SDS—Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 7).

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile; the line described by the signal at an exact m/z.

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock Solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TCDD—Tetrachlorodibenzo-p-dioxin.

TCDF—Tetrachlorodibenzofuran.

VER—See calibration verification standard.

METHOD 1624 REVISION B—VOLATILE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS

1. Scope and Application

1.1 This method is designed to determine the volatile toxic organic pollutants associated with the 1976 Consent Decree and additional compounds amenable to purge and trap gas chromatography-mass spectrometry (GC/MS).

1.2 The chemical compounds listed in table 1 may be determined in municipal and industrial discharges by this method. The methmd is designed to meet the survey requirements of Effluent Guidelines Division (EGD) and the National Pollutants Discharge Elimination System (NPDES) under 40 CFR 136.1 and 136.5. Any modifications of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in table 2 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 the analyses of environmental samples by GC/MS should run the performance tests in reference 1 before beginning.

2. Summary of Method

2.1 Stable isotopically labeled analogs of the compounds of interest are added to a 5 mL water sample. The sample is purged at 20–25 °C with an inert gas in a specially designed chamber. The volatile organic compounds are transferred from the aqueous phase into the gaseous phase where they are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS) (references 2 and 3). 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 spectral masses 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 purge and trap and GC/MS systems.

3. Contamination and Interferences

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from interferences under conditions of the analysis by analyzing blanks initially and with each sample lot (samples analyzed on the same 8 hr shift), as described in Section 8.5.

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 reagent 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. To reduce carry-over, the purging device and sample syringe are rinsed between samples with reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a reagent water blank to check for carry-over. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high levels or purgeable compounds, the purge device is washed with soap solution, rinsed with tap and distilled water, and dried in an oven at 100–125 °C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

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

4. Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. 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 data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 4–6.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5. Apparatus and Materials

5.1 Sample bottles for discrete sampling.

5.1.1 Bottle—25 to 40 mL with screw cap (Pierce 13075, or equivalent). Detergent wash, rinse with tap and distilled water, and dry at >105 °C for one hr minimum before use.

5.1.2 Septum—Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100–200 °C, for one hour minimum.

5.2 Purge and trap device—consists of purging device, trap, and desorber. Complete devices are commercially available.

5.2.1 Purging device—designed to accept 5 mL samples with water column at least 3 cm deep. The volume of the gaseous head space between the water and trap shall be less than 15 mL. The purge gas shall be introduced less than 5 mm from the base of the water column and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shown in Figure 1 meets these criteria.

5.2.2 Trap—25 to 30 cm x 2.5 mm i.d. minimum, containing the following:

5.2.2.1 Methyl silicone packing—one ±0.2 cm, 3 percent OV–1 on 60/80 mesh Chromosorb W, or equivalent.

5.2.2.2 Porous polymer—15 ±1.0 cm, Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.2.2.3 Silica gel—8 ±1.0 cm, Davison Chemical, 35/60 mesh, grade 15, or equivalent. The trap shown in Figure 2 meets these specifications.

5.2.3 Desorber—shall heat the trap to 175 ±5 °C in 45 seconds or less. The polymer section of the trap shall not exceed 180 °C, and the remaining sections shall not exceed 220 °C. The desorber shown in Figure 2 meets these specifications.

5.2.4 The purge and trap device may be a separate unit or coupled to a GC as shown in Figures 3 and 4.

5.3 Gas chromatograph—shall be linearly temperature programmable with initial and final holds, shall contain a glass jet separator as the MS interface, and shall produce results which meet the calibration (Section 7), quality assurance (Section 8), and performance tests (Section 11) of this method.

5.3.1 Column—2.8 ±0.4 m x 2 ±0.5 mm i. d. glass, packekd with one percent SP–1000 on Carbopak B, 60/80 mesh, or equivalent.

5.4 Mass spectrometer—70 eV electron impact ionization; shall repetitively scan from 20 to 250 amu every 2–3 seconds, and produce a unit resolution (valleys between m/z 174–176 less than 10 percent of the height of the m/z 175 peak), background corrected mass spectrum from 50 ng 4-bromo-fluorobenzene (BFB) injected into the GC. The BFB spectrum shall meet the mass-intensity criteria in Table 3. All portions of the GC column, transfer lines, and separator which connect the GC column to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.5 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.

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

5.5.2 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 (Section 7.2).

5.5.3 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, mass chromatograms, and library comparisons are required to verify results.

5.5.4 Response factors and multipoint calibrations—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). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and on-going performance shall be maintained (Sections 8 and 11).

