METHOD 8275

SEMI-VOLATILE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS

1.0 SCOPE AND APPLICATION

1.1 This method is designed to determine semi-volatile toxic organic chemicals and additional compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GC/MS).

1.2 The chemical compounds listed in Tables 1 and 2 may be determined in municipal and industrial discharges by this method. Any modifications of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures.

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in Tables 3 and 4 represent the minimum quantity that can be detected with no interferences present.

1.4 The GC/MS portions of this method are for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GC/MS should run performance tests before beginning.

2.0 SUMMARY OF MEHTOD

2.1 Stable isotopically labeled analogs of the compounds of interest are added to a 1 liter sample. The sample is extracted at pH 12-13, then at pH < 2 with methylene chloride using continuous extraction techniques. The extract is dried over sodium sulfate and concentrated to a volume of one mL. An internal standard is added to the extract, and the extract is injected into the gas chromotograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a compound (qualitative analysis) is performed by comparing the GC retention time and the background corrected characteristic mass spectra with those of authentic standards.

2.3 Quantitative analysis is performed by GC/MS using extracted ion current profile (EICP) areas. Isotope dilution is used when labeled compounds are available; otherwise, an internal standard method is used.

2.4 Quality is assured through reproducible calibration and testing of the GC/MS systems.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing

misinterpretation of chromatograms and spectra. All materials shall be demonstrated to be free from interferences under the conditions of the analysis by running blanks initially and with each sample lot (samples started through the extraction process on a given 8 hour shift, to a maximum of 20). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Non-volumetric glassware should be cleaned by solvent rinse and baking at 450°C for one hour minimum.

3.2 Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from water and carried through the sampling and handling protocol serves as a check on such contamination.

3.3 Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. When an unusually concentrated sample is encountered, it is followed by analysis of a water blank to check for carry-over.

3.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling.

4.1.1 Sampling bottle - amber glass, 1.1 liters minimum. If amber bottles are not available, samples shall be protected from light. Bottles are detergent water washed, then solvent rinsed, and then at 450°C for one hour minimum before use.

4.1.2 Bottle caps - threaded to fit sample bottles. Caps are lined with Teflon. Aluminum foil may be substituted if the sample is not corrosive. Liners are detergent water washed, then water and solvent rinsed, and baked at approximately 200°C for one hour minimum before use.

4.1.3 Compositing equipment - automatic or manual compositing system incorporating glass containers for collection of a minimum 1.1 liters. Sample containers are kept at 0 to 4°C during sampling. Glass or Teflon tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing is thoroughly rinsed with methanol, followed by repeated rinsings with water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

4.2 Continuous liquid-liquid extractor - Teflon or glass connecting joints and stopcocks without lubrication (Hershberg-Wolf Extractor), one liter capacity, (Ace Glass 6841-10, or equivalent).

4.3 Drying column - 15 cm by 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K-D) apparatus, 500-ml.

4.4.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

4.4.3 Snyder column - three ball macro (Kontes K-503000-022, or equivalent.

4.4.4 Snyder column - two ball micro (Kontes K-469002-0219, or equivalent.

4.5 Water bath - heated, with concentric ring cover, capable of temperature control ($\pm$ 2°C), installed in a fume hood.

4.6 Sample vials - amber glass, 2-15 mL with Teflon-lined screw cap.

4.7 Analytical balance - capable of weighing 0.1 mg.

4.8 Gas chromatograph - shall have splitless or on-column injection port for capillary column, temperature program with 30°C hold, and shall meet all the performance specifications.

4.8.1 Column - 30 $\pm$ 5 m x 0.25 $\pm$ 0.02 mm i.d. 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase fused silica capillary column (J & W DB-5, or equivalent).

4.9 Mass spectrometer - 70 eV electron impact ionization, shall repetitively scan from 35 to 450 amu in 0.95 to 1.00 second and shall produce a unite resolution (valleys between m/z 441-442 less 10 percent of the height of the 441 peak), background corrected mass spectrum from 50 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum shall meet the mass-intensity criteria in Table 5. The mass spectrometer shall be interfaced to the GC such that the end of the capillary column terminates within one centimeter of the ion source but does not intercept the electron or the ion beams. All portions of the column which connect the GC to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

4.10 Data system - shall collect and record MS data, store mass intensity data in spectral libraries, process GC/MS data and generate reports, and shall calculate and record response factors.

4.10.1 Data acquisition. Mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

4.10.2 Mass spectral libraries. User created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GC/MS runs for the compounds of interest (Step 7.2).

4.10.3 Data processing. The data system shall be used to search, locate, identify, and quantify the compounds of interest in each GC/MS analysis. Software routines shall be employed to compute retention times and EICP areas. Displays of spectra, or gas chromatograms, and library comparisons are required to verify results.

4.10.4 Response factors and multipoint calibration. The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves (Section 7.0). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and on-going performance shall be maintained.

4.11 Micro syringes - 10, 25, and 100-uL.

4.12 Balance - analytical, capable of weighing 0.1 mg.

4.13 Refrigerator.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.2 Methylene chloride, CH_2Cl_2, distilled in glass (Burdick and Jackson or equivalent).

5.3 Sodium hydroxide (6N), NaOH.

5.4 Sulfuric acid (6N), H_2SO_4.

5.5 Sodium sulfate, Na_2SO_4, granular anhydrous, rinsed with methylene chloride (20 mL/g) and conditioned at 450°C for one hour minimum.

5.6 Stock standard solutions. Purchase as solutions or mixtures with certification to their purity, concentration, and authenticity or prepare from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10°C in screw-

capped vials with Teflon-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is dissolved and solvent is added if solvent loss has occurred.

5.7 Preparation of stock standard solutions. Prepare in methylene chloride, benzene, p-dioxane, or a mixture of these solvents per the steps below. The large number of labeled and unlabeled acid and base/neutral, compounds used for combined calibration and calibration verification require high concentrations (approximately 40 mg/mL) when individual stock solutions are prepared so that dilutions of mixtures will permit calibration with all compounds in a single set of solutions. The working range for most compounds is 10-200 ug/mL. Compounds with a reduced MS response may be prepared at higher concentrations.

5.7.1 Dissolve an apporpriate amount of assayed reference material in a suitable solvent. For example, weigh 400 mg naphthalene in a 10-mL ground glass stoppered volumetric flask and fill to the mark with benzene. After the naphthalene is completely dissolved, transfer the solultion to a 15-mL vial with Teflon-lined cap.

5.7.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards.

5.7.3 Stock standard solutions shall be replaced after six months, or sooner if comparison with quality control check samples indicates a change in concentration.

5.8 Labeled compound spiking solution. Using stock standard solutions prepared as above, or from mixtures, prepare the labeled compound spiking solution at a concentration of 200 ug/mL or at a concentration appropriate to the MS response of each compound.

5.9 Secondary standards. Using stock standard solutions (Step 5.6 and 5.7), prepare a secondary standard containing all of the compounds in Tables 1 and 2 at a concentration of 400 ug/mL or at a higher concentration appropriate to the MS response of the compound.

5.10 Internal standard solution. Prepare 2,2'-difluorobiphenyl (DFB) at a concentration of 10 mg/mL in benzene.

5.11 DFTPP solution. Prepare decafluorotriphenylphosphine at 50 ug/mL acetone.

5.12 Solutions for obtaining authentic mass spectra (Step 7.2). Pprepare mixtures of compounds at concentrations which will assure authentic spectra are obtained for storage in libraries.

5.13 Calibration solutions. Combine 0.5 mL of the labeled compound spiking solution in Step 5.8 with 25, 50, 125, 250, and 500 uL of the

secondary standard solution in Step 5.9 and bring each to 1.00 mL total volume. This will produce calibration solutions of nominal 10, 20, 50, 100 and 200 ug/mL of the chemicals and a constant nominal 100 ug/mL of the labeled compounds. Spike each solution with 10 uL of the internal standard solution (Step 5.10). These calibration solutions permit the relative response (labeled to unlabeled) to be measured as a function of concentration.

5.14 Precision and recovery standards are used for determination of initial and on-going precision and recovery. This solution shall contain all the chemicals and labeled compounds at a nominal concentraion of 100 ug/mL.

5.15 Stability of solutions. All standard solutions (Steps 5.8 - 5.14) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area at the quantitation mass relative to the DFB internal standard remains within $\pm$ 15 percent of the area obtained in the initial analysis of the standard.

5.16 Boiling chips - approximately 10/40 mesh. Extract with methylene chloride and bake at 450°C for one hour.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Collect samples in glass containers following conventional sampling practices. Composite samples are collected in refrigerated glass containers in accordance with the requirements of the sampling program.

6.2 Maintain samples at 0-4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine.

6.3 Begin sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction.

6.4 All sampling plans shall address the issues raised in Chapter Nine.

7.0 PROCEDURES

7.1 Assemble the GC/MS apparatus and establish operating conditions given in Tables 3 and 4. By injecting standards into the GC, demonstrate that the analytical system meets the detection limits in Tables 3 and 4 and the mass-intensity criteria in Table 5 for 50 ng DFTPP.

7.2 Mass spectral libraries. Identification of the compounds of interest are dependent upon the mass spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each chemical labeled compound, and internal standard by analyzing an authentic standard either singly

or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to enhance the spectrum may eliminate distortion, but may also eliminate authentic m/z's or introduce other distortion.

7.2.2 The authentic reference spectrum is obtained under DFTPP tuning conditions (Steps 7.1 and Table 5) to normalize it to spectra from other instruments. See Step 5.12.

7.3 Analytical range. Demonstrate that 25 ng anthracene or phenanthrene produces an area at m/z 178 approximately one-tenth that required to exceed the linear range of the system. The exact value must be determined for each instrument. It is used to match the calibraton range of the instrument to the analytical range and detection limits required and to diagnose instrument sensitivity problems. One uL of the 20 ug/mL calibration standard (Step 5.13) can be used to demonstrate this performance.

