7.13 LABORATORY PERFORMANCE CHECK SOLUTION -- Prepare by accurately weighing 0.0010 g each of chlorothalonil, chlorpyrifos, DCPA, and HCH-delta. Dissolve each analyte in MTBE and dilute to volume in individual 10-mL volumetric flasks. Combine 2 µL of the chloropyrifos stock solution, 50 µL of the DCPA stock solution, 50 µL of the chlorothalonil stock solution, and 40 µL of the HCH-delta stock solution to a 100-mL volumetric flask and dilute to volume with MTBE. Transfer to a TFE-fluorcarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Section 10) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION

8.2.1 Add mercuric chloride (See 7.8) to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a 10 mg/mL solution of mercuric chloride in reagent water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.3 After adding the sample to the bottle containing preservative(s), seal the sample bottle and shake vigorously for 1 min.

8.2.4 Samples must be iced or refrigerated at 4°C from the time of collection until extraction. Preservation study results indicate that most of the target analytes present in the samples are stable for 7 days when stored under these conditions (1). Preservation data for the analytes chlorthalonil, alpha-HCH, delta-HCH, gamma-HCH, cis-permethrin, trans-permethrin, and trifluralin are nondefinitive, and therefore if these are analytes of interest, it is recommended that the samples be analyzed immediately. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.3 EXTRACT STORAGE

8.3.1 Sample extracts should be stored at 4°C away from light. A 14-day maximum extract storage time is recommended. However, analyte stability may be affected by the matrix; therefore, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. CALIBRATION

9.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.8. The GC system must be calibrated using the internal standard technique (Sect. 9.2) or the external standard technique (Sect. 9.3). WARNING: DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-level standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration. Calculate percent breakdown as follows:

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. PCNB has been identified as a suitable internal standard. Data presented in this method were generated using the internal standard calibration procedure.

9.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest and surrogate compound by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The

remaining standards should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector. The calibration standards must bracket the analyte concentrations found in the sample extracts.

9.2.2 Analyze each calibration standard according to the procedure (Sect. 11.4). Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where :

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (μg/L).
C_s = Concentration of the analyte to be measured (μg/L).

9.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. Cs.

9.2.4 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm$ 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that analyte.

9.2.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standards should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.2.6 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

9.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

9.3.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of

interest and surrogate compound by adding volumes of one or more stock standards to a volumetric flask. Dilute to volume with MTBE. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector. The calibration standards must bracket the analyte concentrations found in the sample extracts.

9.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.4 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

9.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hrs.), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

9.3.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standards should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.3.5 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

10. QUALITY CONTROL

10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound

recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples.

10.2 Laboratory Reagent Blanks -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 INITIAL DEMONSTRATION OF CAPABILITY

10.3.1 Select a representative fortified concentration (about 10 times EDL or at the regulatory Maximum Contaminant Level, whichever is lower) for each analyte. Prepare a sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of at least four 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Section 11.

10.3.2 For each analyte the recovery value for all four of these samples must fall in the range of $R \pm 30\%$ (or within $R \pm 3S_R$ if broader) using the values for R and S_R for reagent water in Table 2. For those compounds that meet the acceptance criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

10.4 The analyst is permitted to modify GC columns, GC conditions, GC detectors, continuous extraction techniques, concentration techniques (i.e. evaporation techniques), internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.3.

10.5 ASSESSING SURROGATE RECOVERY

10.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors,

(2) fortifying solutions for degradation, (3) contamination or other obvious abnormalities, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

10.5.2 If a blank extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

10.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract reanalysis continues to fail the surrogate recovery criterion, report all data for that sample as suspect.

10.6 ASSESSING THE INTERNAL STANDARD

10.6.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standards IS response by more than 30%.

10.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

10.6.2.1 If the reinjected aliquot produces an acceptable internal standard response report results for that aliquot.

10.6.2.2 If a deviation of greater than 30% is obtained for the re-injected extract, analysis of the sample should be repeated beginning with Section 11, provided the sample is still available. Otherwise, report results obtained from the re-injected extract, but annotate as suspect.

10.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

10.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 10.6.2 for each sample failing the IS response criterion.

10.6.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 9.

10.7 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANK

10.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every twenty samples or one per sample set (all samples extracted within a 24-h period) whichever is greater. The fortified concentration of each analyte in the LFB should be 10 times EDL or the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 10.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.7.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 10.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery ($\bar{X}$) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$
$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should never exceed those established in Sect. 10.3.2.

10.7.3 It is recommended that the laboratory periodically document and determine its detection limit capabilities for the analytes of interest.

10.7.4 At least quarterly, analyze a QC sample from an outside source.

10.7.5 Laboratories are encouraged to participate in external performance evaluation studies such as the labroatory certification programs offered by many states or the studies conducted by USEPA. Performance evaluation studies serve as independent checks on the analyst's performance.

10.8 ASSESSING METHOD PERFORMANCE - LABORATORY FORTIFIED SAMPLE MATRIX

10.8.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample concentration per set, whichever is greater. The added concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the fortified analyte concentrations should be the same as that used for the LFB

(Section 10.7). Over time, samples from all routine sample sources should be fortified.

10.8.2 Calculate the percent recovery, P of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b) \ /\ \text{fortifying concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. If the analyzed unfortified sample is found to contain NO background concentrations, and the added concentrations are those specified in Sect. 10.7, then the appropriate control limits would be the acceptance limits in Sect. 10.7. If, on the other hand, the analyzed unfortified sample is found to contain background concentration, b, estimate the standard deviation at the background concentration, s_b, using regressions or comparable background data and, similarly, estimate the mean, $\bar{X}_a$, and standard deviation, s_a, of analytical results at the total concentration after fortifying. Then the appropriate percentage control limits would be $\bar{P} \pm 3s_p$, where:

$$\bar{P} = 100\ \bar{X}\ /\ (b + \text{fortifying concentration})$$

$$\text{and } s_p = 100\ \ (s_a^2 + s_b^2)^{1/2} / \text{fortifying concentration}$$

For example, if the background concentration for Analyte A was found to be 1 µg/L and the added amount was also 1 µg/L, and upon analysis the laboratory fortified sample measured 1.6 µ/L, then the calculated P for this sample would be (1.6 µg/L minus 1.0 µg/L)/1 µg/L or 60%. This calculated P is compared to control limits derived from prior reagent water data. Assume it is known that analysis of an interference free sample at 1 µg/L yields an s of 0.12 µg/L and similar analysis at 2.0 µg/L yields X and s of 2.01 µg/L and 0.20 µg/L, respectively. The appropriate limits to judge the reasonableness of the percent recovery, 60%, obtained on the fortified matrix sample is computed as follows:

$$[100\ (2.01\ \mu g/L) \ /\ 2.0\ \mu g/L]$$

$$\pm 3\ (100)\ \ [(0.12\ \mu g/L)^2 + (0.20\ \mu g/L)^2]^{1/2} \ /\ 1.0\ \mu g/L =$$

$$100.5\% \pm 300\ (0.233) =$$

100.5% ± 70% or 30% to 170% recovery of the added analyte.

10.8.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 10.7), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK SAMPLE - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 3. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs.

10.10 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to asses the precision of the environmental measurements or filed reagent blanks may be used to asses contamination of samples under site conditions, transportation and storage.

11. PROCEDURE

11.1 EXTRACTION (MANUAL METHOD)

11.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.6). Add preservative to blanks and QC check standards. Fortify the sample with 50 µL of the surrogate standard fortifying solution. Pour the entire sample into a 2-L separatory funnel.

11.1.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.1.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.4 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from

the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 AUTOMATED EXTRACTION METHOD -- Data presented in this method were generated using the automated extraction procedure with the mechanical tumbler.

11.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.6). Add preservative to blanks and QC check standards. Fortify the sample with 50 µL of the surrogate standard fortifying solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH: add H_2SO_4 or NaOH if necessary.

11.2.3 Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.4 Add 300 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for 1 hour. Complete mixing of the organic and aqueous phases should be observed within about 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from

the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500-mL Erlenmeyer flask.

11.2.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a 25-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Sect. 10.3 are met.

11.3.2 Dry the extract by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Collect the extract in the K-D concentrator, and rinse the column with 20-30 mL methylene chloride. Alternatively, add about 5 g anhydrous sodium sulfate to the extract in the Erlenmeyer flask; swirl flask to dry extract and allow to sit for 15 min. Decant the methylene chloride extract into the K-D concentrator. Rinse the remaining sodium sulfate with two 25-mL portions of methylene chloride and decant the rinses into the K-D concentrator.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 65 to 70°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of MTBE. Add 5-10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of MTBE to the top. Place the micro K-D apparatus on the water bath so that the

concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 5-10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

11.3.5 Transfer extract to an appropriate-sized TFE-fluorocarbon-sealed screw-cap vial and store, refrigerated at 4°C, until analysis by GC-NPD.

11.4 GAS CHROMATOGRAPHY

11.4.1 Sect. 6.8 summarizes the recommended operating conditions for the gas chromatograph. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 10.3 are met.

11.4.2 Calibrate the system daily as described in Sect. 9. The standards and extracts must be in MTBE.

11.4.3 If the internal standard calibration procedure is used, add 5 µL of the internal standard fortifying solution to the sample extract, seal, and shake to distribute the internal standard.

11.4.4 Inject 2 µL of the sample extract. Record the resulting peak size in area units.

11.4.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

11.5 IDENTIFICATION OF ANALYTES

11.5.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.5.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5.3 Identification requires expert judgment when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry, or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.8.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 9.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the calibration curve or response factor (RF) determined in Sect. 9.2 and Equation 2.

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)} \qquad \text{Equation 2}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 9.3.The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 3}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range (1). Analytes were divided into two fortified groups for recovery studies. Analyte EDLs and analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 2.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices (1). Analyte recoveries from the two synthetic matrices are given in Table 2.

14. REFERENCES

1. National Pesticide Survey Method No. 2: Determination of Chlorinated Pesticides in Groundwater by Gas Chromatography with a Electron Capture Detector.

2. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, 1986.

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

4. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

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

6. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, 1986.