5.6 Syringes—5 mL glass hypodermic, with Luer-lok tips.

5.7 Micro syringes—10, 25, and 100 uL.

5.8 Syringe valves—2-way, with Luer ends (Telfon or Kel-F).

5.9 Syringe—5 mL, gas-tight, with shut-off valve.

5.10 Bottles—15 mL., screw-cap with Telfon liner.

5.11 Balance—analytical, capable of weighing 0.1 mg.

6. Reagents and Standards

6.1 Reagent water—water in which the compounds of interest and interfering compounds are not detected by this method (Section 11.7). It may be generated by any of the following methods:

6.1.1 Activated carbon—pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

6.1.2 Water purifier—pass tap water through a purifier (Millipore Super Q, or equivalent).

6.1.3 Boil and purge—heat tap water to 90–100 °C and bubble contaminant free inert gas through it for approx one hour. While still hot, transfer the water to screw-cap bottles and seal with a Teflon-lined cap.

6.2 Sodium thiosulfate—ACS granular.

6.3 Methanol—pesticide quality or equivalent.

6.4 Standard solutions—purchased as solution or mixtures with certification to their purity, concentration, and authenticity, or prepared 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.

6.5 Preparation of stock solutions—prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in Section 4.

6.5.1 Place approx 9.8 mL of methanol in a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 minutes or until all methanol wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids—using a 100 µL syringe, permit 2 drops of liquid to fall into the methanol without contacting the leck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride)—fill a valved 5 mL gas-tight syringe with the compound. Lower the needle to approximately 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

6.5.2 Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (µg/µL) from the weight gain (or density if a known volume was injected).

6.5.3 Transfer the stock solution to a Teflon sealed screw-cap–bottle. Store, with minimal headspace, in the dark at −10 to −20 °C.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

6.6 Labeled compound spiking solution—from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5–10 µL spike into each 5 mL sample, blank, or aqueous standard analyzed will result in a concentration of 20 µg/L of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, and MEK), a concentration of 100 µg/L may be used. Include the internal standards (Section 7.5) in this solution so that a concentration of 20 µg/L in each sample, blank, or aqueous standard will be produced.

6.7 Secondary standards—using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 500 µg/mL For the gases and water soluble compounds (Section 6.6), a concentration of 2.5 mg/mL may be used.

6.7.1 Aqueous calibration standards—using a 25 µL syringe, add 20 µL of the secondary standard (Section 6.7) to 50, 100, 200, 500, and 1000 mL of reagent water to produce concentrations of 200, 100, 50, 20, and 10 µg/L, respectively. If the higher concentration standard for the gases and water soluble compounds was chosen (Section 6.6), these compounds will be at concentrations of 1000, 500, 250, 100, and 50 µg/L in the aqueous calibration standards.

6.7.2 Aqueous performance standard—an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (Section 11). This standard shall contain either 20 or 100 µg/L of the labeled and pollutant gases and water soluble compounds, 10 µg/L BFB, and 20 µg/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 µg/L aqueous calibration standard (Section 6.7.1).

6.7.3 A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge and trap analyses are compared. This standard shall contain either 100 µg/mL or 500 µg/mL of the gases and water soluble compounds, and 100 µg/mL of the remaining pollutants

and internal standards (consistent with the amounts in the aqueous performance standard in 6.7.2).

6.7.4 Other standards which may be needed are those for test of BFB performance (Section 7.1) and for collection of mass spectra for storage in spectral libraries (Section 7.2).

7. Calibration

7.1 Assemble the gas chromatographic apparatus and establish operating conditions given in table 2. By injecting standards into the GC, demonstrate that the analytical system meets the detection limits in table 2 and the mass-intensity criteria in table 3 for 50 ng BFB.

7.2 Mass spectral libraries—detection and identification of the compound of interest are dependent upon the spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each pollutant and labeled compound and each 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.

7.2.3 The authentic reference spectrum is obtained under BFB tuning conditions (Section 7.1 and table 3) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. This spectrum is stored for reverse search and for compound confirmation.

7.3 Assemble the purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at 170–180 °C by backflushing with an inert gas at a flow rate of 20–30 mL/min. Condition traps daily for a minimum of 10 minutes prior to use.

7.3.1 Analyze the aqueous performance standard (Section 6.7.2) according to the purge and trap procedure in Section 10. Compute the area at the primary m/z (table 4) for each compound. Compare these areas to those obtained by injecting one µL of the methanolic standard (Section 6.7.3) to determine compound recovery. The recovery shall be greater than 20 percent for the water soluble compounds, and 60–110 percent for all other compounds. This recovery is demonstrated initially for each purge and trap GC/MS system. The test is repeated only if the purge and trap or GC/MS systems are modified in any way that might result in a change in recovery.

7.3.2 Demonstrate that 100 ng toluene (or toluene-d8) produces an area at m/z 91 (or 99) approx one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required.

7.4 Calibration by isotope dilution—the isotope dilution approach is used for the purgeable 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, internal standard methods (Section 7.5 or 7.6) are used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) vs concentration (µg/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d8 is given in figure 5. Also shown are the ±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 (Section 7.4.4).

7.4.1 The relative response (RR) of pollutant to labeled compound 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 pollutant (figure 6A).

R_y=the isotope ratio of pure labeled compound (figure 6B).

R_m=the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (figure 6C).

