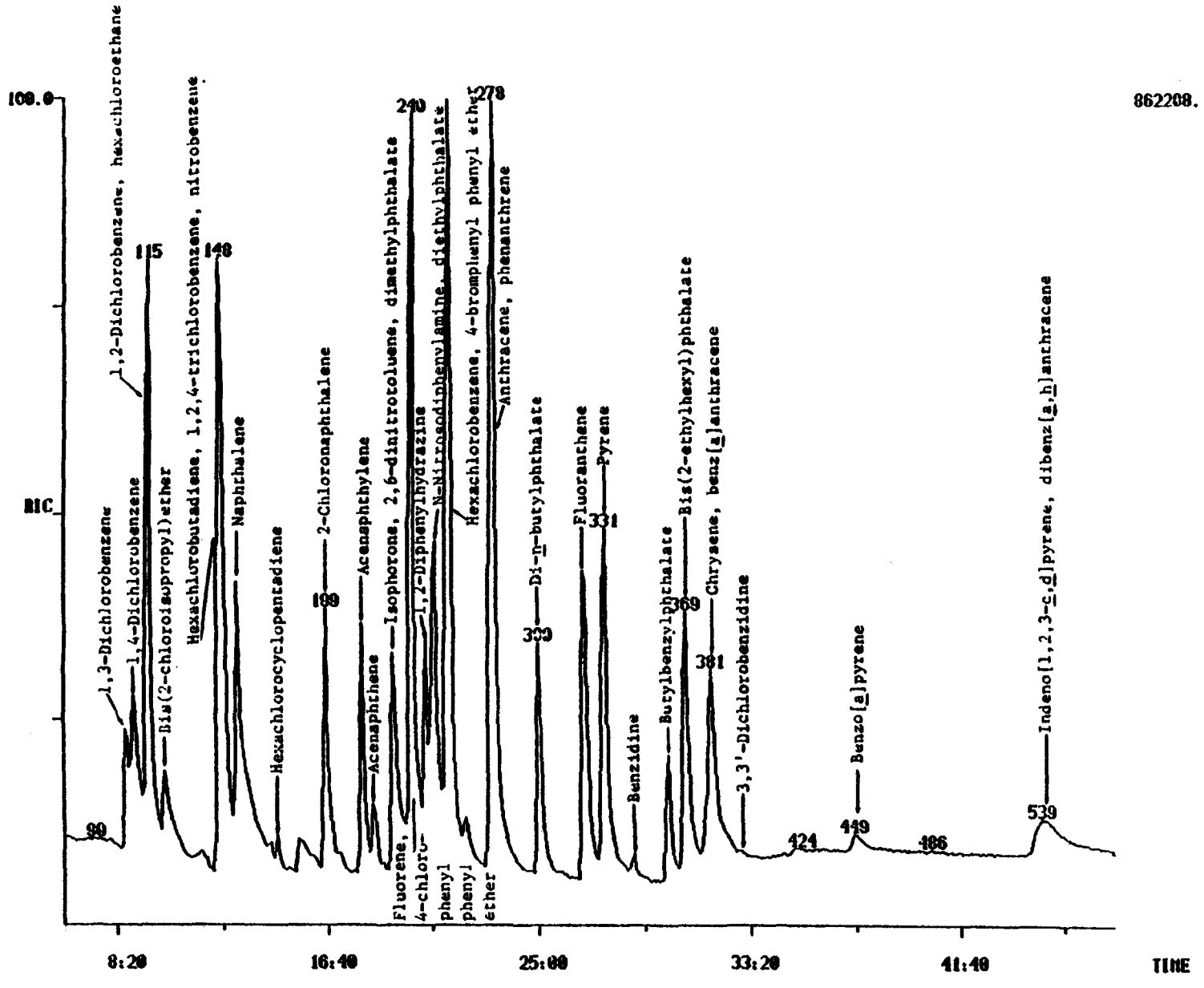

Figure 3. GC/MS chromatogram for the base/neutral compounds on a packed column.