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

	Retention Time[a] (minutes)	
	Primary	Alternative
Etridiazole	23.46	22.78
Chlorneb	25.50	26.18
Propachlor	28.90	30.94
Trifluralin	31.62	(b)
HCH-alpha	31.62	32.98
Hexachlorobenzene	31.96	(b)
HCH-beta	33.32	40.12
HCH-gamma	33.66	35.36
PCNB (internal std.)	34	34
HCH-delta	35.02	41.48
Chlorthalonil	35.36	39.78
Heptachlor	37.74	36.72
Aldrin	40.12	38.08
Chlorpyrifos	40.6	(b)
DCPA	41.14	41.14
Heptachlor epoxide	42.16	42.16
Chlordane-gamma	43.52	43.86
Endosulfan I	44.20	43.52
Chlordane-alpha	44.54	44.54
4,4'-DDE	45.90	44.88
Dieldrin	45.90	45.90
Endrin	46.92	(b)
Endosulfan II	47.60	51.68
Chlorobenzilate	47.94	48.28
4,4'-DDD	48.28	46.92
Endrin aldehyde	48.62	46.92
Endosulfan sulfate	49.98	49.30
4,4'-DDT	50.32	50.32
Methoxychlor	53.38	53.72
cis-Permethrin	58.48	(b)
trans-Permethrin	58.82	(b)
DCB	64.1	(b)

[a] Columns and analytical conditions are described in Sect. 6.8.1 and 6.8.2.
[b] Data not available.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND ESTIMATED DETECTION LIMITS (EDLS) FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[A]

Analyte	EDL[B] µg/L	Conc. µg/L	Reagent Water Rc	Reagent Water S_Rd	Synthetic Water 1[E] R	Synthetic Water 1[E] S_R	Synthetic Water 2[F] R	Synthetic Water 2[F] S_R
Aldrin	0.075	0.15	86	9.5	100	11.0	69	9.0
Chlordane-alpha	0.0015	0.15	99	11.9	96	12.5	99	7.9
Chlordane-gamma	0.0015	0.15	99	11.9	96	12.5	99	6.9
Chlorneb	0.5	5	97	11.6	95	6.7	75	8.3
Chlorobenzilate	5	10	108	5.4	98	10.8	102	9.2
Chlorthalonil	0.025	0.25	91	8.2	103	10.3	71	9.2
DCPA	0.025	0.25	103	12.4	100	13.0	101	6.1
4,4'-DDD	0.0025	0.25	107	6.4	96	8.6	101	7.1
4,4'-DDE	0.01	0.1	99	11.9	96	12.5	99	6.9
4,4'-DDT	0.06	0.6	112	16.8	98	11.8	84	8.4
Dieldrin	0.02	0.2	87	8.7	103	9.3	82	7.4
Endosulfan I	0.015	0.15	87	8.7	102	8.2	84	8.4
Endosulfan sulfate	0.015	0.15	102	15.3	94	1.3	72	12.2
Endrin	0.015	0.15	88	8.8	98	9.8	104	9.4
Endrin aldehyde	0.025	0.25	88	7.9	103	11.3	84	9.2
Endosulfan II	0.024	0.15	92	10.1	98	10.8	76	6.8
Etridiazole	0.025	0.25	103	6.2	91	6.4	98	3.9
HCH-alpha	0.025	0.05	92	10.1	106	7.4	86	7.7
HCH-beta	0.01	0.1	95	6.7	92	5.5	100	6.0
HCH-delta	0.01	0.1	102	11.2	99	11.9	103	6.2
HCH-gamma	0.015	0.15	89	9.8	115	6.9	85	7.7
Heptachlor	0.01	0.1	98	11.8	85	11.1	85	7.7
Heptachlor epoxide	0.015	0.15	87	8.7	103	7.2	82	9.8
Hexachlorobenzene	0.0077	0.05	99	21.8	82	9.8	68	4.8
Methoxychlor	0.05	0.5	105	13.7	101	10.1	104	6.2
cis-Permethrin	0.5	5	91	9.1	96	11.5	86	9.5
trans-Permethrin	0.5	5	111	6.7	97	9.7	102	7.1
Propachlor	0.5	5	103	9.3	116	4.6	95	7.6
Trifluralin	0.025	0.25	103	5.2	86	10.3	87	9.6

TABLE 2. (Continued)

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher. The concentration level used in determining the EDL is not the same as the concentration level presented in this table.

[c] R = average percent recovery.

[d] S_R = standard deviation of the percent recovery.

[e] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[f] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado), was used.

TABLE 3. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/L	Requirements
Sensitivity	Chlorpyrifos	0.0020	Detection ofanalyte;S/N > 3
Chromatographic performance	DCPA	0.0500	PSF between 0.80 and 1.15[a]
Column performance	Chlorothalonil HCH-delta	0.0500 0.0400	Resolution > 0.50[b]

[a] PGF - peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

METHOD 508A. SCREENING FOR POLYCHLORINATED BIPHENYLS BY PERCHLORINATION AND GAS CHROMATOGRAPHY

Revision 1.0

T. A. Bellar - Method 508A, Revision 1.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
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U.S. ENVIRONMENTAL PROTECTION AGENCY
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METHOD 508A

SCREENING FOR POLYCHLORINATED BIPHENYLS BY PERCHLORINATION/GAS CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1. This procedure may be used for screening finished drinking water, raw source water, or drinking water in any treatment stage for polychlorinated biphenyls (PCBs). This procedure is applicable to samples containing PCBs as single congeners or as complex mixtures such as weathered, intact, or mixtures of commercial Aroclors. The procedure is incapable of identifying the parent PCBs because the original PCBs are chemically converted to a common product, decachlorobiphenyl (DCB). The procedure has only been evaluated using Aroclors and 2-chlorobiphenyl as a source of PCBs.

1.2. This procedure is primarily designed to function as a pass/fail test for DCB at 0.5 μg/L. However, it will accurately measure DCB from the method detection limit (MDL) to 5.0 μg/L. It is prone to false positive interferences and can result in a calculated weight of PCBs significantly greater than that of PCB originally present in the sample. If DCB is detected at 0.5 μg/L or above, then an approved method for the analysis of PCBs should be used to accurately identify the source and measure the concentration of the PCBs.

1.3. This procedure can be used to help confirm the presence of PCBs for other methods using electron capture or halogen specific detectors whenever chromatographic patterns are not representative of those described in the method.

2. SUMMARY OF PROCEDURE

2.1. A 1-L water sample is placed into a separatory funnel and extracted with methylene chloride or one of several optional solvents. The extract is dried, concentrated, and the solvent is exchanged to chloroform. The PCBs are then reacted with antimony pentachloride ($SbCl_5$) (in the presence of an iron catalyst and heat) to form DCB. The DCB is extracted with hexane from the reaction mixture; after the extract is purified, an aliquot is injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD) for separation and measurement. The GC is calibrated using DCB as the standard.

3. DEFINITIONS

3.1. Calibration Standard (CAL) -- A solution of DCB used to calibrate the ECD.

3.2. Congener Number -- Throughout this procedure, individual PCBs are described with the number assigned by Ballschmiter and Zell (1).

(This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)

3.3. Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory are analyzed with identical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.

3.4. Laboratory Performance Check Solution (LPC) -- A solution of method analytes used to evaluate the analytical system performance with respect to a defined set of criteria.

3.5. Laboratory Reagent Blank (LRB) -- An aliquot of reagent water that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents and reagents are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.

3.6. Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.7. Quality Control (QC) Sample -- A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst. Preparation of the QC check sample by a laboratory other than the laboratory performing the analysis is highly desirable.

4. INTERFERENCES

4.1. Interferences may be caused by contaminants in solvents reagents, glassware, and other sample processing equipment. Laboratory reagent blanks (LRBs) are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.

4.2. To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry and heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an

appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

4.3. In addition to PCBs, several compounds and classes of compounds will form DCB with varying yields when extracted and perchlorinated according to this procedure. Based upon a literature search (2) such compounds include biphenyl, polyhalogenated biphenyls, hydrogenated biphenyls, and polyhalogenated terphenyls. If such compounds are present in the extract, false positive or positively biased data will be generated.

4.4. A splitless injection capillary column GC can be used but standards and samples should be contained in the same solvent, or results may be significantly biased.

4.5. PCBs are converted to DCB on a mole for mole basis. Converting DCB concentrations back to the original PCB concentration is beyond the scope of this method. For informational purposes and in order to demonstrate the degree of increased weight of PCBs generated by the procedure, Table 1 lists the conversion of 0.5 μg/L of DCB back to various sources of PCBs assuming 100% method recovery.

5. SAFETY

5.1. Chloroform and methylene chloride have been tentatively classified as known or suspected human or mammalian carcinogens. The toxicity or carcinogenicity of the remaining chemicals used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard, and exposure should be reduced to the lowest feasible level. Each laboratory is responsible for safely disposing materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (3-5).

5.2. Polychlorinated biphenyls have been classified as known or suspected human or mammalian carcinogens. Primary standards of these compounds should be prepared in an area specifically designed to handle carcinogens. It is recommended that primary dilutions be obtained from certified sources such as the EPA repository.

5.3. $SbCl_5$ is a corrosive reagent that reacts violently with water. This compound must be used with extreme caution. All operations involving the pure reagent must be performed in a hood because appreciable quantities of volatile, potentially harmful materials will be lost to the atmosphere.

5.4. The perchlorination reaction described in this procedure requires that the sample extract be heated to 205°C for about 30 min while hermetically sealed in a glass test tube. The solvents and volumes described in the procedure should be carefully reproduced; otherwise

dangerous pressures may be generated during perchlorination. The following safety precautions are strongly recommended.

5.4.1. Use only the prescribed perchlorination glassware and visually check for flaws such as chips, strains, or scratches. Discard if any abnormalities are noted.

5.4.2. After cooling the perchlorinated product is still under slight pressure and should be carefully vented in a hood (Sect. 11.2.8.).

5.4.3. The $SbCl_5$ neutralization step involves an exothermic reaction and should be performed in a hood (Sect. 11.2.9.).

5.4.4. An explosion shield should be used during the perchlorination and neutralization procedures along with additional eye protection such as an 8-in. face shield. An oil bath heater should not be substituted for the block digester.

5.5. Storage, labelling and disposal of PCBs must conform to all applicable laws and regulations. See (6) for USEPA requirements. Call the Toxics Substances Control Act hotline for further assistance (1-800-424-9065).

5.6. Methylene chloride is described in the procedure (Sect. 11.1.2) as the extraction solvent; however, hexane, hexane + 15% methylene chloride or hexane + 15% ethylether may be substituted to minimize laboratory personnel exposure to methylene chloride.

5.7. Chloroform is described in the procedure (Sect. 11.2.1) as the solvent for the perchlorination reaction. Other less toxic solvents including methylene chloride and hydrocarbons were evaluated but were found to be unsuitable. Prior to implementing this procedure, all laboratory personnel must be trained in safe handling practices for chloroform.

6. APPARATUS AND EQUIPMENT

6.1. Sampling equipment

6.1.1. Water sample bottles -- Meticulously cleaned 1-L glass bottles fitted with Teflon-lined screw caps.

6.2. Glassware

6.2.1. Separatory Funnel -- 2-L with Teflon stopcock.

6.2.2. Drying Column -- Glass column approximately 400 mm long x 19 mm i.d. with coarse frit filter disc.

6.2.3. Concentrator Tube -- 10-mL graduated Kuderna-Danish design with ground-glass stopper.

6.2.4. Evaporative Flask -- 500-mL Kuderna-Danish design.

6.2.5. Snyder Column -- Three-ball macro Kuderna-Danish design.

6.2.6. Snyder Column -- Three-ball micro Kuderna-Danish design.

6.2.7. Vials -- 10- to 15-mL amber glass with Teflon-lined screw caps.

6.2.8. Screw cap culture test tubes -- 100 mm x 13 mm i.d. Pyrex with a Teflon-lined screw cap, Sargent-Welch #S-79533A or equivalent.

6.2.9. Disposable Pasteur pipettes -- 9-in. heavy wall.

6.2.10. Screw cap test tube -- 15 mL with Teflon-lined screw cap.

6.3. GC System -- Packed column or capillary column.

6.3.1. Isothermal packed column GC equipped with an on-column injector and a linearized ECD capable of generating a linear response for DCB from at least 0.005 to 1.0 ng injected.

6.3.2. Programmable capillary column GC equipped with an on-column or splitless injector and a linearized ECD capable of generating a linear response for DCB from at least 0.005 to 1.0 ng injected. The column oven temperature programmer should have multi-ramp capabilities from at least 60°C to 300°C. For most precise data, an autoinjector should be used.