The correct way to calculate RR is: $RR=(R_y-R_m)\ (R_x+1)/(R_m-R_x)(R_y+1)$ If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by internal or external standard methods (Section 7.5 or 7.6).

7.4.2 In most cases, the retention times of the pollutant and labeled compound are the same and isotope ratios (R's) can be calculated from the EICP areas, where: R=(area at m_1/z)/(area at m_2/z) If either of the areas is zero, it is assigned a value of one in the calculations; that is, if: area of m_1/z=50721, and area of m_2/z=0, then R=50721/1=50720. The m/z's are always selected such that $R_x>R_y$. When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios.

R_x, R_y, and R_m are defined as follows:

R_x=[area m_1/z (at RT_1)]/1

R_y=1/[area m_2/z (at RT_2)]

R_m=[area m_1/z (at RT_1)]/[area m_2/z (at RT_2)]

7.4.3 An example of the above calculations can be taken from the data plotted in figure 6 for toluene and toluene-d8. For these data, R_x=168920/1=168900, R_y=1/60960=0.00001640, and R_m=96868/82508=1.174. The RR for the above data is then calculated using the equation given in Section 7.4.1. For the example, RR=1.174.

NOTE: Not all labeled compounds elute before their pollutant analogs.

7.4.4 To calibrate the analytical system by isotope dilution, analyze a 5 mL aliquot of each of the aqueous calibration standards (Section 6.7.1) spiked with an appropriate constant amount of the labeled compound spiking solution (Section 6.6), using the purge and trap procedure in section 10. Compute the RR at each concentration.

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

7.5 Calibration by internal standard—used when criteria for isotope dilution (Section 7.4) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds. The internal standards used for volatiles analyses are bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluted internal standard, as shown in table 2.

7.5.1 Response factors—calibration requires the determination of response factors (RF) which are defined by the following equation:

$RF=(A_s x C_{is})/(A_{is} x C_s)$, where A_s is the EICP area at the characteristic m/z for the compound in the daily standard. A_{is} is the EICP area at the characteristic m/z for the internal standard.

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

C_s is the concentration of the pollutant in the daily standard.

7.5.2 The response factor is determined at 10, 20, 50, 100, and 200 ug/L for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants—see Section 6.7), in a way analogous to that for calibration by isotope dilution (Section 7.4.4). 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 averaged 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 (Section 6.6) to the aqueous calibration standards (Section 6.7.1), 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 (Section 11.5) by purging the aqueous performance standard (Section 6.7.2). Recalibration is required only if calibration and on-going performance (Section 11.5) criteria cannot be met.

8. Quality Assurance/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, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. 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 Section 8.2.

8.1.2 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 Section 8.2 to demonstrate method performance.

8.1.3 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). The procedures and criteria for analysis of a blank are described in Sections 8.5 and 11.7.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (Section 14.2).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through the analysis of the aqueous performance standard (Section 6.7.2) that the analysis system is in control. This procedure is described in Sections 11.1 and 11.5.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 8.4 and 11.5.2.

8.2 Initial precision and accuracy—to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 Analyze two sets of four 5–mL aliquots (8 aliquots total) of the aqueous performance standard (Section 6.7.2) according to the method beginning in Section 10.

8.2.2 Using results of the first set of four analyses in Section 8.2.1, compute the average recovery ($\bar{X}$) in µg/L and the standard deviation of the recovery (s) in µg/L for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and $\bar{X}$ with the corresponding limits for initial precision and accuracy found in table 5. If s and $\bar{X}$ for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If individual $\bar{X}$ falls outside the range for accuracy, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 5 present a substantial probability that one or more will fail one of the acceptance criteria when all compoulds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and $\bar{X}$ for only those compounds which failed the test of the first set of four analyses (Section 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 (Section 8.2.1).

8.3 The laboratory 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 Section 10.

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

8.3.3 Compare the percent recovery for each compound with the corresponding labeled compound recovery limit in table 5. 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 Section 14.2.

8.4 As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in Section 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 accuracy measurements).

8.5 Blanks—reagent water blanks are analyzed to demonstrate freedom from carryover (Section 3) and contamination.

8.5.1 The level at which the purge and trap system will carry greater than 5 µg/L of a pollutant of interest (table 1) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the 5 µg/L level.

8.5.2 With each sample lot (samples analyzed on the same 8 hr shift), a blank shall be analyzed immediately after analysis of the aqueous performance standard (Section 11.1) to demonstrate freedom from contamination. If any of the compounds of interest (table 1) or any potentially interfering compound is found in a blank at greater than 10 µg/L (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in table 1), 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 (Section 7), calibration verification (Section 11.5) and for initial (Section 8.2) and on-going (Section 11.5) 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 analyses of 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 when internal or external standard methods are used.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples are collected in glass containers having a total volume greater than 20 mL. Fill sample bottles so that no air bubbles pass through the sample as the bottle is filled. Seal each bottle so that no air bubbles are entrapped. Maintain the hermetic seal on the sample bottle until time of analysis.