7.3.1 Polar compound detection. Demonstrate that unlabled pentachlorophenol and benzidine are detectable at the 50 ug/mL level. The 50 ug/mL calibration standard (Step 5.13) can be used to demonsrate this performance.

7.4 Calibration by isotope dilution. The isotope dilution approach is used for organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available, or interferences are present, the internal standard method (Step 7.5) is used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) versus concentration (ug/L) is plotted or computed using a linear regression. An example of a calibration curve for phenol using phenol-d_5 as the isotopic diluent is given in Figure 1. Also shown are the $\pm$ 10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration.

7.4.1 The relative response (RR) of a chemical to its labled analog is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured in the pure chemical (Figure 3A).

R_y = the isotope ratio of pure labeled compound (Figure 3B).

R_m = the isotope ratio measured in the analytical mixture of the chemical and labeled compounds (Figure 3C).

The m/z's are selected such that Rx > Ry. If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method (Step 7.5).

7.4.2 Capillary columns usually separate the chemical-labeled pair with the labeled compound usually eluting first (Figure 2). When there is a difference in retention times (RT) between the chemical and labeled compounds, use the following equations:

$$R_x = \frac{[\text{area } m_1/z]}{1}$$

at the retention time of the chemical (RT_2)

$$Ry = \frac{1}{[\text{area } m_2/z]}$$

at the retention time of the labeled compound (RT_1)

$$Rm = \frac{[\text{area } m_1/z \text{ (at } RT_2)]}{[\text{area } m_2/z \text{ (at } RT_1)]}$$

as measured in the mixture of the chemical and labeled analog.

NOTE: Most but not all compounds elute before their chemical analogs.

RR is computed as follows:

$$RR = \frac{(R_y-R_m)(R_x+1)}{(R_m-R_x)(R_y+1)}$$

7.4.3 Special precautions are taken when the chemical labeled pair is not separated, or when another labeled compound with interfering spectral masses overlaps the chemical (a case which can occur with isomeric compounds). In this case, it is necessary to determine the respective contributions of the chemical and labeled compounds to the respective EICP areas. If the peaks are separated well enough to permit the data system or operator to remove the contributions of the compounds to each other, the equations in Step 7.4.2 apply. This usually occurs when the height of the valley between the two GC peaks at the same m/z is less than 10 percent of the height of the shorter of the two peaks. If significant GC and spectral overlap occur, use the following equations:

For the example given, Rx is measured as shown in Figure 3A, Ry is measured as shown in Figure 3B, and Rm is measured as shown in Figure 3C.

For the unlabeled compound:

$$R_x = \frac{[\text{area } M_1/z]}{[\text{area } M_2/z]}$$

$$R_x = \frac{46100}{4780} = 9.644$$

For the labeled compound

$$R_y = \frac{[\text{area } M_1/z]}{[\text{area } M_2/z]}$$

$$R_y = \frac{2650}{43600} = 0.0608$$

For an equal mixture of labeled and unlabeled compounds:

$$R_m = \frac{[\text{area } M_1/z]}{[\text{area } M_2/z]}$$

$$R_m = \frac{49200}{48300} = 1.019$$

RR is calculated as follows:

$$RR = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

$$RR = 1.114$$

7.4.4 To calibrate the analytical system by isotope dilution, analyze a 5 mL aliquot of each of the calibration standards (Step 5.13) Compute the RR at each concentration.

7.4.5 Linearity. If the ratio of relative response to concentration for any compound is constant (less then 20 percent coefficient of variation) over the 5 point calibration range, an average relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for the compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard. Use internal standard calibration when criteria for isotope dilution (Step 7.4) cannot be met. The internal standard to be used for both acid and base/neutral analyses is 2,2'-difluorobiphenyl. The internal standard method is also applied to determination of compounds having no labeled analog, and to measurement of labeled compounds for intra-laboratory statistics (Step 8.4).

7.5.1 Response factors. Calibration requires the determination of response factore (RF) which are defined by the following equation:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where

A_s is the area at the characteristic mass for the chemical in the daily standard.

A_{is} is the area at the characteristic mass for the internal standard.

C_{is} is the concentration (ug/L) of the internal standard.

C_s is the concentration (ug/L) of the chemical in the daily standard.

7.5.2 The response factor is detemined for at least five concentrations appropriate to the response of each compound ; nominally, 10,20, 50, 100, and 200 ug/mL. The amount of internal standard added to each extract is the same (100 ug/mL) so that C_{is} remains constant. The RF is plotted against concentration for each compound in the standard (C_s) to produce a calibration curve.

7.5.3 Linearity. If the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an average response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration. By adding the isotopically labeled compounds and internal standards to the calibration standards (Step 5.13), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift by analyzing the 125 ug/ml calibration standard (Step 5.13). Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.7 SAMPLE EXTRACTION AND CONCENTRATION

7.7.1 Labeled compound spiking.Measure 1.00 $\pm$ 0.01 liter of sample into a glass container. For untreated effluents and samples which are expected to be difficult to extract and/or concentrate, measure 10.0 $\pm$ 0.01 mL of sample and dilute to a final volume of 1.00 $\pm$ 0.01 liter with water in a glass container.

7.7.1.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 1.00 $\pm$ 0.01 liter aliquots of water in glass containers.

7.7.1.2 Spike 0.5 mL of the labeled compound spiking solution (Step 5.8) into all samples and one water aliquot.

7.7.1.3 Spike 1.0 mL of the precision and recovery standard (Step 5.14) into the two remaining water aliquots.

7.7.1.4 Stir and equilibrate all solutions for 1-2 hours.

7.7.2 Base/neutral extraction. Place 100-150 mL of methylene chloride in each continuous extractor and 200-300 mL in each distilling flask.

7.7.2.1 Pour the sample(s), blank(s), and standard(s) into the extractors. Rinse the glass containers with 50-100 mL of methylene chloride and add the solvent to the respective extractor.

7.7.2.2 Adjust the pH of the samples in the extractors to 12-13 with 6N NaOH while monitoring with a pH meter. Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1-2 drops of methylene chloride per second will fall from the condenser tip into the water. After 1-2 hours of extraction, test the pH and adjust to 12-13 if required. Extract for 18-24 hours.

7.7.2.3 Remove the distilling flask, estimate and record the volume of extract (to the nearest 25 mL), and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the distilling flask with 30-50 mL of methylene chloride and pour through the drying column. Collect the solution in a 500-mL K-D evaporator flask equipped with a 10-mL concentrator tube. Seal, label as the base/neutral fraction, and concentrate per Steps 7.7.4 to 7.7.5.

7.7.3 Acid extraction. Adjust the pH of the samples in the extractors to 2 or less using 6N sulfuric acid. Charge clean distilling flasks with 300-400 mL of methylene chloride. Test and adjust the pH of the samples after the first 1-2 hours of extraction. Extract for 18-24 hours.

7.7.3.1 Repeat Step 7.7.2.3, except label as the acid fraction.

7.7.4 Concentration. Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes.

7.7.4.1 Add 1 or 2 clean boiling chips to the flask and attach a three ball macro Snyder column. Prewet the column by adding approximately 1 mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed in steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

7.7.4.2 For performance standards (Step 8.2) and for blanks (Step 8.5), combine the acid and base/neutral extracts at this point. Do not combine the acid and base/neutral extracts for samples.

7.7.5 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the

water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid reaches an apparent volume of approx 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride using a 1-mL syringe. Adjust the final volume to 1.0 mL.

7.7.6 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid, and mark the level on the vial. Label with the sample number and fraction, and store in the dark at -20 to -10°C until ready for analysis.

7.7.7 GC/MS ANALYSIS

7.7.8 Establish the operating conditions given in Tables 3 or 4 for analysis of the base/neutral or acid extracts, respectively. For analysis of combined extracts (Step 7.7.4.2), use the operating conditions in Table 3.

7.7.9 Bring the concentrated extract (Step 7.7.6) and standards (Steps 5.13 and 5.14) to room temperature and verify that any precipitate has dissolved. Verify the level of the extract (Steps 5.6 and 7.7.6) and bring to the mark with solvent if required.

7.7.10 Add the internal standard solution (Step 5.10) to the extract (use 10 uL of internal standard solution per 1 mL of extract) immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

7.7.11 Inject volumes of the standard solutions or extracts such that 100 ng of the internal standard will be injected, using on-column or splitless injection. For 1 mL extracts, this volume will be 1.0 uL. Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the benzo (ghi) perylene or pentachlorophenol peak elutes for the base/neutral or acid fraction, respectively. Return the column to the initial temperature for analysis of the next sample.

7.8 System Performance.

7.8.1 At the beginning of each 8 hour shift during which analyses are performed, system calibration and performance shall be verified for all chemicals and labeled compounds. For these tests, analysis of the 100 ug/ml calibration standard (Step 5.13) shall be used. Adjustment and/or recalibration shall be performed until performance criteria are met. Only after all performance criteria are met may blanks, samples, and precision and recovery standards be analyzed.

7.8.2 DFTPP spectrum validity. Inject 1 uL of the DFTPP solution (Step 5.11) either separately or within a few seconds of injection of the calibration verification standard (Step 7.8.1) analyzed at the beginning of each shift.

7.8.3 Retention times. The absolute retention time of 2,2'-diflourobiphenyl shall be within the range of 1078 to 1248 seconds and the relative retention times of all chemicals and labeled compounds shall fall within the limits given in Tables 3 and 4.

7.8.4 GC resolution. The valley height between anthracene and phenanthrene at m/z 178 (or the labeled analogs at m/z 188) shall not exceed 10 percent of the taller of the two peaks.

7.8.5 Calibration verification. Compute the concentration of each chemical (Table 1 and 2) by isotope dilution (Step 7.4) for those compounds which have labeled analogs. Compute the concentration of each chemical (Table 1 and 2) which has no labeled analog by the internal standard method (Step 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in Section 7.0. For these tests, analysis of the 100 ug/mL calibration standard (Step 5.13) shall be used.