6.4. GC Columns

6.4.1. Packed Column -- A 2 mm i.d. x 3 m, glass column packed with 3% OV-1 on 80-100 mesh Supelcoport or equivalent.

6.4.2. Capillary Column -- A 30 m x 0.32 mm i.d. fused silica capillary coated with a bonded 0.25 μm film of cross linked phenyl methyl silicone such as Durabond-5 (DB-5).

6.5. Miscellaneous Equipment

6.5.1. Volumetric flask -- 5-mL, 10-mL, and 100 mL with ground glass stoppers.

6.5.2. Microsyringes -- Various standard sizes.

6.5.3. Boiling Chips -- Approximately 10/40 mesh. Heat at 400°C for 30 min or extract with methylene chloride in a Soxhlet apparatus.

6.5.4. Water Bath -- Heated, with concentric ring cover, capable of temperature control with ± 2°C.

6.5.5. Analytical Balance -- Capable of accurately weighing to 0.0001 g.

6.5.6. 1-L graduated cylinder.

6.5.7. Block digestor -- 1.4 cm i.d. x 5 cm deep holes. Operated at 205°C ± 5°C. Note: A Technicon Model BD-40 block digestor with specially fabricated aluminum insert bushings was used to conduct the procedure development research. Block digestors with holes of other dimensions may adversely influence recoveries.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1. Solvents -- High purity, distilled in glass toluene, hexane, methylene chloride, chloroform and methyl alcohol.

7.2. Sodium sulfate -- ACS granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow dish. Store in a glass bottle with a Teflon-lined screw cap.

7.3. $SbCl_5$ > 98%.

7.4. Iron powder - 99.1%.

7.5. PCB Solutions.

7.5.1. Prepare a stock solution of Aroclor 1260 at 5.00 μg/μL in methyl alcohol or obtain a similar mixture from a certified source.

7.5.2. Prepare a stock solution of DCB at 1.00 μg/μL in toluene or obtain a similar mixture from a certified source.

7.5.3. PCB fortification solution. Dilute an aliquot of the Aroclor 1260 stock solution in methyl alcohol to produce about 10 mL of a solution containing 50.0 ng/μL. Store in a 50-90% filled glass bottle with a Teflon-lined screw cap.

7.5.4. Calibration standards. Five calibration solutions containing DCB from 0.01 ng/μL to 1.0 ng/μL in hexane are required to calibrate the detector response. Prepare standards at 0.010, 0.080, 0.10, 0.25 and 1.0 ng/μL in hexane (see 4.4) from the stock solution of DCB. Store in

50-90% filled glass bottles with Teflon-lined screw caps. Monitor for solvent loss due to evaporation.

7.5.5. Extract matrix evaluation solution. Dilute an aliquot of the DCB stock solution to produce about 10 mL of a solution containing 50.0 ng/μL in hexane. Store in a 50-90% filled glass bottle with a Teflon-lined screw cap.

7.6. Hydrochloric Acid Solution 1+1 - Dilute one part concentrated hydrochloric acid with one part distilled water.

7.7. 0.1N Sodium Bicarbonate ($NaHCO_3$) Solution - Dilute 0.84 g of ACS grade $NaHCO_3$ to 100 mL with reagent water.

7.8. Reagent water - Water in which DCB is found to be less than 0.1 μg/L as analyzed by this procedure. Distilled water met this criterion.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample Collection

8.1.1. Collect duplicate samples in clean 1-L glass containers and seal with a Teflon-lined screw cap. Fill the bottles to about 90-95% full.

8.1.2. Because PCBs are hydrophobic they are likely to be adsorbed on suspended solids. If suspended solids are present in the source, a representative portion of solids must be included in the water sample.

8.1.3. When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (about 10 min). Adjust the flow to about 1 L/min and collect the duplicate samples from the flowing stream.

8.1.4. When sampling from an open body of water, fill a 1-gal wide-mouth bottle from a representative area. Carefully fill the duplicate sample bottles from the 1-gal bottle.

8.2. Sample Preservation -- No chemical preservation reagents are recommended. Store the samples at 4°C to retard microbial action until analysis.

8.3. Sample Storage -- Extract samples within 14 days of collection (7). Extracts and perchlorinated extracts may be stored for up to 30 days if protected from solvent volatilization.

9. CALIBRATION -- Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning

and end of each set of samples or 8-hour period during which analyses are performed.

9.1. Initial Calibration

9.1.1. Inject duplicate aliquots (1-3 μL) of each calibration solution into the GC. (Autoinjectors are preferred, especially with splitless injectors.) Inject five additional aliquots of the 0.10 ng/μL standard.

9.1.2. Accurately determine the DCB retention time (RT) and peak area or peak height for each injection.

9.1.3. Determine the average RT and the standard deviation (SD) of RTs for all 15 injections. To be acceptable, the RSD of the RTs should be less than 0.2%.

9.1.4. Determine the response factor (RF) for each of the injections by dividing the amount (ng) injected into the resulting area or peak height or integrator units.

9.1.5. Determine the average RF and its SD and RSD for the seven injections at the 0.10 ng/μL level.

9.1.6. The RSD of the RF should be less than 6% for the seven injections at the 0.1 ng/μL level.

9.1.7. Compare the RF determined for the 0.01, 0.08, 0.25, and 1.0 ng standards to the average RF calculated in 9.1.5 ± 3 SD. If any value falls outside of this range, then the instrument is not being operated within an acceptable linear range and the sample volume injected must be adjusted accordingly. Alternatively, the linear dynamic range can be clearly defined by injecting standards at other concentrations. To be marginally acceptable, the system should function from 0.08 to 0.25 ng injected.

Table II shows typical values obtained during method developmnt.

9.2. For an acceptable continuing calibration check, the 0.1 ng/μL calibration standard must be analyzed before and after a series of samples or at least once after each 8 hours of operation. The RF must be within ± 20% of the mean value determined in 9.1.5, or a new calibration curve must be generated. Additionally, the RT must fall within the mean value ± 3 SD determined in 9.1.3, or a new calibration curve must be generated or the reason for the RT variance must be found and rectified.

9.3. Extract matrix effect evaluation -- It has been found that there may be a matrix effect from the perchlorinated extract which can bias the response on certain GC systems. Until this problem is

understood, an extract matrix effect evaluation should be performed on each gas chromatographic system to determine if the system can be used for this procedure. This test should be repeated each time a modification or change is made to the system.

9.3.1. Extract, perchlorinate, and cleanup duplicate drinking water samples or laboratory reagent blanks according to the procedure halting at step 11.2.13.

9.3.2. Combine the two extracts together in a 25-mL beaker or flask and mix.

9.3.3. Immediately place 5.0 mL in a volumetric flask and seal. Place the remaining solution in a second hermetically sealed container and label MS-1 (mixed sample 1).

9.3.4. Analyze MS-1 in duplicate. If the value for the DCB is $\leq$ 0.05 ng/μL, proceed to 9.3.5. If $\geq$ 0.05 ng/μL, proceed to 9.3.6.

9.3.5. Fortify the contents of the volumetric flask with 10.0 μL of the 50.0 ng/μL extract matrix evaluation solution (Sect. 7.5.5) and label SE-1 (fortified extract 1). Analyze SE-1 in duplicate, then proceed to 9.3.

9.3.6. Fortify the contents of the volumetric flask at three to ten times the concentration found in 9.3.4. If the fortified value plus the MS-1 value found in 9.3.4 exceeds the linear dynamic range of the detector (Sect. 9.1.7), then terminate the test and select another sample. Do not dilute extract matrices to perform this test.

9.3.7. Determine the extract matrix bias according to the following calculation:

$$\frac{(\text{SE-1 ng}/\mu\text{L}) - (\text{MS-1 ng}/\mu\text{L}) \times 100}{(\text{Fortified value ng}/\mu\text{L})} = \% \text{ recovery}$$

Recoveries between 80 and 120% are acceptable. If the recovery is < 80%, the test should be repeated. If the recovery remains < 80%, then another GC system should be used.

10. QUALITY CONTROL

10.1. Laboratory Reagent Blank (LRB) -- Perform all steps in the analytical procedure (Sect. 11) using all glassware, reagents, standards, equipment, apparatus, and solvents that would be used for a sample analysis using 1 L of reagent water.

10.1.1. Prepare and analyze a LRB before any samples are extracted and analyzed.

10.1.2. Prepare and analyze additional LRB whenever new batches or sources of reagents are introduced into the analysis scheme.

10.1.3. Prepare a LRB each time samples are perchlorinated. If large batches of samples are perchlorinated, then prepare and analyze 1 LRB per 10 samples.

10.1.4. An acceptable LRB contains ≤ 0.025 ng/μL of DCB.

10.1.5. Corrective action for unacceptable LRB -- Systematically check solvents, reagents (particularly the $SbCl_5$ and methylene chloride), apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted, perchlorinated, and analyzed. Purify or discard contaminated reagents and solvents.

10.2. Calibration -- Included among initial and continuing calibration procedures are numerous QC checks to ensure that valid data are being acquired (See Sect. 9). Continuing calibration checks are accomplished with results from analysis of one solution, the 0.10 ng/μL calibration solution.

10.2.1. If some criteria are not met for a continuing calibration check after an 8-h period or after a series of samples are analyzed, then those samples must be reanalyzed. Those criteria include the RF criteria and the RT criteria described in Sect. 9.2.

10.3. All sample concentrations must be bracketed by the calibration curve and must be within the linear dynamic range of the detector. (See Sect. 9.1.7.)

10.3.1. Samples that fall outside the linear dynamic range due to excessive concentration must be reanalyzed after appropriate dilution if accurate values for DCB are required.

10.4. All GC systems must be evaluated for extract matrix effect bias according to Sect. 9.3.

10.4.1. Systems that exhibit a bias in excess of + or - 20% should not be used for this determination.

10.5. Initial demonstration of laboratory capability for water analysis.

10.5.1. Prepare one or more solutions containing representative PCB mixtures at a concentration that falls within the

linear dynamic range of the instrument. Reagent water fortified with Aroclor 1260 is recommended for this test.

10.5.2. Fortify four to seven 1-L portions of reagent water with 10.0 μL of the 50 ng/μL PCB solution (Sect. 7.5.3). Extract and analyze the fortified water samples according to the procedure (Sect. 11).

10.5.3. Calculate the recovery according to the following formula:

$$\% \text{ Recovery} = \frac{(\text{Total ng found in extract}) \times 100}{691}$$

$$\text{where } 691 = 500 \text{ ng} \frac{\text{mw DCB (499)}}{\text{mw Aroclor 1260 (361)}}^{a}$$

[a]See Table 1 for the molecular weights of other Aroclors.

10.5.4. Determine the average concentration and the relative SD of the five measurements. Average recovery should be 100% ±20 with a RSD of < 10%.

10.6. Fortify reagent water with varying quantities of the 50 ng/μL PCB solution (Sect. 7.5.3). Analyze at least one fortified sample for each batch of 20 samples. Calculate recovery according to Sect. 10.5.3. Maintain QC charts of these data. Until interlaboratory data are available, the recovery of the fortified sample should be equivalent to that determined in 10.5.4.

10.7. Sample matrix effects have been observed with this procedure and they are significant. Check for sample matrix effects by analyzing one laboratory fortified sample matrix (LFM) for every 20 samples.

10.8. At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy (Sect. 10.5.4), check the entire analytical procedure to locate and correct the problem source.