9.2 Samples are maintained at 0–4 °C from the time of collection until analysis. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL) to the empty sample bottles just prior to shipment to the sample site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (Reference 8). If preservative has been added, shake bottle vigorously for one minute immediately after filling.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven 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 residual chlorine is present, add sodium thiosulfate to a separate sample container and fill as in Section 9.1.

9.4 All samples shall be analyzed within 14 days of collection.

10. Purge, Trap, and GC/MS Analysis

10.1 Remove standards and samples from cold storage and bring to 20–25 °.

10.2 Adjust the purge gas flow rate to 40 ±4 mL/min. Attach the trap inlet to the purging device and set the valve to the purge mode (figure 3). Open the syringe valve located on the purging device sample introduction needle (figure 1).

10.3 Remove the plunger from a 5–mL syringe and attach a closed syringe valve. Open the sample bottle and carefully pour the sample into the syringe barrel until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data. Add an appropriate amount of the labeled compound spiking solution (Section 6.6) through the valve bore, then close the valve.

10.4 Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber.

10.5 Close both valves and purge the sample for 11.0 ±0.1 minutes at 20–25 °C.

10.6 After the 11 minute purge time, attach the trap to the chromatograph and set the purge and trap apparatus to the desorb mode (figure 4). Desorb the trapped compounds into the GC column by heating the trap to 170–180 °C while backflushing with carrier gas at 20–60 mL/min for four minutes. Start MS data acquisition upon start of the desorb cycle, and start the GC column temperature program 3 minutes later. Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and detection limits that were achieved under these conditions. Other columns may be used provided the requirements in Section 8 can be met. If the priority pollutant gases produce GC peaks so broad that the precision and recovery specifications (Section 8.2) cannot be met, the column may be cooled to ambient or sub-ambient temperatures to sharpen these peaks.

10.7 While analysis of the desorbed compounds proceeds, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL portions of reagent water. After the purging device has been emptied, allow the purge gas to vent through the chamber until the frit is dry, so that it is ready for the next sample.

10.8 After desorbing the sample for four minutes, recondition the trap by returning to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 170–180 °C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

11. System Performance

11.1 At the beginning of each 8 hr shift during which analyses are performed, system calibration and performance shall be verified for all pollutants and labeled compounds. For these tests, analysis of the aqueous performance standard (Section 6.7.2) shall be used to verify all performance criteria. Adjustment and/or recalibration (per Section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may blanks and samples be analyzed.

11.2 BFB spectrum validity—the criteria in table 3 shall be met.

11.3 Retention times—the absolute retention times of all compounds shall approximate those given in Table 2.

11.4 GC resolution—the valley height between toluene and toluene-d8 (at m/z 91 and 99 plotted on the same graph) shall be less than 10 percent of the taller of the two peaks.

11.5 Calibration verification and on-going precision and accuracy—compute the concentration of each polutant (Table 1) by isotope dilution (Section 7.4) for those compmunds which have labeled analogs. Compute the concentration of each pollutant (Table 1) which has no labeled analog by the internal standard method (Section 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.

11.5.1 For each pollutant and labeled compound, compare the concentration with the corresponding limit for on-going accuracy in Table 5. If all compmunds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound.

NOTE: The large number of compounds in Table 5 present a substantial probability that one or more will fail 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:

11.5.1.1 Analyze a second aliquot of the aqueous performance standard (Section 6.7.2).

11.5.1.2 Compute the concentration for only those compounds which failed the first test (Section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds and analyses of blanks and samples 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 (Section 7), and repeat the entire test (Section 11.1) for all compounds.

11.5.2 Add results which pass the specification in 11.5.1.2 to initial (Section 8.2) and previous on-going data. Update QC charts to form a graphic representation of laboratory performance (Figure 7). Develop a statement of accuracy for each pollutant and labeled compound by calculating the average percentage 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.

12. Qualitative Determination—Accomplished by Comparison of Data from Analysis of a Sample or Blank with Data from Analysis of the Shift Standard (Section 11.1). Identification is Confirmed When Spectra and Retention Times Agree Per the Criteria Below

12.1 Labeled compounds and pollutants having no labeled analog:

12.1.1 The signals for all characteristic masses stored in the spectral library (Section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.1.2 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.

12.1.3 The retention time relative to the nearest eluted internal standard shall be within ±7 scans or ±20 seconds, whichever is greater.

12.2 Pollutants having a labeled analog:

12.2.1 The signals for all characteristic masses stored in the spectral library (Section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.2.2 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 for all masses stored in the spectral library.

12.2.3 The retention time difference between the pollutant and its labeled analog shall agree within ±2 scans or ±6 seconds (whichever is greater) of this difference in the shift standard (Section 11.1).

12.3 Masses present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, an experienced spectrometrist (Section 1.4) is to determine the presence or absence of the compound.