7.8.5.1 For each chemical and labeled compound being tested, compare the concentration with the corresponding limit for calibration verification in Table 8. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks, precision and recovery standards, and samples may proceed. If any individual value falls outside the range given, system performance is unacceptable for that compound. The large number of compounds in Table 8 presents a substantial probability that one or more will fall outside of the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure may be attributed to probability, proceed as follows:

7.8.5.1.1 Analyze a freshly prepared calibration verification standard.

7.8.5.1.2 Compute the concentration for only those compounds which failed the first test (Step 7.8.5.1). If these compounds now pass, system performance is acceptable for all compounds and analyses of blanks, samples, and precision and recovery standards may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the system and repeat the entire performance series (Step 7.8.1 to 7.8.5.1.2) for all compounds.

7.8.6 On-going precision and accuracy.

7.8.6.1 Analyze the extract of one of the pair of precision and recovery standards (Step 7.7.1.3) prior to analysis of samples from the same lot.

7.8.6.2 Compute the concentration of each chemical (Tables 1 and 2) by isotope dilution (Step 7.4) for those compounds which have labeled analogs. Compute the concentration of each chemical which has no labeled analog by the internal standard method (Step 7.5). Compute the concentration of the labled compounds by the internal standard method.

7.8.6.3 For each chemical and labeled compound, compare the concentration with the limits for on-going accuracy in Table 8. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, system performance is unacceptable for that compound. The large number of compounds in Table 8 present a substantial probability that one or more will fail when all compounds are analyzed. To determine if the extraction/concentration system is out of control, or if the failure is caused by probability, proceed as follows:

7.8.6.4 Analyze a second aliquot of the pair of precision and recovery standards (Step 7.7.1.3).

7.8.6.5 Compute the concentration for only those chemicals or labeled compounds that failed the previous test (Step 7.8.7.3). If these compounds now pass, the extraction/concentration processes are in control and analyses of blanks and samples may proceed. If, however, any of the same compounds fail again, the extraction/concentration processes are not being peformed properly for these compounds. In this event, correct the problem, extract the samples again (Step 7.7) and repeat the on-going precision and recovery test (Step 7.8.6).

7.8.7 Add results which pass the specifications in Steps 7.8.5 and 7.8.6 to initial and on-going data (Step 8.2). Update QC charts to form a graphic representation of laboratory performance (Figure 5). Develop a statement of accuracy for each chemical and labeled compound by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85-105 percent.

7.9 Qualitative determination is accomplished by comparison of data from analysis of a sample with data from analysis of the daily calibration verification standard (Step 7.8.1) and with data stored in spectral libraries (Step 7.2). Identification is confirmed when mass spectra and retention times agree per the criteria below.

7.9.1 Labeled compounds and chemicals having no labeled analog:

7.9.1.1 The signals for all characteristic masses stored in the spectral library (Step 7.2.1) shall be present and shall maximize within the same two consecutive scans.

7.9.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

7.9.1.3 The retention time difference relative to the nearest eluted internal standard shall be within $\pm$ 20 seconds of this retention time difference in the daily calibration verification standard (Step 7.8.1).

7.9.2 Chemicals having a labeled analog:

7.9.2.1 The signals for all characteristic masses stored in the spectral library (Step 7.2.1) shall be present and shall maximize within the same two consecutive scans.

7.9.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the spectral library.

7.9.2.3 The retention time difference between the chemical and its labeled analog shall agree within $\pm$ 6 seconds of this difference in the daily calibration verification standard (Step 7.8.1).

7.9.3 Masses present in the sample mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the sample mass spectrum is contaminated, an experienced spectrometrist shall determine the presence or absence of the compound.

7.10 Quantitative determination.

7.10.1 Isotope dilution. By adding a known amount of a labeled compound to every sample prior to extracting, correction for recovery of the chemical can be made because the chemical and its labeled analog should exhibit the same effects upon extraction, concentration, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in Step 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the phenol example given in Figure 1 and Step 7.4.3, RR would be equal to 1.114. For this RR value, the phenol calibration curve given in Figure 1 indicates a concentration of 27 ug/mL in the sample extract (C_{ex}).

7.10.2 Internal standard. Calculate the concentration in the extract using the response factor determined from calibration data (Step 7.5) and the following equation:

$$\text{Concentration} = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

where the terms are as defined in Step 7.5.1.

7.10.3 The concentration of the chemical in the original sample is computed using the volumes of the original sample (Step 7.7.10) and the final extract volume (Step 7.7.5), as follows:

$$C_o(ug/L) = \frac{C_{ex} \times V_{ex}}{V_s}$$

where

V_{ex} is the extract volume in mL
V_s is the sample volume in liters
C_{ex} is the concentration in the extract
C_o is the concentration in the original sample

7.10.3.1 If the EICP area at the quantitiation mass for any compound exceeds the calibration range of the system, the extract of the dilute aliquot (Step 7.7.1) is analyzed by the isotope dilution method. Alternatively, the extract is diluted by a factor of 10, 9 uL of internal standard solution (Step 5.10) is added to a 1.0 mL aliquot, and this diluted extract is analzed by the internal standard method (Step 7.5). Quantify each compound at the highest concentration level within the calibration range.

7.10.4 Report results for all chemicals and labeled compounds (Table 1 and 2) found in all standards, blanks, and samples in ug/L, to three significant figures. Results for samples which have been diluted are reported at the least diluted level at which the area at the quantitation mass is within the calibration range and the labeled compound recovery is within the normal range for the method .

7.11 Analysis of complex samples.

7.11.1 Untreated effluents and other samples frequently contain high levels (> 1000 ug/L) of the compounds of interest and of interfering compounds. Some samples will not concentrate to 1.0 mL; others will overload the GC column and/or mass spectrometer.

7.11.2 Analyze the dilute aliquot (Step 7.7.1) when the sample will not concentrate to 1.0 mL. If a dilute aliquot was not extracted, and the sample holding time (Step 6.3) has not been exceeded, dilute an aliquot of the sample with water and extract (Step 7.7); otherwise, dilute the extract (Step 7.7.5) and analyze by the internal standard method (Step 7.5.2).

7.11.3 Recovery of internal standard. The EICP area of the internal standard should be within a factor of two of the area of the daily calibration verification standard (Step 7.9). If the absolute area of the labeled compounds are within a factor of two of the respective areas in the calibration verification standard, and the internal standard area is less than one-half of its respective area, then internal standard loss in the extract has occurred. In this case, use one of the labeled compounds (preferably a polynuclear aromatic hydrocarbon) to compute the concentration of a chemical with no labeled analog.

7.11.4 Recovery of labeled compounds. In most samples, labeled compound recoveries will be similar to those from water (Step 7.7.1.2). If the labeled compound recovery is outside the limits given in Table 8, the dilute extract (Step 7.7.1) is analyzed. If the recoveries of all labeled compounds and the internal standard are low (per the criteria above), then a loss in instrument sensitivity is the most likely cause. In this case, the 100 ug/mL calibration verification standard (Step 7.9) shall be analyzed and calibration verified. If a loss in sensitivy has occurred, the instrument shall be repaired, the performance specifications in Step 7.9 shall be met, and the extract reanalyzed. If a loss in instrument sensitivity has not occurred, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (Step 8.2), analysis of samples spiked with labeled compounds to evaluate and document data quality (Step 8.3), analysis of blanks (Step 8.5), and tests of continued performance (Step 8.1.5). Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Step 8.2. The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in Step 8.2 to demonstrate method performance.

8.1.2 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Step 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (Step 7.11.2).

8.1.3 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Steps 8.4.

8.1.4 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis (Section 3.0). The procedures and criteria for analysis of blanks are described in Step 8.5.

8.1.5 The laboratory shall, on an on-going basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (Step 5.14) that the analysis system is in control. These procedures are described in Steps 7.8.5 and 7.8.6.

8.2 Initial precision and accuracy (method performance). To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 Extract, concentrate, and analyze two sets of four, 1-liter aliquots (8 aliquots total) of the precision and recovery standard (Step 5.14) according to the method beginining in Step 7.7.

8.2.2 Using results of the first set of four analyses, compute the average recovery (X) in ug/mL and the standard deviation of the recovery(s) in ug/mL for each compound by isotope dilution for chemicals with a labeled analog, and by internal standard for labeled compounds and chemicals with no labeled analog.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy found in Table 8. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. The large number of compounds in Table 8 presents a substantial probability that one or more compounds will fail one of the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.3.1 Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (Step 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for the compound(s) in question. In this event, correct the problem and repeat the entire test (Step 8.2).

8.3 The analyst shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Spike and analyze each sample according to the method beginning in Step 7.7.

8.3.2 Compute the average percent recovery (P) of the labeled compounds using the internal standard method (Step 7.5).

8.3.3 Compare the percent recovery for each labeled compound with the corresponding labeled recovery limit in Table 8. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample matrix is complex and the sample is to be diluted and reanalyzed, per Step 7.11.2.

8.4 As part of the Quality Assurance program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five samples for which recovery of the labeled compounds pass the test in Step 8.3.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from P - $2s_p$ to P + $2s_p$. For example, if P = 90% and s_p = 10%, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each compound on a regular basis (e.g. after each 5-10 new measurements).

8.5 Blanks are analyzed to demonstrate freedom from carry-over (Section 3.0) and contamination.

8.5.1 Extract and concentrate a blank with each analytical batch (samples started through the extraction process on the same 8 hour shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the precision and recovery standard (Step 7.8.6) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (Tables 1 and 2), or any potentially interfering compound is found in a blank greater than 10 ug/L (assuming a response factor of 1 relative to the internal standard for compounds not listed in Tables 1 and 2), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (Sections 7.4 and 7.5), calibration verification (Step 7.8.5), and for initial (Step 8.2) and on-going (Step 8.1.5) precision and accuracy should be identical, so that the most precise results will be obtained. The GC/MS instrument, in particular, will provide the most reproducible results if dedicated to the settings and conditions required for the anlayses of semi-volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis.