10.9. Qualitative identification of DCB in the samples is based on the average RT for DCB determined in Sect. 9.1.3. For a positive identification, the DCB peak must elute within the window bracketed by the average retention ± 3 SD. If DCB appears to fall outside of this window, then further analyses of samples should be halted and Sect. 9.2 initiated.

10.10. It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference

materials and participate in relevant performance evaluation studies.

11. PROCEDURE

11.1. Sample Extraction

11.1.1. Mark the sample meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

11.1.2. Add 60 mL of methylene chloride (See Sect. 5.6) to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Wait at least 10 min to allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, use mechanical techniques (such as stirring, filtration of emulsion through glass wool, or centrifugation) to complete phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.3. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

11.1.4. Pour the combined extract into a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Rinse the Erlenmeyer flask with a 20 to 30 mL portion of methylene chloride adding the rinse to the drying column. Collect the combined extract in the K-D concentrator.

11.1.5. Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.1.6. Remove the 10-mL concentrator tube from the 500-mL evaporative flask and attach a 3-ball micro Snyder column. After wetting the column with about 0.5 mL of methylene chloride, continue concentrating the extract down to about 2 mL.

11.1.7. Determine the original sample volume by refilling the sample bottle with water to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2. Perchlorination (8,9)

11.2.1. Quantitatively transfer the extract to a 100 mm x 13 mm i.d. screw cap test tube. Rinse the KD ampul three times with 250 μL of chloroform adding the rinse to the test tube.

11.2.2. Concentrate the extract to about 0.1 mL (0.1 mL is about the volume of one drop of water) by directing a stream of nitrogen flowing at about 100 mL/m into the test tube while warming the base of the test tube in a 50°C water bath.

11.2.2.1. Do not allow to go to dryness.

11.2.2.2. Disposable pipettes are a convenient means of directing the nitrogen into the test tube. In an effort to minimize cross contamination, a new pipette should be used for each sample.

11.2.3. Add an additional 2 mL of chloroform and again concentrate to 0.1 mL using the nitrogen blow-down technique.

11.2.4. Add 100 mg of iron powder to the extract.

11.2.5. Using a disposable pipette, carefully add 25 drops of $SbCl_5$ to the extract. (See Sect. 5.3). Seal immediately.

11.2.6. Heat to 205°C ± 5°C for a minimum of 30 min but do not exceed 45 min. Perform the reaction in the hood behind an explosion shield.

11.2.7. Allow the mixture to cool to room temperature.

11.2.8. Carefully open in a hood. (The extract will be under a slight pressure.)

11.2.9. Slowly add 0.5 mL of 1+1 diluted hydrochloric acid to the perchlorinated extract in a hood. Caution: The remaining $SbCl_5$ will react exothermally with the HCl. If a white

precipitate is present, add additional hydrochloric acid solution until it dissolves.

11.2.10. Add 2.0 mL of hexane to the contents of the test tube. Seal and shake for 2 min. Allow the two phases to separate. Decant the top layer into a 5.0-mL volumetric flask. Reextract the mixture two additional times: First with 2.0 mL of hexane, then with 1.0 mL of hexane, adding the extracts to the 5.0-mL volumetric flask. Carefully adjust the volume to 5.0 mL using hexane.

11.2.11. Add 4 mL of 0.1 N $NaHCO_3$ to a 15-mL test tube with a Teflon-lined screw cap. Pour the contents of the 5-mL volumetric flask into the test tube. (Note: Do not rinse the volumetric flask with additional solvent.) Seal and shake for 1 min. Allow the two phases to separate.

11.2.12. Decant the top layer into a second 15-mL test tube. Add 4 mL of reagent water. Seal and shake for 1 min.

11.2.13. Decant the top layer and store in a hermetically sealed container for GC analysis.

11.3. GC -- Packed - on-column injection ECD, capillary - on-column injection electron capture and capillary splitless injection ECD GC systems have been evaluated and found to generate acceptable data for DCB as long as Sect. 10.4 criteria are met. The following conditions were used to generate the single-laboratory accuracy and precision data listed in Sect. 13. The values given are for guidance because slight modifications may be necessary to optimize specific GC systems.

11.3.1. The packed column GC was operated with a glass column 3 m long with an i.d. of 2 mm. The column was packed with 3% OV-1 coated on 80-100 mesh Supelcoport. 3.0 μL volumes of each sample was injected directly on column using an autosampler. The injection port was held at 200°C while the column was maintained isothermally at 235°C with an Argon +5% methane carrier gas flowing at 50 mL/min. The ECD was maintained at 300°C with no auxiliary make-up gas.

Under these conditions, the average RT for DCB was 9.49 min with a SD of 0.014. DCB was adequately resolved from other perchlorination reaction byproducts to generate accurate data for drinking water samples. Highly contaminated raw source water generated complex chromatograms with late eluting components that interfered with DCB measurements.

11.3.2. The capillary column on-column GC was operated with a DB-5 fused silica column 30 m long with a 0.32 mm i.d. and a 0.25 μm film thickness. The helium carrier gas was

adjusted to flow at 29 cm/sec at 60°C. Three microliter sample volumes were injected on-column into a 0.5 mm i.d. x 10 cm fused silica retention gap using an autoinjector. The retention gap was maintained at 60°C during injection.

The capillary column was maintained at 60°C until one minute after injection, then programmed at 20°/min to 180°C. After a 2 minute hold, the column was again programmed at 20°C/min to 290°C and held there until all compounds eluted. The ECD was operated at 300°C with an Argon +5% methane makeup gas flowing at 20 mL/min.

Under these conditions the average RT for DCB was 21.85 min with a SD of 0.021. DCB was adequately resolved from other perchlorination byproducts to generate accurate data for both finished drinking water and raw source water samples.

11.3.3. The capillary column splitless injection GC was operated with a DB-5 fused silica column 30 m long with an i.d. of 0.32 mm and a 0.25 μm film thickness. The helium carrier gas was adjusted to flow at 29 cm/sec at 180°C. Three μL injection volumes were delivered by an autoinjector into the splitless injector operated at 250°C. The splitless time was set for 30 sec.

The capillary column was maintained at 180°C until one minute after injection, then programmed at 20°C/min to 290°C and held for 20 min or until all late eluting compounds eluted. The electron capture was operated at 300°C with an argon + 5% methane makeup gas flowing at 20 mL/min.

Under these conditions the average RT for DCB was 24.75 min with a SD of 0.009. DCB was adequately resolved from other perchlorination byproducts to generate accurate data for both finished drinking water and raw source water samples.

12. CALCULATIONS

12.1. Calculate the concentration of the DCB found in each extract using an automated data system or according to the formula.

12.1.1. Extract concentration ng/μL = $\dfrac{\dfrac{\text{Area Sample}}{\mu\text{L Injected}}}{\text{RF}}$

12.1.2. Sample concentration ng/L = $\dfrac{(\text{Concentration ng}/\mu\text{L})\ (5000)}{\text{volume of sample (L)}}$

where: area sample = area, peak height or

integrator units

μL injected = volume of sample injected into GC

5000 = final volume of extract in μL (Sect. 11.2.10)

Volume of sample (L) = volume of sample extracted in liters (Sect. 11.1.7)

RF = average RF (9.1.4) for the 0.1 ng/μL standard.

12.1.3. Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 μg/L, two significant figures for concentrations between 0.1-99 μg/L, and one significant figure for lower concentrations.

12.1.4. Do not subtract method blanks from the sample data unless otherwise required in the procedure.

13. **METHOD PERFORMANCE** -- To obtain single-laboratory accuracy and precision data for method analytes, seven 1-L aliquots of chlorinated tap water, groundwater and river water were fortified with 500 ng of PCBs from several sources. The samples were extracted, perchlorinated and analyzed according to Sect. 11. Tables 3 and 4 list the resulting data.

14. **REFERENCES**

1. Ballschmiter, K. and M. Zell, Fresenius Z. Anal. Chem., 302, 20, 1980.

2. DeKok, A., et al., Intern. J. Environ. Anal. Chem., Vol. 11, pp. 17-41, 1982.

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

4. "OSHA Safety and Health Standards," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206.

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 4th Edition, 1985.

6. 40 CFR Part 761.60; .65; .40; .45 40 CFR Part 761, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce and Use Prohibitions.

7. Bellar, T.A. and Lichtenberg, J. J., "Some Factors Affecting Recovery of Polychlorinated Biphenyls from Water and Bottom Samples," ASTM, STP 573, Water Quality Parameters, 1975.

8. H. Steinwandter, Brune, H. Fresenius Z. Anal. Chem. 314, 160, 1983.

9. H. Steinwandter, Fresenius Z. Anal. Chem. 317, 869-871, 1984.

10. Armour, J., JOAC, 56, 4, 987-993, 1973.

11. Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol. 15 1426, 1981.

TABLE 1. DECACHLOROBIPHENYL EQUIVALENT OF COMMON PCB SOURCES

Compound	Congener Number	Molecular Weight[a]	Concentration[b] (μg/L)	Decachloro-biphenyl Equivalent(%)[c]
2-Chlorobiphenyl	1	188.5	0.19	263
Aroclor 1221	N/A	188.5	0.19	263
Aroclor 1232	N/A	223	0.23	217
Aroclor 1242	N/A	257.5	0.26	192
Aroclor 1016	N/A	257.5	0.26	192
Aroclor 1248	N/A	292	0.30	167
Aroclor 1254	N/A	326.4	0.33	152
Aroclor 1260	N/A	361	0.36	139
Dechlorobiphenyl	209	499	0.50	100

[a] Values from (10).
[b] μg/L of various PCBs required to generate a value of 0.50 μg/L DCB (assuming 100% method recovery).
[c] The decachlorobiphenyl produced by perchlorination will be this percentage greater than the original concentration of the PCB/Aroclor listed.

TABLE 2. CALIBRATION CURVE LINEARITY TEST AND RETENTION DATA

Standard Concentration (ng/μL)	Retention Time (min)	Response Factor (area/ng)		
0.01	24.74	48790		
0.01	24.74	50650		
0.08	24.74	48240		
0.08	24.73	47260		
0.1	24.75	48300	Average	48030
0.1	24.75	49550	Standard	
0.1	24.75	51170	Deviation	2500
0.1	24.75	49160		
0.1	24.75	43220	Relative	
0.1	24.74	47490	Standard	5.2%
0.1	24.74	47320	Deviation	
0.25	24.76	49960		
0.25	24.76	48240		
1.0	24.76	47230		
1.0	24.76	48410		

Average RT = 24.75
SD = 0.009
Relative Standard Deviation = 0.038%

TABLE 3. SPLITLESS CAPILLARY COLUMN SINGLE LABORATORY ACCURACY AND PRECISION FOR FORTIFIED TAP WATER

Source of PCBs	MDL[11] µg/L	Concentration (µg/L)	Accuracy[ae] (%)	Precision[ae] RSD, (%)
2-Chlorobiphenyl	0.08	0.50	85; (96)[b]	5.0; (9.9)[b]
Aroclor 1221	0.14	0.50	99	8.4
Aroclor 1232	0.23	0.50	124	11.3
Aroclor 1242	0.21	0.50	82	13.1
Aroclor 1248	0.15	0.50	136	8.6
Aroclor 1254	0.14	0.50	122; (137)[c]	6.4; (7.6)[c]
Aroclor 1260	0.14	0.50	113; (96)[b]	6.5; (6.9)[b]
Biphenyl[d]		0.50	109; (75)[c]	4.8; (5.8)[c]

[a]Data corrected for source water background. Average value over study = 0.11 µg/L

[b]Data collected by on-column capillary column GC.