13. Quantitative Determination

13.1 Isotope dilution—by adding a known amount of a labeled compound to every sample prior to purging, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in Section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the toluene example given in Figure 6 (Section 7.4.3), RR would be equal to 1.174. For this RR value, the toluene

calibration curve given in Figure 5 indicates a concentration of 31.8 μg/L.

13.2 Internal standard—calculate the concentration using the response factor determined from calibration data (Section 7.5) and the following equation:

Concentration $=(A_s \times C_{is})/(A_{is} \times RF)$ where the terms are as defined in Section 7.5.1.

13.3 If the EICP area at the quantitation mass for any compound exceeds the calibration range of the system, the sample is diluted by successive factors of 10 and these dilutions are analyzed until the area is within the calibration range.

13.4 Report results for all pollutants and labeled compounds (Table 1) found in all standards, blanks, and samples, in μg/L to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation mass is within the calibration range (Section 13.3) and the labeled compound recovery is within the normal range for the Method (Section 14.2).

14. Analysis of Complex Samples

14.1 Untreated effluents and other samples frequently contain high levels (>1000 μg/L) of the compounds of interest and of interfering compounds. Some samples will foam excessively when purged; others will overload the trap/or GC column.

14.2 Dilute 0.5 mL of sample with 4.5 mL of reagent water and analyze this diluted sample when labeled compound recovery is outside the range given in Table 5. If the recovery remains outside of the range for this diluted sample, the aqueous performance standard shall be analyzed (Section 11) and calibration verified (Section 11.5). If the recovery for the labeled compmund in the aqueous performance standard is outside the range given in Table 5, the analytical system is out of control. In this case, the instrumelt shall be repaired, the performance specifications in Section 11 shall be met, and the analysis of the undiluted sample shall be repeated. If the recovery for the aqueous performance standard is within the range given in Table 5, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

14.3 Reverse search computer programs can misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra when a high level of the pollutant is present. Examine each chromatogram for peaks greater than the height of the internal standard peaks. These peaks can obscure the compounds of interest.

15. Method Performance

15.1 The specifications for this method were taken from the inter-laboratory validation of EPA Method 624 (reference 9). Method 1624 has been shown to yield slightly better performance on treated effluents than Method 624. Additional method performance data can be found in Reference 10.

References

1. ''Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories,'' USEPA, EMSL/Cincinnati, OH 45268, EPA–600/4–80–025 (April 1980).

2. Bellar, T.A. and Lichtenberg, J.J., ''Journal American Water Works Association,'' *66,* 739 (1974).

3. Bellar, T.A. and Lichtenberg, J.J., ''Semi-automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds,'' in *Measurement of Organic Pollutants Water and Wastewater,* C.E. VanHall, ed., American Society for Testing Materials, Philadelphia, PA, Special Technical Publication 686, (1978).

4. ''Working with Carcinogens,'' DHEW, PHS, NIOSH, Publication 77–206 (1977).

5. ''OSHA Safety and Health Standards, General Industry,'' 29 CFR part 1910, OSHA 2206, (1976).

6. ''Safety in Academic Chemistry Laboratories,'' American Chemical Society Publication, Committee on Chemical Safety (1979).

7. ''Handbook of Analytical Quality Control in Water and Wastewater Laboratories,'' USEPA, EMSL/Cincinnati, OH 45268, EPA–4–79–019 (March 1979).

8. ''Methods 330.4 and 330.5 for Total Residual Chlorine,'' USEPA, EMSL/Cincinnati, OH 45268, EPA–4–79–020 (March 1979).

9. ''EPA Method Study 29 EPA Method 624—Purgeables,'' EPA 600/4–84–054, National Technical Information Service, PB84–209915, Springfield, Virginia 22161, June 1984.

10. ''Colby, B.N., Beimer, R.G., Rushneck, D.R., and Telliard, W.A., ''Isotope Dilution Gas Chromatography-Mass Spectrometry for the Determination of Priority Pollutants in Industrial Effluents,'' USEPA, Effluent Guidelines Division, Washington, DC 20460 (1980).

TABLE 1—VOLATILE ORGANIC COMPOUNDS ANALYZED BY ISOTOPE DILUTION GC/MS

Compound	Storet	CAS registry	EPA–EGD	NPDES
Acetone	81552	67–64–1	516 V	.....
Acrolein	34210	107–02–8	002 V	001 V
Acrylonitrile	34215	107–13–1	003 V	002 V
Benzene	34030	71–43–2	004 V	003 V