9.0 METHOD PERFORMANCE

9.1 Interlaboratory performance for this method is detailed in references 1 and 4.

9.2 Performance requirements are found in Steps 7.1, 7.3, 7.3.1, 7.8, 7.9, 7.11.3, 7.11.4, Section 8.0, and Tables 3, 4, 5, and 8.

10.0 REFERENCES

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3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories; U.S. Environmental Protection Agency. Office of Research and Developmnent. Enviornmental Monitoring and Support Laboratory. ORD Publications Office of Center for Environmental Research Information: Cincinnati, OH, 1979; EPA-600/4-79-019.

4. "Inter-laboratory Validation of U.S. Enviornmental Protection Agency Method 1625"; U.S. Enviornmental Protection Agency. Effluent Guidelines Division. U.S. Government Printing Office: Washington, DC, 1984.

5. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Devlopment. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

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7. Rohrbough, W. G.; et al. Reagent Chemicals, American Chemical Society Specificationsn, 7th ed.; American Chemical Society: Washington, DC, 1986.

8. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitory and Support Laboratory. ORD Publication Offices of Center for Enviornmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

9. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specifications for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

TABLE 5

DFTPP Mass-intensity Specifications

MASS	INTENSITY REQUIRED
51	30-60 percent of mass 198
68	<2 percent of mass 69
70	<2 percent of mass 69
127	40-60 percent of mass 198
197	<1 percent of mass 198
198	base peak, 100 percent abundance
199	5-9 percent of mass 198
275	10-30 percent of mass 198
365	>1 percent of mass 198
441	present but less than mass 443
442	>40 percent of mass 198
443	17-23 percent of mass 442

TABLE 6

Base/Neutral Extractable Compound
Characteristic Masses

COMPOUND	LABELED ANALOG	PRIMARY M/Z'S
acenaphthene	d_{10}	154/164
acenaphthylene	d_8	152/160
anthracene	d_{10}	178/188
benzidine	d_8	184/192
benzo(a)anthracene	d_{12}	228/240
benzo(b)fluoroanthene	d_{12}	252/264
benzo(k)fluoroanthene	d_{12}	252/264
benzo(a)pyrene	d_{12}	252/264
benzo(ghi)perylene	d_{12}	276/288
bipheynyl	d_{10}	154/164
bis(2-chloroethyl) ether	d_8	93/101
bis(2-chloroethoxy) methane	d_8	93
bis(2-chloroisopropyl) ether	d_{12}	121/131
bis(2-ethylhexyl) phthalate	d_4	149/153
4-bromophenyl phenyl ether	d_5	248
butyl benzyl phthalate	d_4	149
n-decane	d_{22}	55/66
n-dodecane	d_{26}	55/66
n-tetradecane		55
n-hexadecane	d_{34}	55/56
n-octadecane		55
n-licosane	d_{42}	55/56
n-docosane		56
n-tetracosane	d_{50}	55/66
n-hexacosane		55
n-octacosane		55
n-triacontane	d_{62}	55/56
carbazole	d_8	167/175
2-chloronaphthalene	d_7	162/169
4-chlorophenyl phenyl ether	d_5	204/209
chrysene	d_{12}	228/240
p-cymene	d_{14}	119/130
dibenzo(a,h) anthracene	d_{14}	278
dibenzofuran	d_8	168/176
dibenzothiophene (Synfuel)	d_8	184/192
di-n-butyl phthalate	d_4	149/153
1,2-dichlorobenzene	d_4	146/152
1,3-dichlorobenzene	d_4	146/152
1,4-dichlorobenzene	d_4	146/152
3,3-dichlorobenzene	d_6	252/258
diethyl phthalate	d_4	149/153
2,4-dimethylphenol	d_3	122/125
dimethyl phthalate	d_4	163/167
2,4-dinitrotoluene	d_3	165/168
2,6-dinitrotoluene	d_3	165/167

TABLE 6 (continued)

Base/Neutral Extractable Compound
Characteristic Masses

COMPOUND	LABELED ANALOG	PRIMARY M/Z'S
di-n-octyl phthalate	d_4	149/153
diphenylamine	d_{10}	169/179
diphenyl ether	d_{10}	170/180
1,2-diphenythydrazine (1)	d_{10}	77/82
fluoranthene	d_{10}	202/212
fluorene	d_{10}	166/176
hexachlorobenzene	$^{13}C_6$	284/292
hexachlorobutadiene	$^{13}C_4$	225/231
hexachloroethane	^{13}C	201/204
hexachlorocyclopentadiene	$^{13}C_4$	237/241
ideno(1,2,3-cd) pyrene		276
isophorone	d_8	82/88
naphthalene	d_8	128/136
beta-naphthylamine	d_7	143/150
nitrobenzene	d_5	123/128
N-nitrosodimethylamine	d_6	74
N-nitrosodi-n-proplylamine	d_{14}	70
N-nitrosodiphenylamine (2)	d_6	169/175
phenanthrene	d_{10}	178/188
phenol	d_5	94/71
alpha-picoline (Synfuel)	d_7	93/100
pyrene	d_{10}	202/212
styrene	d_5	104/109
alpha-terpineol	d_3	59/62
1,2,3-trichlorobenzene	d_3	180/183
1,2,4-trichlorobenzene	d_3	180/183

(1) detected as azobenzene
(2) detected as diphenylamine

TABLE 7

Acid Extractable Compound
Characteristic Masses

COMPOUND	LABELED ANALOG	PRIMARY M/Z'S
4-chloro--methylphenol	d_2	107/109
2-chlorophenol	d_4	128/132
2,4-dichlorophenol	d_3	162/167
2,4-dinitrophenol	d_3	184/187
2-methyl-4,6-dinitrophenol	d_2	198/200
2-nitrophenol	d_4	139/143
4-nitrophenol	d_4	139/143
pentachlorophenol	$^{13}C_6$	266/272
2,3,6-trichlorophenol	d_2	196/200
2,4,5-trichlorophenol	d_2	196/200
2,4,6-trichlorophenol	d_2	196/200

TABLE 8

Acceptance Criteria for Performance Test

COMPOUND	INITIAL PRECISION AND ACCURACY (ug/L) s	X	LABELED COMPOUND RECOVERY P(%)	CALIBRATION VERIFICATION (ug/mL)	ON-GOING ACCURACY R(ug/L)
acenaphthene (1)	21	79-134		80-125	72-144
acenaphthene-d_{10}	38	38-147	20-270	71-141	30-180
acenaphthylene (1)	38	69-186		60-166	61-207
acenaphthylene-d_8	31	39-146	23-239	66-152	33-168
anthracene (1)	41	58-174		60-168	50-199
anthracene-d_{10}	49	31-194	14-419	58-171	23-242
benzidine (1)	119	16-518		34-296	11-672
benzidine-d_8	269	ns-ns	ns-ns	ns-ns	ns-ns
benzo(a)anthracene (1)	20	65-168		70-142	62-176
benzo(a)anthracene-d_{12}	41	25-298	12-605	28-357	22-329
benzo(b)fluoroanthene (1)	183	32-545		61-164	20-ns
benzo(b)fluoroanthene-d_{12}	168	11-577	ns-ns	14-ns	ns-ns
benzo(k)fluoroanthene (1)	26	59-143		13-ns	53-155
benzo(k)fluoroanthene-d_{12}	114	15-514	ns-ns	13-ns	ns-685
benzo(a)pyrene (1)	26	62-195		78-129	59-206
benzo(a)pyrene-d_{12}	24	35-181	21-290	12-ns	32-194
benzo(ghi)perylene (1)	21	72-160		69-145	58-168
benzo(ghi)perylene-d_{12}	45	29-268	14-529	13-ns	25-303
bipheynyl (1)	41	75-148		58-171	62-176
bipheynyl-d_{10}	43	28-165	ns-ns	52-192	17-267
bis(2-chloroethyl) ether (1)	34	55-196		61-164	50-213
bis(2-chloroethyl) ether-d_8	33	29-196		15-372	25-222
bis(2-chloroethoxy) methane	27	43-153		44-228	39-166
bis(2-chloroisopropyl) ether (1)	17	81-138		67-148	77-145
bis(2-chloroisopropyl) ether-d_{12}	27	35-149	20-260	44-229	30-169
bis(2-ethylhexyl) phthalate (1)	31	69-220		76-131	64-232
bis(2-ethylhexyl) phthalate-d_4	29	32-205	18-364	43-232	28-224
4-bromophenyl phenyl ether	44	44-140		52-193	35-172
butyl benzyl phthalate	31	37-183		22-450	35-195
n-decane (1)	51	24-195		42-235	19-237
n-decane-d_{22}	70	ns-298	ns-ns	44-227	29-424
n-dodecane (1)	74	35-369		60-166	29-424
n-dodecane-d_{28}	53	ns-331	ns-ns	41-242	ns-408
n-tetradecane	109	ns-985		37-268	ns-ns
n-hexadecane (1)	33	80-162		72-138	71-181
n-hexadecane-d_{34}	46	37-162	18-308	54-186	28-202
n-octadecane	39	42-131		40-249	35-167
n-eicosane (1)	59	53-263		54-184	46-301
n-eicosane-d_{42}	34	34-172	19-306	62-162	29-198
n-docosane	31	41-184		40-249	39-195
n-tetracosane (1)	11	80-139		65-154	78-142
n-tetracosane-d_{50}	28	27-211	15-376	50-199	25-229

TABLE 8 (CONTINUED)