[c]Data collected by packed column GC.

[d]Potential method interference compound.

[e]Fortified matrix effect bias (See Sect. 9.3)

Splitless capillary column	103, 113
Packed column	93, 95
Splitless on-column	(not performed)

TABLE 4. SPLITLESS CAPILLARY COLUMN SINGLE LABORATORY ACCURACY AND PRECISION FOR RAW SOURCE WATERS

Raw Source Water	Source of PCBs Aroclor	Concentration (µg/L)	Extraction Solvent	Source Water Background (µg/L)	Accuracy (%)	Precision RSD (%)
Ohio River	1221	0.50	CH_2Cl_2	0.54	114	8.4
Spring	1260	0.50	CH_2Cl_2	0.19	101	7.9
Ohio River	1221	0.50	Hexane	0.16	123	7.5
Little Miami River	1260	5.0	Hexane	0.14	91	5.8
Ohio River	1260	5.0	Hexane	0.29	100	5.4

METHOD 515.1. DETERMINATION OF CHLORINATED ACIDS IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

Revision 4.0

R.C. Dressman and J.J. Lichtenberg - EPA 600/4-81-053, Revision 1.0 (1981)

J.W. Hodgeson - Method 515, Revision 2.0 (1986)

T. Engels (Battelle Columbus Laboratories) - National Pesticide Survey Method 3, Revision 3.0 (1987)

R.L. Graves - Method 515.1, Revision 4.0 (1989)

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METHOD 515.1

DETERMINATION OF CHLORINATED ACIDS IN WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR

1. SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water.(1) The following compounds can be determined by this method:

Analyte	Chemical Abstract Services Registry Number
Acifluorfen*	50594-66-6
Bentazon	25057-89-0
Chloramben*	133-90-4
2,4-D	94-75-7
Dalapon*	75-99-0
2,4-DB	94-82-6
DCPA acid metabolites(a)	
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
4-Nitrophenol*	100-02-7
Pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP	93-72-1

(a)DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies.

*These compounds are only qualitatively identified in the National Pesticides Survey (NPS) Program. These compounds are not quantitated because control over precision has not been accomplished.

1.2 This method may be applicable to the determination of salts and esters of analyte acids. The form of each acid is not distinguished by this method. Results are calculated and reported for each listed analyte as the total free acid.

1.3 This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for the analytes above (Sect.13). Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Sect. 10.3.

1.5 Analytes that are not separated chromatographically i.e., which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternate technique for identification and quantitation exist (Sect. 11.8).

1.6 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is adjusted to pH 12 with 6 N sodium hydroxide and shaken for 1 hr to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed, and the esters are determined by capillary column/GC using an electron capture detector (ECD).

2.2 The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered.

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated

exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are

used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 10.2.

4.1.1 Glassware must be scrupulously cleaned.(2) Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 hr. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

4.2 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with 1N hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.4 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.(3,4)

4.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. Between-sample rinsing of the sample syringe and associated equipment with methyl-t-butyl-ether (MTBE) can minimize sample cross contamination. After analysis of a sample containing high concentrations of analytes, one or more injections of MTBE should be made to ensure that accurate values are obtained for the next sample.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all analytes listed in the Scope and Application Section are not resolved from each other on any one column, i.e., one analyte of interest may be an interferant for another analyte of interest. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. The procedures in Sect. 11 can be used to overcome many of these interferences. Positive identifications should be confirmed (Sect. 11.8).

4.7 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must 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 material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (6-8) for the information of the analyst.

5.2 DIAZOMETHANE -- A toxic carcinogen which can explode under certain conditions. The following precautions must be followed:

5.2.1 Use only a well ventilated hood -- do not breath vapors.

5.2.2 Use a safety screen.

5.2.3 Use mechanical pipetting aides.

5.2.4 Do not heat above 90°C -- **EXPLOSION** may result.

5.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers -- **EXPLOSION** may result.

5.2.6 Store away from alkali metals -- **EXPLOSION** may result.

5.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5.2.8 The diazomethane generation apparatus used in the esterification procedures (Sect. 11.4 and 11.5) produces micromolar amounts of diazomethane to minimize safety hazards.

5.3 ETHYL ETHER -- Nanograde, redistilled in glass, if necessary.

5.3.1 Ethyl ether is an extremely flammable solvent. If a mechanical device is used for sample extraction, the device should be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.

5.3.2 Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers).

5.4 WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6. **APPARATUS AND EQUIPMENT** (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLE BOTTLE -- Borosilicate, 1-L volume with graduations (Wheaton Media/Lab bottle 219820 or equivalent), fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in Sect. 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2 GLASSWARE

6.2.1 Separatory funnel -- 2000-mL, with TFE-fluorocarbon stop-cocks, ground glass or TFE-fluorocarbon stoppers.

6.2.2 Tumbler bottle -- 1.7-L (Wheaton Roller Culture Vessel or equivalent), with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736) and extracted with methanol overnight prior to use.

6.2.3 Concentrator tube, Kuderna-Danish (K-D) -- 10- or 25-mL, graduated (Kontes K-570050-2525 or Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stoppers are used to prevent evaporation of extracts.

6.2.4 Evaporative flask, K-D -- 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.5 Snyder column, K-D -- three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.6 Snyder column, K-D -- two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.7 Flask, round-bottom -- 500-mL with 24/40 ground glass joint.

6.2.8 Vials -- glass, 5- to 10-mL capacity with TFE-fluorocarbon lined screw cap.

6.2.9 Disposable pipets -- sterile plugged borosilicate glass, 5-mL capacity (Corning 7078-5N or equivalent).

6.3 SEPARATORY FUNNEL SHAKER -- Capable of holding 2-L separatory funnels and shaking them with rocking motion to achieve thorough mixing of separatory funnel contents (available from Eberbach Co. in Ann Arbor, MI or other suppliers).

6.4 TUMBLER -- Capable of holding tumbler bottles and tumbling them end-over-end at 30 turns/min (Associated Design and Mfg. Co., Alexandria, VA and other suppliers).

6.5 BOILING STONES -- Teflon, Chemware (Norton Performance Plastics No. 015021 and other suppliers).

6.6 WATER BATH -- Heated, capable of temperature control (± 2°C). The bath should be used in a hood.

6.7 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.8 DIAZOMETHANE GENERATOR -- Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen as shown in Figure 1 (available from Aldrich Chemical Co.). When esterification is performed using diazomethane solution, the diazomethane collector is cooled in an approximately 2-L thermos for ice bath or a cryogenically cooled vessel (Thermoelectrics Unlimited Model SK-12 or equivalent).

6.9 GLASS WOOL -- Acid washed (Supelco 2-0383 or equivalent) and heated at 450°C for 4 hr.

6.10 GAS CHROMATOGRAPH -- Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.10.1 Column 1 (Primary column) -- 30 m long x 0.25 mm I.D. DB-5 bonded fused silica column, 0.25 μm film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 μL splitless mode with 45 second delay. The injector temperature was 250°C and the detector was 320°C. Alternative columns may be used in accordance with the provisions described in Sect. 10.2.

6.10.2 Column 2 (Confirmation column) -- 30 m long x 0.25 mm I.D. DB-1701 bonded fused silica column, 0.25 um film thickness (J&W Scientific). Helium carrier gas flow is established at 30 cm/sec linear velocity and oven temperature is programmed from 60°C to 300°C at 4°C/min.

6.10.3 Detector -- Electron capture. This detector has proven effective in the analysis of fortified reagent and artificial ground waters. An ECD was used to generate the validation data presented in this method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Sect. 10.3.

7. <u>REAGENTS AND CONSUMABLE MATERIALS</u> - WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

7.1 ACETONE, METHANOL, METHYLENE CHLORIDE, MTBE -- Pesticide quality or equivalent.

7.2 ETHYL ETHER, UNPRESERVED -- Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. PI126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips.

7.3 SODIUM SULFATE, GRANULAR, ANHYDROUS, ACS GRADE -- Heat treat in a shallow tray at 450°C for a minimum of 4 hr to remove interfering organic substances. Acidify by slurrying 100 g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.1 mL concentrated

sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. The pH must be below pH 4. Store at 130°C.

7.4 SODIUM THIOSULFATE, GRANULAR, ANHYDROUS -- ACS grade.

7.5 SODIUM HYDROXIDE (NAOH), PELLETS -- ACS grade.

7.5.1 NaOH, 6 N -- Dissolve 216 g NaOH in 900 mL reagent water.

7.6 SULFURIC ACID, CONCENTRATED -- ACS grade,sp. gr. 1.84.

7.6.1 Sulfuric acid, 12 N -- Slowly add 335 mL concentrated sulfuric acid to 665 mL of reagent water.

7.7 POTASSIUM HYDROXIDE (KOH), PELLETS -- ACS grade.

7.7.1 KOH, 37% (w/v) -- Dissolve 37 g KOH pellets in reagent water and dilute to 100 mL.

7.8 CARBITOL (DIETHYLENE GLYCOL MONOETHYL ETHER) -- ACS grade. Available from Aldrich Chemical Co.

7.9 DIAZALD, ACS grade -- Available from Aldrich Chemical Co.

7.10 DIAZALD SOLUTION -- Prepare a solution containing 10 g Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber bottle with a Teflon-lined screw cap.

7.11 SODIUM CHLORIDE (NACL), CRYSTAL, ACS GRADE -- Heat treat in a shallow tray at 450°C for a minimum of 4 hr to remove interfering organic substances.

7.12 4,4'-DIBROMOOCTAFLUOROBIPHENYL (DBOB) -- 99% purity, for use as internal standard (available from Aldrich Chemical Co).

7.13 2,4-DICHLOROPHENYLACETIC ACID (DCAA) -- 99% purity, for use as surrogate standard (available from Aldrich Chemical Co).

7.14 MERCURIC CHLORIDE -- ACS grade (Aldrich Chemical Co.) - for use as a bacteriocide. If any other bactericide can be shown to work as well as mercuric chloride, it may be used instead.

7.15 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., Columbus, Ohio.

7.16 SILICIC ACID, ACS GRADE.

7.17 FLORISIL -- 60-100/PR mesh (Sigma No. F-9127). Activate by heating in a shallow container at 150°C for at least 24 and not more than 48 hr.

7.18 STOCK STANDARD SOLUTIONS (1.00 µg/µL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.18.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.18.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap amber vials. Store at room temperature and protect from light.

7.18.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.19 INTERNAL STANDARD SOLUTION -- Prepare an internal standard solution by accurately weighing approximately 0.0010 g of pure DBOB. Dissolve the DBOB in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 25 µL of the internal standard solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/mL. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem. Note that DBOB has been shown to be an effective internal standard for the method analytes(1), but other compounds may be used if the quality control requirements in Sect. 10 are met.

7.20 SURROGATE STANDARD SOLUTION -- Prepare a surrogate standard solution by accurately weighing approximately 0.0010 g of pure DCAA. Dissolve the DCAA in MTBE and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 µL of the surrogate standard solution to a 1-L sample prior to extraction results in a surrogate standard concentration in the sample of 5 µg/L and, assuming quantitative recovery of DCAA, a surrogate standard concentration in the final extract of 0.5 µg/mL. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem. Note DCAA has been shown to be an effective surrogate standard for the method analytes(1), but other compounds may be used if the quality control requirements in Sect. 10.4 are met.