TABLE 1—VOLATILE ORGANIC COMPOUNDS ANALYZED BY ISOTOPE DILUTION GC/MS—Continued

Compound	Storet	CAS registry	EPA–EGD	NPDES
Bromodichloromethane	32101	75–27–4	048 V	012 V
Bromoform	32104	75–25–2	047 V	005 V
Bromomethane	34413	74–83–9	046 V	020 V
Carbon tetrachloride	32102	56–23–5	006 V	006 V
Chlorobenzene	34301	108–90–7	007 V	007 V
Chloroethane	34311	75–00–3	016 V	009 V
2-chloroethylvinyl ether	34576	110–75–8	019 V	010 V
Chloroform	32106	67–66–1	023 V	011 V
Chloromethane	34418	74–87–3	045 V	021 V
Dibromochloromethane	32105	124–48–1	051 V	008 V
1,1-dichloroethane	34496	75–34–3	013 V	014 V
1,2-dichloroethane	34536	107–06–2	010 V	015 V
1,1-dichloroethene	34501	75–35–4	029 V	016 V
Trans-1,2-dichloroethane	34546	156–60–5	030 V	026 V
1,2-dichloropropane	34541	78–87–5	032 V	017 V
Cis-1,3-dichloropropene	34704	10061–01–5	.....	.....
Trans-1,3-dichloropropene	34699	10061–02–6	033 V	.....
Diethyl ether	81576	60–29–7	515 V	.....
P-dioxane	81582	123–91–1	527 V	.....
Ethylbenzene	34371	100–41–4	038 V	019 V
Methylene chloride	34423	75–09–2	044 V	022 V
Methyl ethyl ketone	81595	78–93–3	514 V	.....
1,1,2,2-tetrachloroethane	34516	79–34–5	015 V	023 V
Tetrachlorethene	34475	127–18–4	085 V	024 V
Toluene	34010	108–88–3	086 V	025 V
1,1,1-trichloroethane	34506	71–55–6	011 V	027 V
1,1,2-trichloroethane	34511	79–00–5	014 V	028 V
Trichloroethene	39180	79–01–6	087 V	029 V
Vinyl chloride	39175	75–01–4	088 V	031 V

TABLE 2—GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS

EGD No. (1)	Compound	Ref EGD No.	Mean retention time (sec)	Minimum level (2) (µg/L)
181	Bromochloromethane (I.S.)	181	730	10
245	Chloromethane-d3	181	147	50
345	Chloromethane	245	148	50
246	Bromomethane-d3	181	243	50
346	Bromomethane	246	246	50
288	Vinyl chloride-d3	181	301	50
388	Vinyl chloride	288	304	10
216	Chloroethane-d5	181	378	50
316	Chloroethane	216	386	50
244	Methylene chloride-d2	181	512	10
344	Methylene chloride	244	517	10
616	Acetone-d6	181	554	50
716	Acetone	616	565	50
002	Acrolein	181	566	50
203	Acrylonitrile-d3	181	606	50
303	Acrylonitrile	203	612	50
229	1,1-dichloroethene-d2	181	696	10
329	1,1-dichloroethene	229	696	10
213	1,1-dichloroethane-d3	181	778	10
313	1,1-dichloroethane	213	786	10
615	Diethyl ether-d10	181	804	50
715	Diethyl ether	615	820	50
230	Trans-1,2-dichloroethene-d2	181	821	10
330	Trans-1,2-dichloroethene	230	821	10
614	Methyl ethyl ketone-d3	181	840	50
714	Methyl ethyl ketone	614	848	50
223	Chloroform-13C1	181	861	10
323	Chloroform	223	861	10
210	1,2-dichloroethane-d4	181	901	10

TABLE 2—GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS—Continued

EGD No. (1)	Compound	Ref EGD No.	Mean retention time (sec)	Minimum level (2) (µg/L)
310	1,2-dichloroethane	210	910	10
211	1,1,1-trichloroethane-13C2	181	989	10
311	1,1,1-trichloroethane	211	999	10
527	p-dioxane	181	1001	10
206	Carbon tetrachloride-13C1	182	1018	10
306	Carbon tetrachloride	206	1018	10
248	Bromodichloromethane-13C1	182	1045	10
348	Bromodichloromethane	248	1045	10
232	1,2-dichloropropane-d6	182	1123	10
332	1.2-dichloropropane	232	1134	10
233	Trans-1,3-dichloropropene-d4	182	1138	10
333	Trans-1,3-dichloropropene	233	1138	10
287	Trichloroethene-13C1	182	1172	10
387	Trichloroethene	287	1187	10
204	Benzene-d6	182	1200	10
304	Benzene	204	1212	10
251	Chlorodibromemethane-13C1	182	1222	10
351	Chlorodibromomethane	251	1222	10
214	1,1,2-trichloroethane-13C2	182	1224	10
314	1,1,2-trichloroethane	214	1224	10
019	2-chloroethylvinyl ether	182	1278	10
182	2-bromo-1-chloropropane (I.S.)	182	1306	10
247	Bromoform-13C1	182	1386	10
347	Bromoform	247	1386	10
215	1,1,2,2-tetrachloroethane-d2	183	1525	10
315	1,1,2,2-tetrachloroethane	215	1525	10
285	Tetrachloroethene-13C2	183	1528	10
385	Tetrachloroethene	285	1528	10
183	1,4-dichlorobutale (int std)	183	1555	10