Acceptance Criteria for Performance Test

COMPOUND	INITIAL PRECISION AND ACCURACY (ug/L) s	X	LABELED COMPOUND RECOVERY P(%)	CALIBRATION VERIFICATION (ug/mL)	ON-GOING ACCURACY R(ug/L)
n-hexacosane	35	35-193		26-392	31-212
n-octacosane	35	35-193		26-392	31-212
n-triacontane (1)	32	61-200		66-152	56-215
n-triacontane-d_{62}	41	27-242	13-479	24-423	23-274
carbazole	38	36-165		44-227	31-188
2-chloronaphthalene (1)	100	46-357		58-171	35-442
2-chloronaphthalene-d_7	41	30-168	15-324	72-139	24-204
4-chloro-3-methylphenol	37	76-131		85-115	62-159
4-chloro-3-methylphenol-d_2	111	30-174	ns-613	68-147	14-314
2-chlorophenol	13	79-135		78-129	76-138
2-chlorophenol-d_4	24	36-162	23-255	55-180	33-176
4-chlorophenyl phenyl ether (1)	42	75-166		71-142	63-194
4-chlorophenyl phenyl ether-d_2	52	40-161	19-325	57-175	29-212
chrysene (1)	51	59-186		70-142	48-221
chrysene-d_{12}	69	33-219	13-512	24-411	23-290
p-cymene (1)	18	76-140		79-127	72-147
p-cymene-d_{14}	67	ns-359	ns-ns	66-152	ns-468
dibenzo(a,h) anthracene	55	23-299		13-761	19-340
dibenzofuran (1)	20	85-136		73-136	79-146
dibenzofuran-d_8	31	47-136	28-220	66-150	39-160
dibenzothiophene (1)	31	79-150		72-140	70-168
dibenzothiophene-d_8	31	48-130	29-215	69-145	40-156
di-n-butyl phthalate (1)	15	76-165		71-142	74-169
di-n-butyl phthalate-d_4	23	23-195	13-346	52-192	22-209
1,2-dichlorobenzene (1)	17	73-146		74-135	70-152
1,2-dichlorobenzene-d_4	35	14-212	ns-494	61-164	11-247
1,3-dichlorobenzene (1)	43	63-201		65-154	55-225
1,3-dichlorobenzene-d_4	48	13-203	ns-550	52-192	ns-260
1,4-dichlorobenzene (1)	42	61-194		62-161	53-219
1,4-dichlorobenzene-d_4	48	15-193	ns-474	65-153	11-245
3,3'-dichlorobenzidene (1)	26	68-174		77-130	64-185
3,3'-dichlorobenzidene-d_6	80	ns-562	ns-ns	18-558	ns-ns
2,4-dichlorophenol	12	85-131		67-149	83-135
2,4-dichlorophenol-d_3	28	38-164	24-260	64-157	34-182
diethyl phthalate (1)	44	75-196		74-135	65-222
diethyl phthalate-d_4	78	ns-260	ns-ns	47-211	ns-ns
2,4-dimethylphenol (1)	13	62-153		67-150	60-156
2,4-dimethylphenol-d_3	22	15-228	ns-449	58-172	14-242
dimethyl phthalate (1)	36	74-188		73-137	67-207
dimethyl phthalate-d_4	108	ns-640	ns-ns	50-201	ns-ns
2,4-dinitrophenol	18	72-134		75-133	68-141

TABLE 8 (CONTINUED)

Acceptance Criteria for Performance Test

COMPOUND	INITIAL PRECISION AND ACCURACY (ug/L) s	X	LABELED COMPOUND RECOVERY P(%)	CALIBRATION VERIFICATION (ug/mL)	ON-GOING ACCURACY R(ug/L)
2,4-dinitrophenol-d_3	66	22-308	ns-ns	39-256	17-378
2,4-dinitrotoluene (1)	18	72-134		75-133	68-141
2,4-dinitrotoluene-d_3	37	22-245	10-514	53-187	19-275
2,6-dinitrotoluene (1)	30	80-141		55-183	70-159
2,6-dinitrotoluene-d_3	59	44-184	17-442	36-278	31-250
di-n-octyl phthalate (1)	16	77-161		71-140	74-166
di-n-octyl phthalate-d_4	46	12-383	ns-ns	21-467	10-433
diphenylamine (1)	45	58-205		57-176	51-231
diphenylamine-d_{10}	42	27-206	11-488	59-169	21-249
diphenyl ether (1)	19	82-136		83-120	77-144
diphenyl ether-d_{10}	37	36-155	19-281	77-129	29-186
1,2-diphenylhydrazine (1)(3)	73	49-308		75-134	40-360
1,2-diphenylhydrazine-d_{10}	35	31-173	17-316	58-174	26-200
fluoranthene (1)	33	71-177		67-149	64-194
fluoranthene-d_{10}	35	36-161	20-278	47-215	30-187
fluorene (1)	29	81-132		74-135	70-151
fluorene-d_{10}	43	51-131	27-238	61-164	38-172
hexachlorobenzene (1)	16	90-124		78-128	85-132
hexachlorobenzene-$^{13}C_5$	81	36-228	13-595	38-265	23-321
hexachlorobutadiene (1)	56	51-251		74-135	43-287
hexachlorobutadiene-$^{13}C_4$	63	ns-316	ns-ns	68-148	ns-413
hexachloroethane (1)	227	21-ns		71-141	13-ns
hexachloroethane-$^{13}C_1$	77	ns-400	ns-ns	47-212	ns-563
hexachlorocyclopentadiene (1)	15	69-144		77-129	67-148
hexachlorocyclopentadiene-$^{13}C_4$	60	ns-ns	ns-ns	47-211	ns-ns
indeno(1,2,3-cd)pyrene	55	23-299		13-761	19-340
isophorone (1)	25	76-156		70-142	70-168
isophorone-d_8	23	49-133	33-193	52-194	44-147
2-methyl-4,6-dinatrophenol	19	77-133		69-145	72-142
2-methyl-4,6-dinatrophenol-d_2	64	36-247	16-527	56-177	28-307
naphthalene (1)	20	80-139		73-137	75-149
naphthalene-d_8	39	28-157	14-305	71-141	22-192
beta-naphthylamine (1)	49	10-ns		39-256	ns-ns
beta-naphthylamine-d_7	33	ns-ns	ns-ns	44-230	ns-ns
nitrobenzene (1)	25	69-161		85-115	65-169
nitrobenzene-d_5	28	18-265	ns-ns	46-219	15-314
2-nitrophenol	15	78-140		77-129	75-145
2-nitrophenol-d_4	23	41-145	27-217	61-163	37-158
4-nitrophenol	42	62-146		55-183	51-175
4-nitrophenol-d_4	188	14-398	ns-ns	35-287	ns-ns
N-nitrosodimethylamine	198	21-472		40-249	12-ns

TABLE 8 (CONTINUED)

Acceptance Criteria for Performance Test

COMPOUND	INITIAL PRECISION AND ACCURACY (ug/L) s	X	LABELED COMPOUND RECOVERY P(%)	CALIBRATION VERIFICATION (ug/mL)	ON-GOING ACCURACY R(ug/L)
N-nitrosodi-n-proplylamine	198	21-472		40-249	12-ns
N-nitrosodiphenylamine (1)(4)	45	65-142		68-148	53-173
N-nitrosodiphenylamine-d_6	37	54-126	26-256	59-170	40-166
pentachlorophenol	21	76-140		77-130	71-150
pentachlorophenol-$^{13}C_6$	49	37-212	18-412	42-237	29-254
phenanthrene (1)	13	93-119		75-133	87-126
phenanthrene-d_{10}	40	45-130	24-241	67-149	34-168
phenol (1)	36	77-127		65-155	62-154
phenol-d_5	161	21-210	ns-ns	48-208	ns-ns
alpha-picoline (Synfuel) (1)	38	59-149		60-165	50-174
alpha-picoline (Synfuel)-d_7	138	11-380	ns-ns	31-324	ns-608
pyrene (1)	19	76-152		76-132	72-159
pyrene-d_{10}	29	32-176	18-303	48-210	28-196
styrene (1)	42	53-221		65-153	48-244
styrene-d_5	49	ns-281	ns-ns	44-228	ns-348
alpha-terpineol (1)	44	42-234		54-186	38-258
alpha-terpineol-d_3	48	22-292	ns-672	20-502	18-339
1,2,3-trichlorobenzene	69	15-229		60-167	11-297
1,2,4-trichlorobenzene (1)	19	82-136		78-128	77-144
1,2,4-trichlorobenzene-d_3	57	15-212	ns-592	61-163	10-282
2,3,6-trichlorophenol	30	58-137		56-180	51-153
2,4,5-trichlorophenol	30	58-137		56-180	51-153
2,4,6-trichlorophenol	57	59-205		81-123	48-244
2,3,6-trichlorophenol-d_2	47	43-183	21-363	69-144	34-226

ns = no specification, limit is outside the range that can be measured realibly.

Figure 1

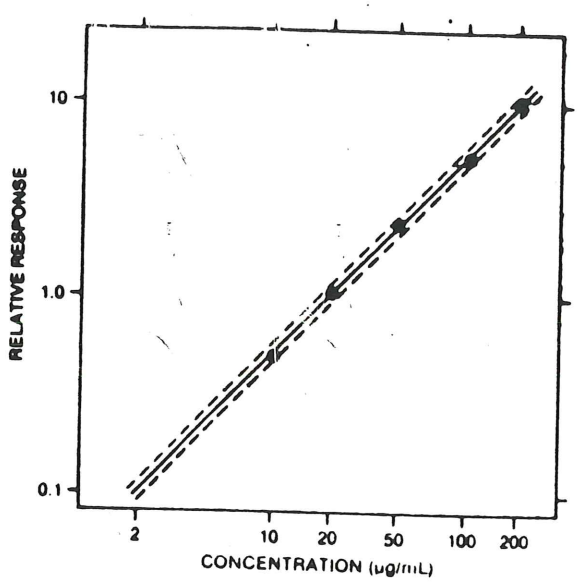

FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a ± 10 Percent Error Window.

Figure 2

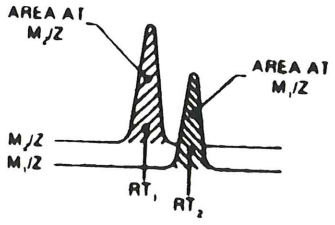

FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled (m_2/z) and Unlabeled (m_1/z) Pairs.