7.21 LABORATORY PERFORMANCE CHECK SOLUTIONS -- Prepare a diluted dinoseb solution by adding 10 µL of the 1.0 µg/µL dinoseb stock solution to the MTBE and diluting to volume in a 10-mL volumetric flask. To prepare the check solution, add 40 µL of the diluted dinoseb solution, 16 µL of the 4-nitrophenol stock solution, 6 µL of the 3,5-dichlorobenzoic acid stock solution, 50 µL of the surrogate standard solution, 25 µL of the internal standard solution, and 250 µL of methanol to a 5-mL volumetric flask and dilute to volume with MTBE. Methylate sample as described in Sects. 11.4 or 11.5. Dilute the sample to 10 mL in MTBE. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION AND STORAGE

8.2.1 Add mercuric chloride (See 7.14) to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a 10 mg/mL solution of mercuric chloride in water to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; mercuric chloride must be handled with caution, and samples containing mercuric chloride must be disposed of properly.

8.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.3 After the sample is collected in the bottle containing preservative(s), seal the bottle and shake vigorously for 1 min.

8.2.4 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicate that the analytes (measured as total acid) present in samples are stable for 14 days when stored under these conditions.(1) However, analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.3 EXTRACT STORAGE

8.3.1 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days(1); however, the analyst should verify appropriate extract holding times applicable to the samples under study.

9. CALIBRATION

9.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.10. The GC system may be calibrated using either the internal standard technique (Sect. 9.2) or the external standard technique (Sect. 9.3). NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE -- To use this approach, the analyst must select one or more internal standards compatible in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.. DBOB has been identified as a suitable internal standard.

9.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more of the internal standards and 250 μL methanol, and dilute to volume with MTBE. Esterify acids with diazomethane as described in Sect. 11.4 or 11.5. The lowest standard should represent analyte concentrations near, but above, the respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

9.2.2 Analyze each calibration standard according to the procedure (Sect. 11.7). Tabulate response (peak height or area) against concentration for each compound and internal standard. Calculate the response factor (RF) for each analyte and surrogate using Equation 1.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)} \qquad \text{Equation 1}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (μg/L).
C_s = Concentration of the analyte to be measured (μg/L).

9.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

9.2.4 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the repetition also fails, a new calibration curve must be generated for that analyte using freshly prepared standards.

9.3.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standards should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.2.6 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

9.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

9.3.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest and surrogate compound by adding volumes of one or more stock standards and 250 μL methanol to a volumetric flask. Dilute to volume with MTBE. Esterify acids with diazomethane as described in Sect. 11.4 or 11.5. The best standard should represent analyte concentrations near, but above, the respective EDL. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

9.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.7 and tabulate response (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (20% RSD or less), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

9.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than 8 hr), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte

varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 9.3.3.

9.3.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards in MTBE. The single point standards should be prepared at a concentration that produces a response that deviates from the sample extract response by no more than 20%.

9.2.5 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

10. QUALITY CONTROL

10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples.

10.2 LABORATORY REAGENT BLANKS (LRB). Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 Initial Demonstration of Capability.

10.3.1 Select a representative fortified concentration (about 10 times EDL) for each analyte. Prepare a sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 1 mL of the concentrate to each of at least four 1-L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

10.3.2 For each analyte the recovery value for all four of these samples must fall in the range of R ± 30% (or within R ± $3S_R$ if broader) using the values for R and S_R for reagent water in Table 2. For those compounds that meet the acceptable criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these

criteria, this procedure must be reported using five fresh samples until satisfactory performance has been demonstrated.

10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

10.4 The analyst is permitted to modify GC columns, GC conditions, detectors, continuous extraction techniques, concentration techniques (i.e., evaporation techniques), internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 10.3

10.5 ASSESSING SURROGATE RECOVERY.

10.5.1 When surrogate recovery from a sample or method blank is <70% or >130%, check (1) calculations to locate possible errors, (2) spiking solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

10.5.2 If a blank extract reanalysis fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

10.5.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the analyzed extract. If sample extract continues to fail the recovery criterion, report all data for that sample as suspect.

10.6 ASSESSING THE INTERNAL STANDARD

10.6.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard's IS response by more than 30%.

10.6.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

10.6.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

10.6.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the samples

should be repeated beginning with Sect. 11, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

10.6.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

10.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Sect. 10.6.2 for each sample failing the IS response criterion.

10.6.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Sect. 9.

10.7 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANK

10.7.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples extracted within a 24-hr period) whichever is greater. The concentration of each analyte in the LFB should be 10 times EDL or the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 10.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.7.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 10.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery ($\bar{X}$) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{X} + 3S$$
$$\text{LOWER CONTROL LIMIT} = \bar{X} - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should never exceed those established in Section 10.3.2.

10.7.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for the analytes of interest.

10.7.4 At least quarterly, analyze a QC sample from an outside source.

10.7.5 Laboratories are encouraged to participate in external performance evaluation studies such as the laboratory certification programs offered by many states or the studies conducted by USEPA. Performance evaluation studies serve as independent checks on the analyst's performance.

10.8 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.8.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample concentration per set, whichever is greater. The concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 10.7). Over time, samples from all routine sample sources should be fortified.

10.8.2 Calculate the percent recovery, P of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b) \ /\ \text{fortifying concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. If the analyzed unfortified sample is found to contain NO background concentrations, and the added concentrations are those specified in Sect. 10.7, then the appropriate control limits would be the acceptance limits in Sect. 10.7. If, on the other hand, the analyzed unfortified sample is found to contain background concentration, b, estimate the standard deviation at the background concentration, s_b, using regressions or comparable background data and, similarly, estimate the mean, $\bar{X}_a$ and standard deviation, s_a, of analytical results at the total concentration after fortifying. Then the appropriate percentage control limits would be $\bar{P} \pm 3s_P$, where:

$$\bar{P} = 100\ \bar{X}\ /\ (b + \text{fortifying concentration})$$

$$\text{and } s_P = 100\ (s_a^2 + s_b^2)^{1/2} \ /\text{fortifying concentration}$$

For example, if the background concentration for Analyte A was found to be 1 μg/L and the added amount was also 1 μg/L, and upon analysis the laboratory fortified sample measured 1.6 μ/L, then the calculated P for this sample would be (1.6

μg/L minus 1.0 μg/L)/1 μg/L or 60%. This calculated P is compared to control limits derived from prior reagent water data. Assume it is known that analysis of an interference free sample at 1 μg/L yields an s of 0.12 μg/L and similar analysis at 2.0 μg/L yields $\bar{X}$ and s of 2.01 μg/L and 0.20 μg/L, respectively. The appropriate limits to judge the reasonableness of the percent recovery, 60%, obtained on the fortified matrix sample is computed as follows:

$$[100\ (2.01\ \mu g/L)\ /\ 2.0\ \mu g/L]$$

$$\pm\ 3\ (100)\ \ [(0.12\ \mu g/L)^2 + (0.20\ \mu g/L)^2]^{1/2}\ /\ 1.0\ \mu g/L =$$

$$100.5\% \pm 300\ (0.233) =$$

100.5% ± 70% or 30% to 170% recovery of the added analyte.

10.8.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 10.7), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.9 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK SAMPLE - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 3. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs.

10.10 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11. PROCEDURE

11.1 MANUAL HYDROLYSIS, PREPARATION, AND EXTRACTION.

11.1.1 Add preservative to blanks and QC check standards. Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.1.9). Pour

the entire sample into a 2-L separatory funnel. Fortify sample with 50 µL of the surrogate standard solution.

11.1.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

11.1.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature for 1 hr, shaking the separatory funnel and contents periodically.

11.1.4 Add 60 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

11.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

11.1.6 Add 17 mL of 12 N H_2SO_4 to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H_2SO_4.

11.1.7 Add 120 mL ethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ethyl ether phase in a 500-mL round-bottom flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

11.1.8 Return the aqueous phase to the separatory funnel, add a 60-mL volume of ethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL erlenmeyer flask. Perform a third extraction with 60 mL of ethyl ether in the same manner.

11.1.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 AUTOMATED HYDROLYSIS, PREPARATION, AND EXTRACTION. -- Data presented in this method were generated using the automated extraction procedure with the mechanical separatory funnel shaker.

11.2.1 Add preservative (Sect. 8.2) to any samples not previously preserved, e.g., blanks and QC check standards. Mark the water meniscus on the side of the sample bottle for later determination of sample volume (Sect. 11.2.9). Fortify sample with 50 µL of the surrogate standard solution. If the mechanical separatory funnel shaker is used, pour the entire sample into a 2-L separatory funnel. If the mechanical tumbler is used, pour the entire sample into a tumbler bottle.

11.2.2 Add 250 g NaCl to the sample, seal, and shake to dissolve salt.

11.2.3 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper; if the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Shake sample for 1 hr using the appropriate mechanical mixing device.

11.2.4 Add 300 mL methylene chloride to the sample bottle to rinse the bottle, transfer the methylene chloride to the separatory funnel or tumbler bottle, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble the sample for 1 hr. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.2.5 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and

discard the organic phase. If the tumbler is used, return the aqueous phase to the tumbler bottle.

11.2.6 Add 17 mL of 12 N H_2SO_4 to the sample, seal, and shake to mix. Check the pH of the sample with pH paper; if the sample does not have a pH less than or equal to 2, adjust the pH by adding more 12 N H_2SO_4.

11.2.7 Add 300 mL ethyl ether to the sample, seal, and shake for 10 s, venting periodically. Repeat shaking and venting until pressure release is not observed during venting. Reseal and place sample container in appropriate mechanical mixing device. Shake or tumble sample for 1 hr. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

11.2.8 Remove the sample container from the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2-L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Drain and discard the aqueous phase. Collect the extract in a 500-mL round-bottom flask containing about 10 g of acidified anhydrous sodium sulfate. Periodically vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

11.2.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 EXTRACT CONCENTRATION

11.3.1 Assemble a K-D concentrator by attaching a concentrator tube to a 500-mL evaporative flask.

11.3.2 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the round-bottom flask and funnel with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

11.3.3 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the

concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether. Add 2 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 250 µL of methanol. If the gaseous diazomethane procedure (Sect. 11.4) is used for esterification of pesticides, rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. If the pesticides will be esterified using the diazomethane solution (Sect. 11.5), rinse the walls of the concentrator tube while adjusting the volume to 4.5 mL with MTBE.

11.4 ESTERIFICATION OF ACIDS USING GASEOUS DIAZOMETHANE -- Results presented in this method were generated using the gaseous diazomethane derivatization procedure. See Section 11.5 for an alternative procedure.

11.4.1 Assemble the diazomethane generator (Figure 1) in a hood.

11.4.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.2 grams Diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 1 min. Remove first sample. Rinse the tip of the diazomethane generator with ethyl ether after methylation of each sample. Bubble diazomethane through the second sample extract for 1 min. Diazomethane reaction mixture should be used to esterify only two samples; prepare new reaction mixture in Tube 2 to esterify each two additional samples. Samples should turn yellow after addition of diazomethane and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

11.4.3 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

11.4.4 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.5 ESTERIFICATION OF ACIDS USING DIAZOMETHANE SOLUTION -- Alternative procedure.

11.5.1 Assemble the diazomethane generator (Figure 2) in a hood. The collection vessel is a 10- or 15-mL vial, equipped with a Teflon-lined screw cap and maintained at 0-5C.