TABLE 2—GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS—Continued

EGD No. (1)	Compound	Ref EGD No.	Mean retention time (sec)	Minimum level (2) (µg/L)
286	Toluene-d8	183	1603	10
386	Toluene	286	1619	10
207	Chlorobenzene-d5	183	1679	10
307	Chlorobenzene	207	1679	10
238	Ethylbenzene-d10	183	1802	10
338	Ethylbenzene	238	1820	10
185	Bromofluorobenzene	183	1985	10

(1) Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. Column: 2.4m (8 ft) x 2 mm i.d. glass, packed with one percent SP–1000 coated on 60/80 Carbopak B. Carrier gas: helium at 40 mL/min. Temperature program: 3 min at 45 °C, 8 °C per min to 240 °C, hold at 240 °C for 15 minutes.

NOTE: The specifications in this table were developed from data collected from three wastewater laboratories.

TABLE 3—BFB MASS-INTENSITY SPECIFICATIONS

Mass	Intensity required
50	15 to 40 percent of mass 95.
75	30 to 60 percent of mass 95.
95	base peak, 100 percent.
96	5 to 9 percent of mass 95.
173	<2 percent of mass 174.
174	>50 percent of mass 95.
175	5 to 9 percent of mass 174
176	95 to 101 percent of mass 174
177	5 to 9 percent of mass 176.

TABLE 4—VOLATILE ORGANIC COMPOUND CHARACTERISTIC MASSES

Labeled compound	Analog	Primary m/z's
Acetone	d6	58/64
Acrolein	d2	56/58
Acrylonitrile	d3	53/56
Benzene	d6	78/84
Bromodichloromethane	13C	83/86
Bromoform	13C	173/176
Bromomethale	d3	96/99
Carbon tetrachloride	13C	47/48
Chlorobenzene	d5	112/117
Chloroethane	d5	64/71
2-chloroethylvinyl ether	d7	106/113
Chloroform	13C	85/86
Chloromethane	d3	50/53
Dibromochloromethane	13C	129/130
1,1-dichloroethane	d3	63/66
1,2-dichloroethane	d4	62/67
1,1-dichloroethene	d2	61/65
Trans-1,2-dichloroethene	d2	61/65
1,2-dichloropropane	d6	63/67
Cis-1,3-dichloropropene	d4	75/79
Trans-1,3-dichloropropene	d4	75/79
Diethyl ether	d10	74/84
p-dioxane	d8	88/96
Ethylbenzene	d10	106/116
Methylene chloride	d2	84/88
Methyl ethyl ketone	d3	72/75
1,1,2,2-tetrachloroethane	d2	83/84
Tetrachloroethene	13C2	166/172
Toluene	d8	92/99
1,1,1-trichloroethane	d3	97/102
1,1,2-trichloroethane	13C2	83/84
Trichloroethene	13C	95/133
Vinyl chloride	d3	62/65

TABLE 5—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

Compound	Acceptance criteria at 20 µg/L			
	Initial precision and accuracy section 8.2.3		Labeled compound recovery sec. 8.3 and 14.2	On-going accuracy sec. 11.5
	s (µg/L)	$\bar{X}$ (µg/L)	P (percent)	R (µg/L)
Acetone		Note 1		
Acrolein		Note 2		
Acrylonitrile		Note 2		
Benzene	9.0	13.0–28.2	ns–196	4–33
Bromodichloromethane	8.2	6.5–31.5	ns–199	4–34
Bromoform	7.0	7.4–35.1	ns–214	6–36
Bromomethane	25.0	d–54.3	ns–414	d–61
Carbon tetrachloride	6.9	15.9–24.8	42–165	12–30
Chlorobenzene	8.2	14.2–29.6	ns–205	4–35
Chloroethane	14.8	2.1–46.7	ns–308	d–51
2–chloroethylvinyl ether	36.0	d–69.8	ns–554	d–79
Chloroform	7.9	11.6–26.3	18–172	8–30
Chloromethane	26.0	d–55.5	ns–410	d–64
Dibromochloromethane	7.9	11.2–29.1	16–185	8–32
1,1-dichloroethane	6.7	11.4–31.4	23–191	9–33
1,2-dichloroethane	7.7	11.6–30.1	12–192	8–33
1,1-dichloroethene	11.7	d–49.8	ns–315	d–52