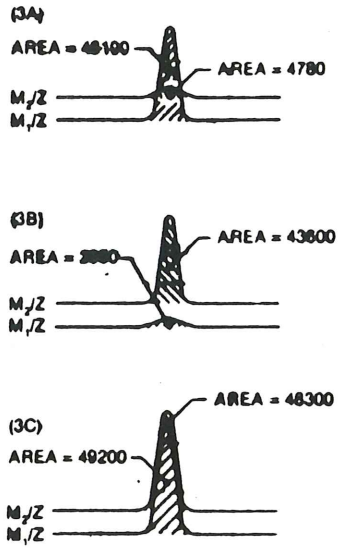

FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

Figure 4

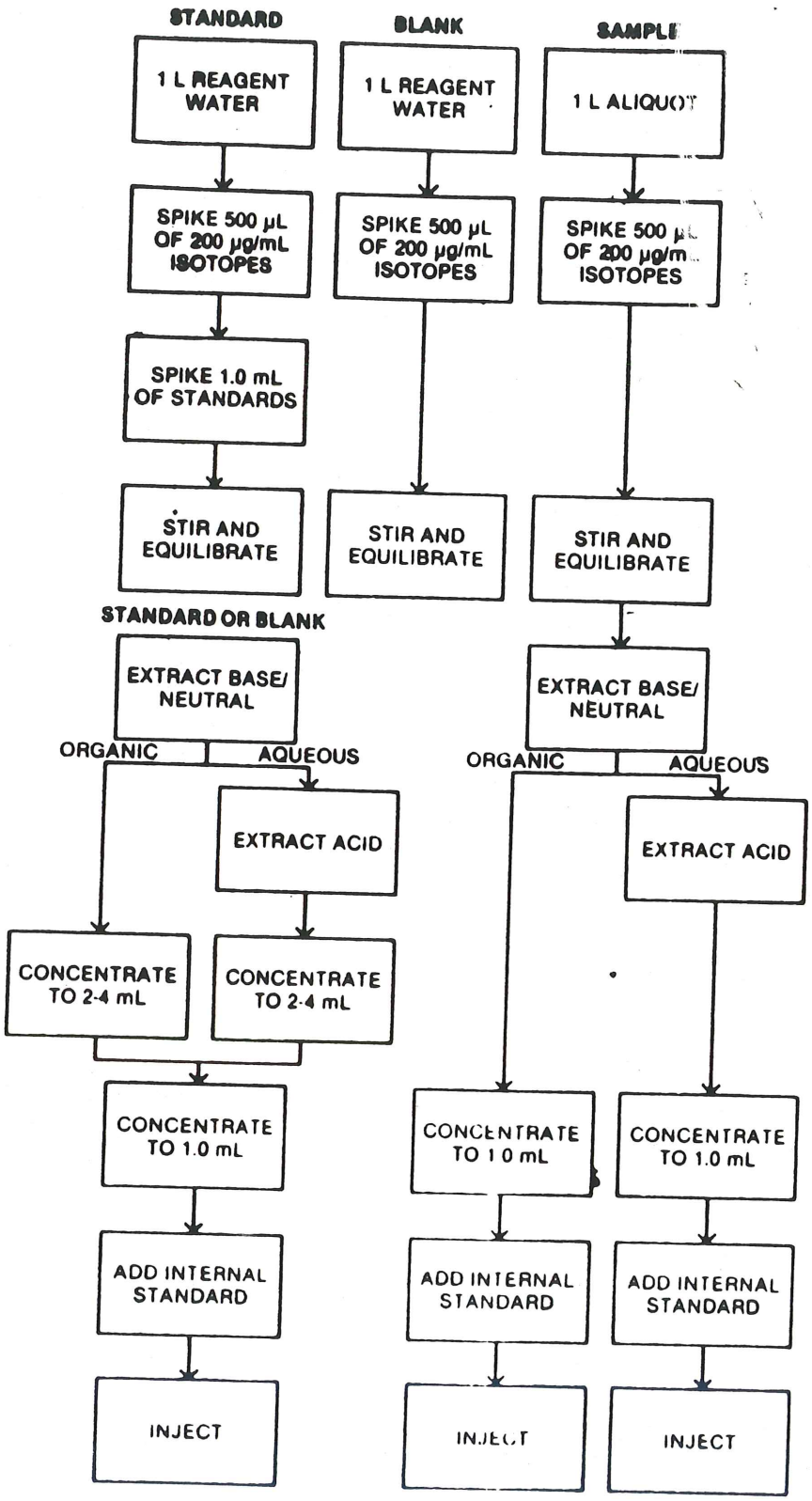

FIGURE 4 Flow Chart for Extraction/Concentration of Precision and Recovery Standard, Blank, and Sample

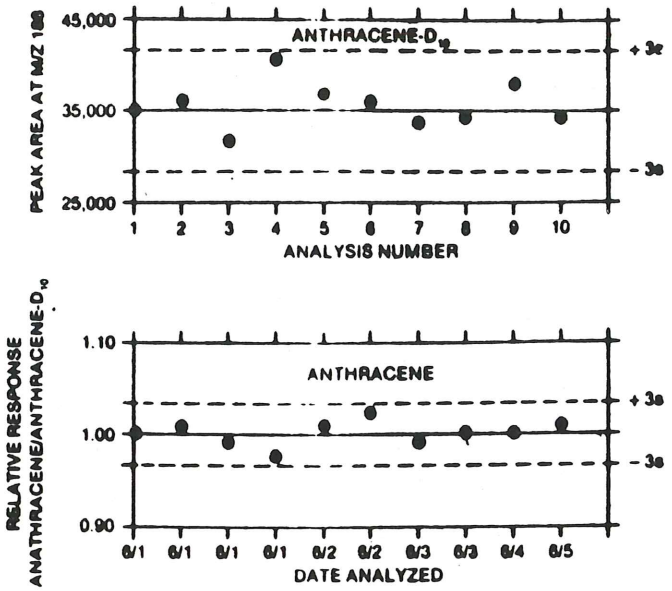

FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d_{10} (lower graph) Plotted as a Function of Time or Analysis Number.

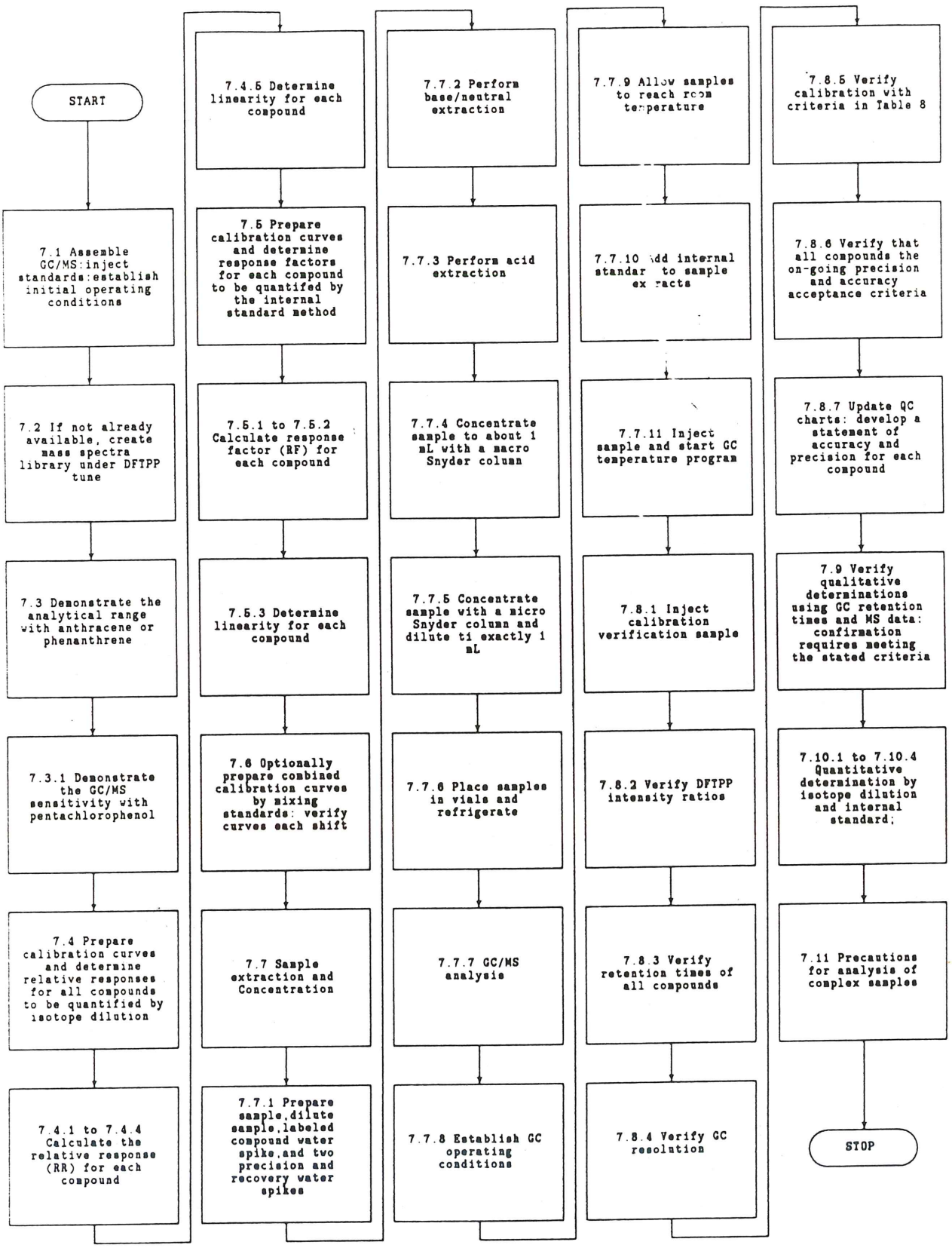
START
7.1 Assemble GC/MS:inject standards:establish initial operating conditions
7.2 If not already available, create mass spectra library under DFTPP tune
7.3 Demonstrate the analytical range with anthracene or phenanthrene
7.3.1 Demonstrate the GC/MS sensitivity with pentachlorophenol
7.4 Prepare calibration curves and determine relative responses for all compounds to be quantified by isotope dilution
7.4.1 to 7.4.4 Calculate the relative response (RR) for each compound
7.4.5 Determine linearity for each compound
7.5 Prepare calibration curves and determine response factors for each compound to be quantifed by the internal standard method
7.5.1 to 7.5.2 Calculate response factor (RF) for each compound
7.5.3 Determine linearity for each compound
7.6 Optionally prepare combined calibration curves by mixing standards: verify curves each shift
7.7 Sample extraction and Concentration
7.7.1 Prepare sample,dilute sample,labeled compound water spike,and two precision and recovery water spikes
7.7.2 Perform base/neutral extraction
7.7.3 Perform acid extraction
7.7.4 Concentrate sample to about 1 mL with a macro Snyder column
7.7.5 Concentrate sample with a micro Snyder column and dilute ti exactly 1 mL
7.7.6 Place samples in vials and refrigerate
7.7.7 GC/MS analysis
7.7.8 Establish GC operating conditions
7.7.9 Allow samples to reach room temperature
7.7.10 Add internal standar to sample ex racts
7.7.11 Inject sample and start GC temperature program
7.8.1 Inject calibration verification sample
7.8.2 Verify DFTPP intensity ratios
7.8.3 Verify retention times of all compounds
7.8.4 Verify GC resolution
7.8.5 Verify calibration with criteria in Table 8
7.8.6 Verify that all compounds the on-going precision and accuracy acceptance criteria
7.8.7 Update QC charts: develop a statement of accuracy and precision for each compound
7.9 Verify qualitative determinations using GC retention times and MS data: confirmation requires meeting the stated criteria
7.10.1 to 7.10.4 Quantitative determination by isotope dilution and internal standard;
7.11 Precautions for analysis of complex samples
STOP