11.5.2 Add a sufficient amount of ethyl ether to tube 1 to cover the first impinger. Add 5 mL of MTBE to the collection vial. Set the nitrogen flow at 5-10 mL/min. Add 2 mL Diazald solution (Sect. 7.10) and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the nitrogen flow to purge the diazomethane from the reaction vessel into the collection vial for 30 min. Cap the vial when collection is complete and maintain at 0-5°C. When stored at 0-5°C this diazomethane solution may be used over a period of 48 hr.

11.5.3 To each concentrator tube containing sample or standard, add 0.5 mL diazomethane solution. Samples should turn yellow after addition of the diazomethane solution and remain yellow for at least 2 min. Repeat methylation procedure if necessary.

11.5.4 Seal concentrator tubes with stoppers. Store at room temperature in a hood for 30 min.

11.5.5 Destroy any unreacted diazomethane by adding 0.1 to 0.2 grams silicic acid to the concentrator tubes. Allow to stand until the evolution of nitrogen gas has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

11.6 FLORISIL SEPARATION

11.6.1 Place a small plug of glass wool into a 5-mL disposable glass pipet. Tare the pipet, and measure 1 g of activated Florisil into the pipet.

11.6.2 Apply 5 mL of 5 percent methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.

11.6.3 Apply 5 mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.

11.6.4 Add 1 mL of 5 percent methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column leaving silicic acid in the tube. Collect eluate in a K-D tube. Repeat with 1-mL and 3-mL aliquots of 5 percent methanol in MTBE, collecting eluates in K-D tube.

11.6.5 If necessary, dilute eluate to 10 mL with 5 percent methanol in MTBE.

11.6.6 Seal the vial and store in a refrigerator if further processing will not be performed immediately. Analyze by GC-ECD.

11.7 GAS CHROMATOGRAPHY

11.7.1 Sect. 6.10 summarizes the recommended operating conditions for the GC. Included in Table 1 are retention times observed using this method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 10.4 are met.

11.7.2 Calibrate the system daily as described in Sect. 9. The standards and extracts must be in MTBE.

11.7.3 If the internal standard calibration procedure is used, fortify the extract with 25 μL of internal standard solution. Thoroughly mix sample and place aliquot in a GC vial for subsequent analysis.

11.7.4 Inject 2 μL of the sample extract. Record the resulting peak size in area units.

11.7.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

11.8 IDENTIFICATION OF ANALYTES

11.8.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.8.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.8.3 Identification requires expert judgement when sample components are not resolved chromatographically. When GC

peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima, or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternative techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used, e.g., mass spectrometry, or the use of a second chromatography column. A suggested alternative column in described in Sect. 6.10.

12. CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 9.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the response factor (RF) determined in Sect. 9.2 and Equation 2, or determine sample concentration from the calibration curve.

$$C\ (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)} \qquad \text{Equation 2.}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

12.3 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Sect. 9.3. The concentration (C) in the sample can be calculated from Equation 3.

$$C\ (\mu g/L) = \frac{(A)(V_t)}{(V_i)(V_s)} \qquad \text{Equation 3.}$$

where:

A = Amount of material injected (ng).
V_i = Volume of extract injected (μL).
V_t = Volume of total extract (μL).
V_s = Volume of water extracted (mL).

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range.(1) Analyte EDLs and analyte recoveries and standard deviation about the percent recoveries at one concentration are given in Table 2.

13.2 In a single laboratory, analyte recoveries from one standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices.(1) Analyte recoveries from the one synthetic matrix are given in Table 2.

14. REFERENCES

1. National Pesticide Survey Method No. 3, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector."

2. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

3. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 86, 1986.

4. Giam, C. S., Chan, H. S., and Nef, G. S. "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," Analytical Chemistry, 47, 2225 (1975).

5. Giam, C. S., and Chan, H. S. "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.

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

7. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

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

9. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 130, 1986.

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] (minutes) Primary	Confirmation
Dalapon	3.4	4.7
3,5-Dichlorobenzoic acid	18.6	17.7
4-Nitrophenol	18.6	20.5
DCAA (surrogate)	22.0	14.9
Dicamba	22.1	22.6
Dichlorprop	25.0	25.6
2,4-D	25.5	27.0
DBOB (int. std.)	27.5	27.6
Pentachlorophenol (PCP)	28.3	27.0
Chloramben	29.7	32.8
2,4,5-TP	29.7	29.5
5-Hydroxydicamba	30.0	30.7
2,4,5-T	30.5	30.9
2,4-DB	32.2	32.2
Dinoseb	32.4	34.1
Bentazon	33.3	34.6
Picloram	34.4	37.5
DCPA acid metabolites	35.8	37.8
Acifluorfen	41.5	42.8

[a] Columns and analytical conditions are described in Sect. 6.10.1 and 6.10.2.

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND ESTIMATED DETECTION LIMITS (EDLS) FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[A]

Analyte	EDL µg/L[b]	Concentration µg/L	Reagent Water R[c]	Reagent Water S_R[d]	Synthetic Water 1[e] R	Synthetic Water 1[e] S_R
Acifluorfen	0.096	0.2	121	15.7	103	20.6
Bentazon	0.2	1	120	16.8	82	37.7
Chloramben	0.093	0.4	111	14.4	112	10.1
2,4-D	0.2	1	131	27.5	110	5.5
Dalapon	1.3	10	100	20.0	128	30.7
2,4-DB	0.8	4	87	13.1	0	0
DCPA acid metabolites	0.02	0.2	74	9.7	81	21.9
Dicamba	0.081	0.4	135	32.4	92	17.5
3,5-Dichlorobenzoic acid	0.061	0.6	102	16.3	82	7.4
Dichlorprop	0.26	2	107	20.3	106	5.3
Dinoseb	0.19	0.4	42	14.3	89	13.4
5-Hydroxydicamba	0.04	0.2	103	16.5	88	5.3
4-Nitrophenol	0.13	1	131	23.6	127	34.3
Pentachlorophenol (PCP)	0.076	0.04	130	31.2	84	9.2
Picloram	0.14	0.6	91	15.5	97	23.3
2,4,5-T	0.08	0.4	117	16.4	96	3.8
2,4,5-TP	0.075	0.2	134	30.8	105	6.3

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] EDL = estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher. The concentration used in determining the EDL is not the same as the concentration presented in this table.

[c] R = average percent recovery.

[d] S_r = standard deviation of the percent recovery

[e] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

TABLE 3. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	Dinoseb	0.004	Detection of analyte; S/N > 3
Chromatographic performance	4-Nitrophenol	1.6	0.70 <PGF<1.05[b]
Column performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 1.6	Resolution >0.40[b]

[a] PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

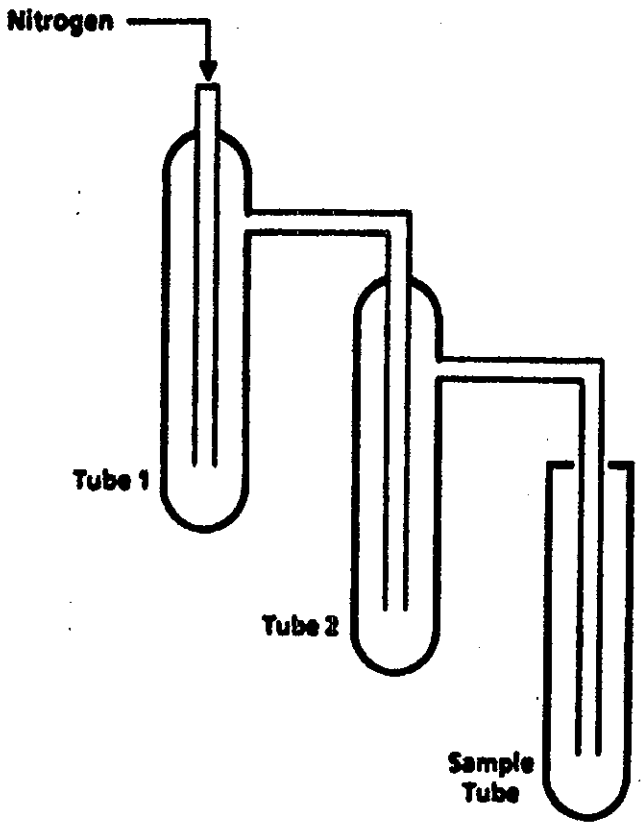

FIGURE 1. GASEOUS DIAZOMETHANE GENERATOR

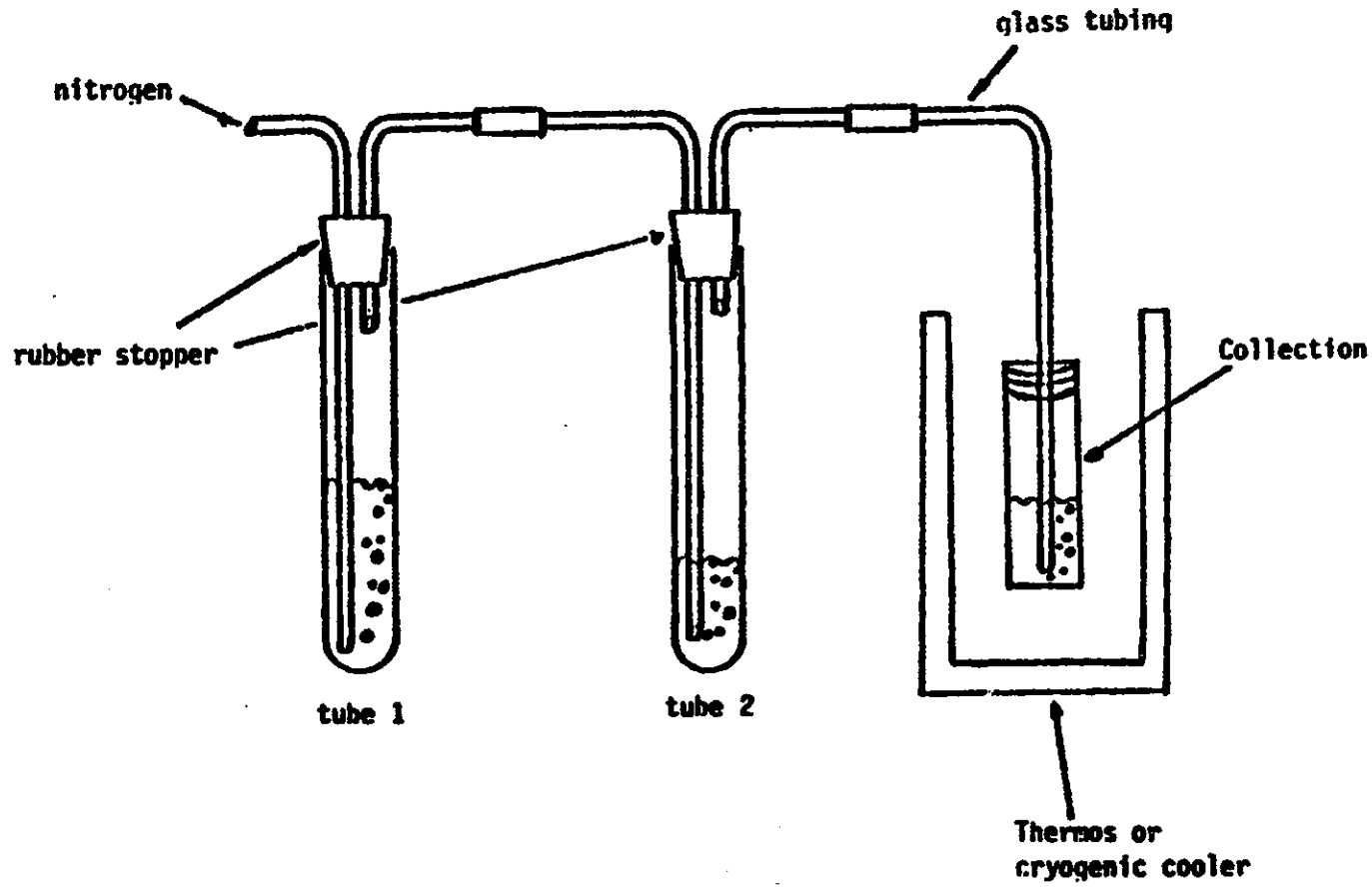

FIGURE 2. DIAZOMETHANE SOLUTION GENERATOR

METHOD 524.1. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY PACKED COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 3.0

A. Alford-Stevens, J. W. Eichelberger, W. L. Budde - Method 524, Revision 1.0 (1983)

J. E. Longbottom, R. W. Slater, Jr. - Method 524.1, Revision 2.0 (1986)

J. W. Eichelberger, W. L. Budde - Method 524.1, Revision 3.0 (1989)

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METHOD 524.1

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY PACKED COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. The following compounds are method analytes, and single-laboratory accuracy, precision, and method detection limit data have been determined with this method for 31 of them[a].