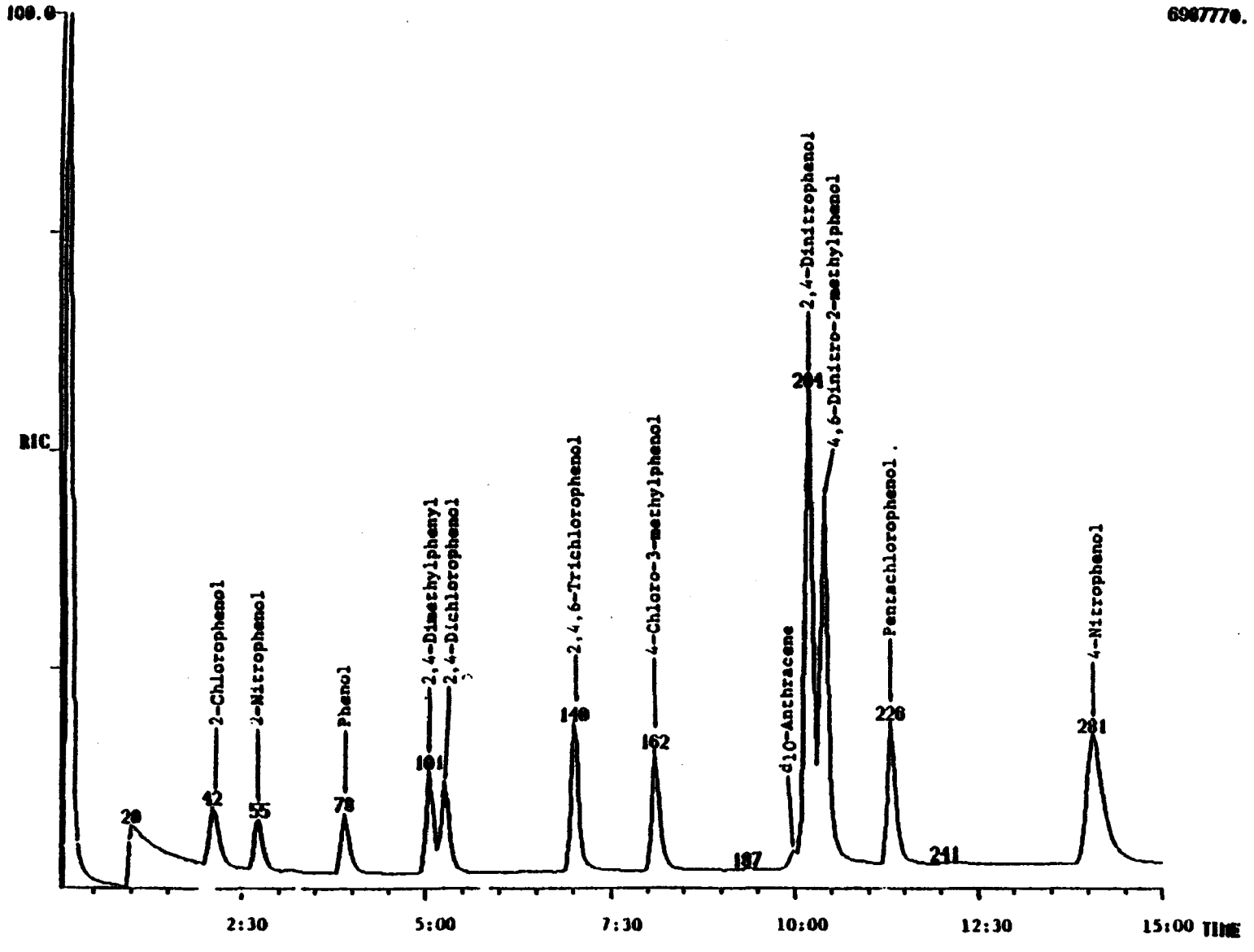

Figure 4. GC/MS chromatogram of the acidic compounds.