TABLE 5—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS—Continued

Compound	Acceptance criteria at 20 μg/L			
	Initial precision and accuracy section 8.2.3		Labeled compound recovery sec. 8.3 and 14.2	On-going accuracy sec. 11.5
	s (μg/L)	$\bar{X}$ (μg/L)	P (percent)	R (μg/L)
Trans-1,2–dichloroethene	7.4	10.5–31.5	15–195	8–34
1,2-dichloropropane	19.2	d–46.8	ns–343	d–51
Cis–1,3–dichloropropene	22.1	d–51.0	ns–381	d–56
Trans–1,3–dichloropropene	14.5	d–40.2	ns–284	d–44
Diethyl ether		Note 1		
P–dioxane		Note 1		
Ethyl benzene	9.6	15.6–28.5	ns–203	5–35
Methylene chloride	9.7	d–49.8	ns–316	d–50
Methyl ethyl ketone		Note 1		
1,1,2,2-tetrachloroethane	9.6	10.7–30.0	5–199	7–34
Tetrachloroethene	6.6	15.1–28.5	31–181	11–32
Toluene	6.3	14.5–28.7	4–193	6–33
1,1,1-trichloroethane	5.9	10.5–33.4	12–200	8–35
1,1,2-trichloroethane	7.1	11.8–29.7	21–184	9–32
Trichloroethene	8.9	16.6–29.5	35–196	12–34
Vinyl chloride	27.9	d–58.5	ns–452	d–65

d = detected; result must be greater than zero.
ns = no specification; limit would be below detection limit.

NOTE 1: Specifications not available for these compounds at time of release of this method.
NOTE 2: Specifications not developed for these compounds; use method 603.

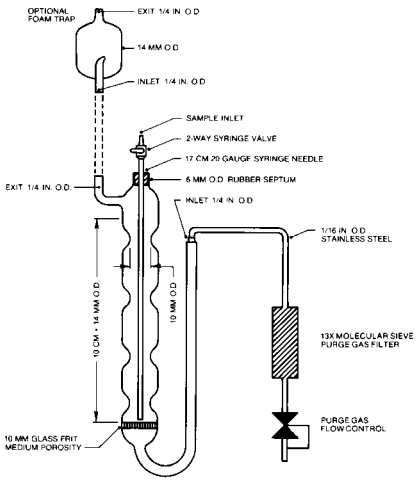

FIGURE 1 Purging Device.

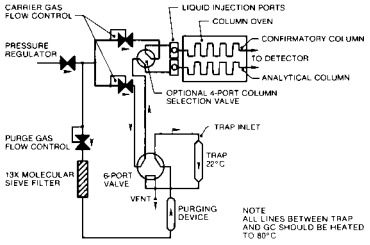

FIGURE 3 Schematic of Purge and Trap Device—Purge Mode.

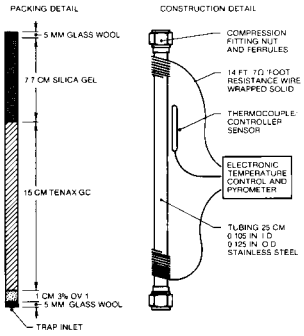

FIGURE 2 Trap Packings and Construction to Include Desorb Capability.

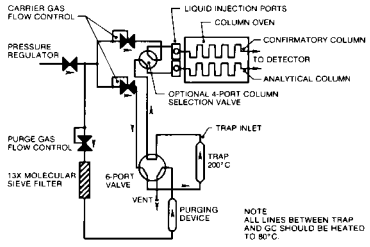

FIGURE 4 Schematic of Purge and Trap Device—Desorb Mode.

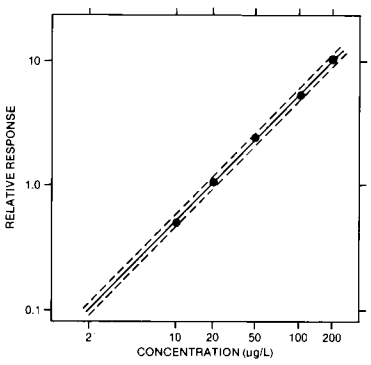

FIGURE 5 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a ±10 Percent Error Window.

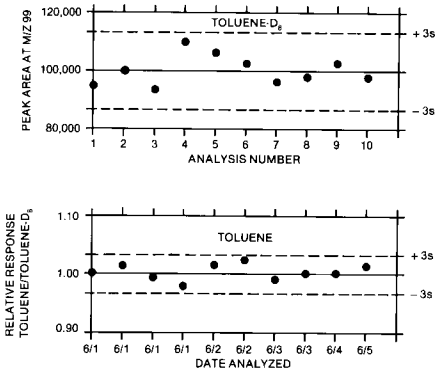

FIGURE 7 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d_8 (lower graph) Plotted as a Function of Time or Analysis Number.

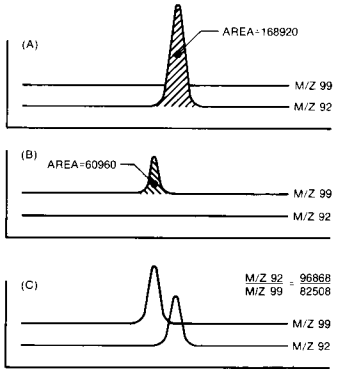

FIGURE 6 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-d_8, and a Mixture of Toluene and Toluene-d_8.

METHOD 1625 REVISION B—SEMIVOLATILE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS

1. Scope and Application

1.1 This method is designed to determine the semivolatile toxic organic pollutants associated with the 1976 Consent Decree 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. The method is designed to meet the survey