TABLE 1

Semi-volatile Organic Compounds by Isotope Dilution GC/MS
Base/Neutal Extractable Compounds

COMPOUND	CAS	LABELED ANALOG	CAS
acenaphthene	87-24-9	d_{10}	15067-20-2
acenaphthylene	208-96-8	d_8	93951-97-4
anthracene	120-12-7	d_{10}	1719-06-8
benzidine	92-87-5	d_8	92890-63-6
benzo(a)anthracene	56-55-1	d_{12}	1718-53-2
benzo(b)fluoroanthene	205-99-2	d_{12}	93951-98-5
benzo(k)fluoroanthene	205-08-9	d_{12}	93952-01-3
benzo(a)pyrene	50-32-B	d_{12}	63466-71-1
benzo(ghi)perylene	191-24-2	d_{12}	93951-66-7
bipheynyl	92-54-4	d_{10}	1486-01-7
bis(2-chloroethyl) ether	111-44-4	d_8	93952-02-4
bis(2-chloroethoxy) methane	111-91-1	d_8	93966-78-0
bis(2-chloroisopropyl) ether	108-60-1	d_{12}	93951-67-8
bis(2-ethylhexyl) phthalate	117-81-7	d_4	93951-87-2
4-bromophenyl phenyl ether	101-55-3	d_5	93951-83-8
butyl benzyl phthalate	85-68-7	d_4	93951-88-3
n-decane	124-18-5	d_{22}	16416-29-8
n-dodecane	112-40-3	d_{26}	16416-30-1
n-tetradecane	629-59-4		
n-hexadecane	544-76-3	d_{34}	15716-08-2
n-octadecane	593-45-3		
n-licosane	112-95-8	d_{42}	62369-67-9
n-docosane	629-97-9		
n-tetracosane	646-31-1	d_{50}	16416-32-3
n-hexacosane	630-01-3		
n-octacosane	630-02-4		
n-triacontane	638-68-6	d_{62}	93952-07-9
carbazole	86-74-8	d_8	38537-24-5
2-chloronaphthalene	81-58-7	d_7	93951-84-9
4-chlorophenyl phenyl ether	7005-72-3	d_5	93951-85-0
chrysene	218-01-9	d_{12}	1719-03-5
p-cymene	99-87-6	d_{14}	93952-03-5
dibenzo(a,h) anthracene	53-70-3	d_{14}	13250-98-1
dibenzofuran	132-64-9	d_8	93952-04-6
dibenzothiophene (Synfuel)	132-65-0	d_8	33262-29-2
di-n-butyl phthalate	84-74-2	d_4	93952-11-5
1,2-dichlorobenzene	95-50-1	d_4	2199-69-1
1,3-dichlorobenzene	541-73-1	d_4	2199-70-4
1,4-dichlorobenzene	106-46-7	d_4	3855-82-1
3,3-dichlorobenzene	91-94-1	d_6	93951-91-8
diethyl phthalate	84-66-2	d_4	93952-12-6
2,4-dimethylphenol	105-67-9	d_3	93951-75-8
dimethyl phthalate	131-11-3	d_4	93951-89-4
2,4-dinitrotoluene	121-14-2	d_3	93951-68-9
2,6-dinitrotoluene	606-20-2	d_3	93951-90-7

TABLE 1 (continued)

Semi-volatile Organic Compounds by Isotope Dilution GC/MS
Base/Neutal Extractable Compounds

COMPOUND	CAS	LABELED ANALOG	CAS
di-n-octyl phthalate	117-84-0	d_4	93952-13-7
diphenylamine	122-9-4	d_{10}	37055-51-9
diphenyl ether	101-84-8	d_{10}	93952-05-7
1,2-diphenythydrazine	122-66-7	d_{10}	93951-92-9
fluoranthene	206-44-0	d_{10}	93951-69-0
fluorene	86-37-7	d_{10}	81103-79-9
hexachlorobenzene	118-74-1	$^{13}C_6$	93952-14-8
hexachlorobutadiene	87-68-3	$^{13}C_4$	93951-70-3
hexachloroethane	67-72-1	^{13}C	93952-15-9
hexachlorocyclopentadiene	77-47-4	$^{13}C_4$	93951-71-4
ideno(1,2,3-cd) pyrene	193-39-5		
isophorone	78-59-1	d_8	93952-16-0
naphthalene	91-20-3	d_8	1146-65-2
beta-naphthylamine	91-59-8	d_7	93951-94-1
nitrobenzene	98-95-3	d_5	4165-60-0
N-nitrosodimethylamine	62-75-9	d_6	17829-05-9
N-nitrosodi-n-proplylamine	621-64-7	d_{14}	93951-96-3
N-nitrosodiphenylamine	86-30-6	d_6	93951-95-2
phenanthrene	85-01-8	d_{10}	1517-22-2
phenol	108-95-2	d_5	4165-62-2
alpha-picoline (Synfuel)	109-06-8	d_7	93951-93-0
pyrene	129-00-0	d_{10}	1718-52-1
styrene	100-42-5	d_5	5161-29-5
alpha-terpineol	98-55-5	d_3	93952-06-8
1,2,3-trichlorobenzene	87-61-6	d_3	3907-98-0
1,2,4-trichlorobenzene	120-82-1	d_3	93952-16-0

TABLE 2

Acid Extractable Compounds

COMPOUND	CAS	LABELED ANALOG	CAS
4-chloro--methylphenol	59-50-7	d_2	93951-72-5
2-chlorophenol	95-57-8	d_4	93951-73-6
2,4-dichlorophenol	120-8-2	d_3	93951-74-7
2,4-dinitrophenol	51-28-5	d_3	93951-77-0
2-methyl-4,6-dinitrophenol	534-52-1	d_2	93951-76-9
2-nitrophenol	88-75-5	d_4	93951-75-1
4-nitrophenol	100-02-7	d_4	93951-79-2
pentachlorophenol	87-86-5	$^{13}C_6$	85380-74-1
2,3,6-trichlorophenol	933-75-5	d_2	93951-81-6
2,4,5-trichlorophenol	95-95-4	d_2	93951-82-7
2,4,6-trichlorophenol	88-06-2	d_2	93951-80-5

TABLE 3

Gas Chromatography of Base/Neutral Extractable Compounds

COMPOUND	RETENTION TIME MEAN (SEC)	RETENTION TIME RELATIVE	DETECTION LIMIT(2) (ug/L)
acenaphthene (1)	1304	0.999-1.0009	10
acenaphthene-d_{10}	1298	1.107-1.125	10
acenaphthylene (1)	1247	1.000-1.004	10
acenaphthylene-d_8	1265	1.080-1.095	10
anthracene (1)	1592	0.998-1.006	10
anthracene-d_{10}	1588	1.342-1.388	10
benzidine (1)	1853	1.000-1.002	50
benzidine-d_8	1854	1.549-1.632	50
benzo(a)anthracene (1)	2090	0.999-1.007	10
benzo(a)anthracene-d_{12}	2082	1.735-1.846	10
benzo(b)fluoroanthene (1)	2293	1.000-1.005	10
benzo(b)fluoroanthene-d_{12}	2281	1.902-2.025	10
benzo(k)fluoroanthene (1)	2293	1.000-1.005	10
benzo(k)fluoroanthene-d_{12}	2287	1.906-2.033	10
benzo(a)pyrene (1)	2350	1.000-1.004	10
benzo(a)pyrene-d_{12}	2351	1.954-2.008	10
benzo(ghi)perylene (1)	2750	1.001-1.006	21
benzo(ghi)perylene-d_{12}	2741	2.187-2.524	20
bipheynyl (1)	1195	1.001-1.006	10
bipheynyl-d_{10}	1205	1.016-1.027	10
bis(2-chloroethyl) ether (1)	704	1.007-1.016	10
bis(2-chloroethyl) ether-d_8	696	0.584-0.607	10
bis(2-chloroethoxy) methane (5)	939	0.799-0.815	10
bis(2-chloroisopropyl) ether (1)	799	1.010-1.016	10
bis(2-chloroisopropyl) ether-d_{12}	788	0.664-0.691	10
bis(2-ethylhexyl) phthalate (1)	2124	1.000-1.002	10
bis(2-ethylhexyl) phthalate-d_4	2123	1.771-1.880	10
4-bromophenyl phenyl ether	1498	1.271-1.307	10
butyl benzyl phthalate (5)	2060	1.724-1.816	10
n-decane (1)	720	1.022-1.038	10
n-decane-d_{22}	698	0.585-0.615	10
n-dodecane (1)	961	0.986-1.051	10
n-dodecane-d_{28}	953	0.730-0.908	10
n-tetradecane (5)	1203	1.015-1.026	10
n-hexadecane (1)	1469	1.013-1.020	10
n-hexadecane-d_{34}	1447	1.010-1.478	10
n-octadecane (5)	1580	1.335-1.381	10
n-eicosane (1)	1677	1.010-1.021	10
n-eicosane-d_{42}	1655	1.184-1.662	10
n-docosane (5)	1889	1.578-1.671	10
n-tetracosane (1)	2025	1.012-1.015	10
n-tetracosane-d_{50}	1997	1.671-1.764	10
n-hexacosane (5)	2147	1.791-1.901	10
n-octacosane (5)	2272	1.880-2.004	10

TABLE 3 (continued)

Gas Chromatography of Base/Neutral Extractable Compounds

COMPOUND	RETENTION TIME MEAN (SEC)	RETENTION TIME RELATIVE	DETECTION LIMIT(2) (ug/L)
n-triacontane (1)	2429	1.011-1.028	10
n-triacontane-d_{62}	2384	1.972-2.127	10
carbazole (5)	1650	1.180-1.660	20
2-chloronaphthalene (1)	1200	0.997-1.007	10
2-chloronaphthalene-d_7	1185	1.014-1.024	10
4-chlorophenyl phenyl ether (1)	1409	0.990-1.015	10
4-chlorophenyl phenyl ether-d_2	1406	1.194-1.223	10
chrysene (1)	2083	1.000-1.004	10
chrysene-d_{12}	2081	1.743-1.837	10
p-cymene (1)	755	1.008-1.023	10
p-cymene-d_{14}	742	0.624-0.652	10
dibenzo(a,h) anthracene (5)	2660	2.121-2.358	20
dibenzofuran (1)	1335	0.998-1.007	10
dibenzofuran-d_8	1331	0.998-1.007	10
dibenzothiophene (1)	1564	1.000-1.006	10
dibenzothiophene-d_8	1559	1.314-1.361	10
di-n-butyl phthalate (1)	1723	1.000-1.003	10
di-n-butyl phthalate-d_4	1719	1.446-1.510	10
1,2-dichlorobenzene (1)	760	0.995-1.008	10
1,2-dichlorobenzene-d_4	758	0.632-0.667	10
1,3-dichlorobenzene (1)	724	0.998-1.006	10
1,3-dichlorobenzene-d_4	722	0.605-0.636	10
1,4-dichlorobenzene (1)	740	0.997-1.009	10
1,4-dichlorobenzene-d_4	737	0.601-0.666	10
3,3'-dichlorobenzidene (1)	2086	1.000-1.001	50
3,3'-dichlorobenzidene-d_6	2088	1.744-1.848	50
diethyl phthalate (1)	1414	0.996-1.006	10
diethyl phthalate-d_4	1409	1.197-1.229	10
2,4-dimethylphenol (1)	924	0.999-1.003	10
2,4-dimethylphenol-d_3	921	0.781-0.803	10
dimethyl phthalate (1)	1273	0.998-1.005	10
dimethyl phthalate-d_4	1269	1.083-1.102	10
2,4-dinitrotoluene (1)	1344	1.000-1.002	10
2,4-dinitrotoluene-d_3	1359	1.152-1.181	10
2,6-dinitrotoluene (1)	1300	1.001-1.005	10
2,6-dinitrotoluene-d_3	1283	1.090-1.112	10
di-n-octyl phthalate (1)	2240	1.000-1.002	10
di-n-octyl phthalate-d_4	2239	1.867-1.982	10
diphenylamine (1)	1439	1.000-1.007	20
diphenylamine-d_{10}	1437	1.213-1.249	20
diphenyl ether (1)	1216	0.997-1.009	10
diphenyl ether-d_{10}	1211	1.035-1.047	10
1,2-diphenylhydrazine (1)(3)	1439	0.999-1.009	20
1,2-diphenylhydrazine-d_8	1433	1.216-1.248	20
fluoranthene (1)	1817	1.000-1.004	10

TABLE 3 (continued)

Gas Chromatography of Base/Neutral Extractable Compounds

COMPOUND	RETENTION TIME MEAN (SEC)	RETENTION TIME RELATIVE	DETECTION LIMIT(2) (ug/L)
fluoranthene-d_{10}	1813	1.522-1.596	10
fluorene (1)	1401	0.999-1.008	10
fluorene-d_{10}	1395	1.185-1.214	10
hexachlorobenzene (1)	1522	0.999-1.001	10
hexachlorobenzene-$^{13}C_5$	1521	1.288-1.327	10
hexachlorobutadiene (1)	1006	0.999-1.002	10
hexachlorobutadiene-$^{13}C_4$	1005	0.856-0.871	10
hexachloroethane (1)	823	0.999-1.001	10
hexachloroethane-$^{13}C_1$	819	0.690-0.717	10
hexachlorocyclopentadiene (1)	1142	0.999-1.001	10
hexachlorocyclopentadiene-$^{13}C_4$	1147	0.976-0.986	10
indeno(1,2,3-cd)pyrene (5)	2650	2.119-2.356	20
isophorone (1)	889	0.999-1.017	10
isophorone-d_8	881	0.747-0.767	10
naphthalene (1)	967	1.001-1.006	10
naphthalene-d_8	963	0.819-0.836	10
beta-naphthylamine (1)	1371	0.996-1.007	10
beta-naphthylamine-d_7	1368	1.163-1.189	10
nitrobenzene (1)	849	1.002-1.007	10
nitrobenzene-d_5	845	0.706-0.727	10
N-nitrosodimethylamine (5)	385	0.264-0.398	50
N-nitrosodi-n-proplylamine (5)	830	0.701-0.721	20
N-nitrosodiphenylamine (1)(4)	1464	1.000-1.002	20
N-nitrosodiphenylamine-d_6	1447	1.225-1.252	20
phenanthrene (1)	1583	1.000-1.005	10
phenanthrene-d_{10}	1580	1.335-1.381	10
phenol (1)	700	0.995-1.010	10
phenol-d_5	696	0.584-0.613	10
alpha-picoline (Synfuel) (1)	426	1.006-1.028	50
alpha-picoline (Synfuel)-d_7	417	0.326-0.393	50
pyrene (1)	1852	1.001-1.003	10
pyrene-d_{10}	1844	1.523-1.644	10
styrene (1)	549	1.002-1.009	10
styrene-d_5	546	0.450-0.488	10
alpha-terpineol (1)	975	0.998-1.008	10
alpha-terpineol-d_3	973	0.829-0.844	10
1,2,3-trichlorobenzene (5)	1003	0.855-0.870	10
1,2,4-trichlorobenzene (1)	958	1.000-1.005	10
1,2,4-trichlorobenzene-d_3	955	0.813-0.830	10
2,2'-difluorobiphenyl	1163	1.000-1.000	10

TABLE 3 (continued)

Gas Chromatography of Base/Neutral Extractable Compounds

(1) Indicates a chemical quantified by isotope dilution.
(2) This is a minimum level at which the entire GC/MS system must give recognizable mass spectra (background corrected) and acceptable calibration points.
(3) Detected as azobenzene.
(4) Detected as diphenylamine.
(5) Specification derived from related compound.
Column: 30 ± 2 m x 0.25 ± 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary.
Temperature program: 5 minutes at 30°C, 30 - 280°C at 8°C per minute, isothermal at 280°C until benzo(ghi)perylene elutes.
Gas velocity: 30 ± 5 cm/sec.

TABLE 4

Gas Chromatography of Acid Extractable Compounds

COMPOUND	RETENTION TIME MEAN	RETENTION TIME RELATIVE	DETECTION LIMIT (2) (ug/L)
4-chloro-3-methylphenol (1)	1091	0.998-1.003	10
4-chloro-3-methylphenol-d_2	1086	0.930-0.943	10
2-chlorophenol (1)	705	0.997-1.010	10
2-chlorophenol-d_4	701	0.587-0.618	10
2,4-dichlorophenol (1)	947	0.997-1.006	10
2,4-dichlorophenol-d_3	944	0.802-0.822	10
2,4-dinitrophenol (1)	1325	1.000-1.005	50
2,4-dinitrophenol-d_3	1323	1.127-1.149	50
2-methyl-4,6-dinitrophenol (1)	1435	1.000-1.002	20
2-methyl-4,6-dinitrophenol-d_2	1433	1.216-1.249	20
2-nitrophenol (1)	900	0.994-1.009	20
2-nitrophenol-d_4	898	0.761-0.783	20
4-nitrophenol (1)	1354	0.997-1.006	50
4-nitrophenol-d_4	1349	1.147-1.175	50
pentachlorophenol (1)	1561	0.998-1.002	50
pentachlorophenol-$^{13}C_6$	1559	1.320-1.363	50
2,3,6-trichlorophenol (5)	1195	1.016-1.140	10
2,4,5-trichlorophenol (5)	1170	0.996-1.016	10
2,4,6-trichlorophenol (1)	1165	0.998-1.004	10
2,4,6-trichlorophenol-d_2	1162	0.994-1.005	10
2,2'-difluorobiphenyl	1163	1.000-1.000	10

(1) Indicates a chemical quantified by isotope dilution.
(2) This is a minimum level at which the entire GC/MS system must give recognizable mass spectra (background corrected) and acceptable calibration points.
(5) Specification derived from related compound.
Column: 30 ± 2 m x 0.25 ± 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary.
Temperature program: 5 minutes at 30°C, 30 - 280°C at 8°C per minute, isothermal at 280°C until pentachlorophenol elutes.
Gas velocity: 30 ± 5 cm/sec.