Compound	Chemical Abstract Service Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
* Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
* Bromomethane	74-83-9
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
* Chloroethane	75-00-3
Chloroform	67-66-3
* Chloromethane	74-87-3
* 2-Chlorotoluene	95-49-8
* 4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
* 1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
* cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9

*	2,2-Dichloropropane	590-20-7
*	1,1-Dichloropropene	563-58-6
*	cis-1,3-Dichloropropene	10061-01-5
*	trans-1,3-Dichloropropene	10061-02-6
*	Ethylbenzene	100-41-4
	Methylene chloride	75-09-2
	Styrene	100-42-5
*	1,1,1,2-Tetrachloroethane	630-20-6
	1,1,2,2-Tetrachloroethane	79-34-5
	Tetrachloroethene	127-18-4
	Toluene	108-88-3
	1,1,1-Trichloroethane	71-55-6
*	1,1,2-Trichloroethane	79-00-5
	Trichloroethene	79-01-6
	Trichlorofluoromethane	75-69-4
*	1,2,3-Trichloropropane	96-18-4
	Vinyl chloride	75-01-4
	o-Xylene	95-47-6
*	m-Xylene	108-38-3
	p-Xylene	106-42-3

[a] Compounds preceded by an asterisk are known to be amenable to purge and trap extraction (see Method 524.2), and chromatography on the packed gas chromatography column used in this method, but precision, accuracy, retention time, and method detection limit data is not provided in this method.

1.2 Method detection limits (MDLs) (2) are compound and instrument dependent and vary from approximately 0.1-2 µg/L. The applicable concentration range of this method is also compound and instrument dependent and is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and non-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample (Sect. 11.9.2). Table 1 lists primary and secondary quantitation ions for each analyte. Analytes which have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect.11.9.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Cis- and trans-1,2-dichloroethene, two of the three isomeric xylenes, and two of the three dichlorobenzenes are three examples of structural isomers that cannot be explicitly identified if more than one member of the isomeric group is present. These groups of isomers must be reported as isomeric pairs (see Method 524.2 for an alternative approach).

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a packed gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to separate the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of one or more compounds used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (3-5) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS -- 60-mL to 120-mL screw cap vials (Pierce #19832 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12718 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (<15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of <3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily

conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to ≈ 180°C. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Figure 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven may require cooling to <30°C; therefore, a subambient oven controller may be required. The GC usually is interfaced to the MS with an all-glass enrichment device and an all-glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in this method can be achieved.

6.3.2 Gas Chromatography Column -- 1.5 to 2.5 m x 2 mm ID stainless steel or glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or the equivalent.

6.3.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 260 amu with a complete scan cycle time (including scan overhead) of 7 seconds or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 2 when 50 ng or less of 4-bromofluoro-benzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by

recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 9.2.6 (or construction of a second or third order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 One 25-μL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

6.4.4 Micro syringes - 10, 100 μL.

6.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers - 15-mL bottles with PTFE-lined screw caps.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) - OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

7.2 COLUMN PACKING MATERIALS

7.2.1 1% SP-1000 on 60/80 mesh Carbopack-B or equivalent.

7.3 REAGENTS

7.3.1 Methanol -- Demonstrated to be free of analytes.

7.3.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

7.3.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.3.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and 99.9% pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.3.5 Ascorbic Acid -- ACS reagent grade, granular.

7.4 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.4.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.4.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.4.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from

liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

7.5 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern and the surrogates (but not the internal standard!) in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.4.4 also apply to primary dilution standard solutions.

7.6 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.6.1 A solution containing the internal standard and surrogates is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each. A 10-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 2 µg/L of each. A 10-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 10 µg/L of each. Additional internal standards and surrogate analytes are optional.

7.6.2 A solution of the internal standard alone is required to prepare calibration standards, laboratory fortified blanks, etc. The internal standard should be in methanol at a concentration of 5 µg/mL.

7.7 PREPARATION OF LABORATORY REAGENT BLANK -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject 10 µL of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.8 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard. See Sect. 7.9.

7.9 PREPARATION OF CALIBRATION STANDARDS

7.9.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL

solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50 use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern and each surrogate at a concentration of 2-10 times the method detection limit (Table 3) for that compound. The other CAL standards should contain each analyte of concern and each surrogate at concentrations that define the range of the method. Every CAL solution contains the internal standard at the same concentration (10 µg/L suggested).

7.9.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hr. unless transferred to a sample bottle and sealed immediately.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid to the sample bottle before filling. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

8.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

8.1.4 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field

samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

8.2 SAMPLE STORAGE

8.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS

8.3.1 Duplicate field reagent blanks must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION

9.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hr period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

9.2 INITIAL CALIBRATION

9.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 9.2.2.

9.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 50 ng of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 2, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the

GC peak may be used to evaluate the performance of the system.

9.2.3 Purge a medium CAL solution, for example 10-20 μg/L, using the procedure given in Sect. 11.

9.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software. Figure 3 shows an acceptable total ion chromatogram.

9.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are broad, or sensitivity poor, replace or repack the column. During handling, packing, and programming, active sites can be exposed on the Carbopack-B packing which can result in tailing peak geometry and poor resolution of many constituents. Pneumatic shocks and rough treatment of packed columns will cause excessive fracturing of the packing. If pressure in excess of 60 psi is required to obtain 40 mL/min carrier flow, the column should be repacked. With the column connected to the MS interface, a pressure below about 10^{-5} mm of Hg indicates the jet separator is clogged.

9.2.4.2 MS sensitivity. The GC/MS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 9.3.6.

9.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

9.2.6 Calculate a response factor (RF) for each analyte, surrogate, and isomer pair, for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.4), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.

A_{is} = integrated abundance of the quantitation ion of the internal standard.
Q_x = quantity of analyte purged in ng or concentration units.
Q_{is} = quantity of internal standard purged in ng or concentration units.

9.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appro-priate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Sect. 9.2.7.

9.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a second or third order regression calibration curve.

9.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 8 hr work shift during which analyses are performed using the following procedure.

9.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 50 ng of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 2), the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

9.3.2 Purge a medium concentration CAL solution and analyze with the same conditions used during the initial calibration.

9.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 9.2.4.

9.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 9.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

9.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a second or third order regression is used, the point from the continuing calibration check for each analyte and surrogate must fall, within the analyst's judgment, on the curve from the initial calibration. If these conditions do not exist, remedial action must be taken which may require reinitial calibration.

9.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

9.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

9.3.6.2 Prepare fresh CAL solutions, and repeat the initial calibration step.

9.3.6.3 Clean the MS ion source and rods (if a quadrupole).

9.3.6.4 Replace the MS electron multiplier, or any other faulty components.

9.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

9.4.1 Fill the purging device with 25.0 mL of reagent water or aqueous calibration standard.

9.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 μL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 μL/min. If the injection of the standard is made through the aqueous sample inlet part, flush the head volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

9.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in μg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in μg/L;
C = Concentration of gaseous standard in ppm (v/v);

V = Volume of standard injected in milliliters.

10. QUALITY CONTROL

10.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbants, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general background from method analytes should be below the method detection limit.

10.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 0.2-5 µg/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte. Calculate the MDL of each analyte using the procedures described in Sect. 13.2 (2).

10.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes. The method detection limits must be sufficient to detect analytes at the required levels. If these

ent to detect analytes at the required levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

10.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

10.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks. These should remain reasonably constant over time. A drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected. These integrated areas should also be reasonably constant in laboratory fortified blanks and samples.

10.5 LABORATORY REAGENT BLANKS. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination. A FRB (Sect. 10.7) may be used in place of an LRB.

10.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in 10.3. If more than 20 samples are included in a batch, analyze one LFB for every 20 samples. Use the procedures described in 10.3.3 to evaluate the accuracy of the measurements, and to estimate whether the method detection limits can be obtained. If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Add these results to the on-going control charts to document data quality.

10.7 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. If the FRB shows unacceptable contamination, a LRB must be measured to define the source of the impurities.

10.8 At least quarterly, replicates of laboratory fortified blanks should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

10.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

10.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, and ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required. It is recommended that sample matrix effects be evaluated at least quarterly using the QCS described in 10.9.

10.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING -- This method is designed for a 25-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0 mL (or 5-mL). For samples and blanks, add 10 µL of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. For calibration standards and laboratory fortified blanks, add 10 µL of the fortification solution containing the internal standard only. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

11.4 SAMPLE DESORPTION -- After the 11-min purge, place the purge and trap system in the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for about 4. min. Simultaneously with the start of desorption, begin the temperature program of the gas chromatograph, and start data acquisition. While the extracted sample is being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave syringe

valve open to allow the purge gas to vent through the sample introduction needle.

11.5 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data from m/z 35-260 with a total cycle time (including scan overhead time) of 7 sec or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak. Adjust the helium carrier gas flow rate to about 40 mL/min. The column temperature is programmed to hold at 45°C for three min, increase to 220°C at 8°C/min, and hold at 220°C for 15 min or until all expected compounds have eluted.

11.6 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.7 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.8 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.8.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.8.2 Identification requires expert judgement when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining

plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.8.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Cis- and trans-1,2-dichloroethene, two of the three isomeric xylenes, and two of the three dichlorobenzenes are three examples of structural isomers that cannot be explicitly identified if both members of the isomeric pair are present. These groups of isomers must be reported as isomeric pairs (see Method 524.2 for an alternative approach).

11.8.4 Methylene chloride and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12. CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. For example, although two listed analytes, carbon tetrachloride and bromodichloromethane, were not resolved with the GC conditions used, concentrations were calculated by measuring the non-interfering quantitation ions.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal

standard added to the water sample.
V = original water sample volume in mL.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the second or third order regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations in µg/L.

13. ACCURACY AND PRECISION

13.1 Single laboratory accuracy and precision data were obtained for 31 of the method analytes using laboratory fortified blanks with analytes at concentrations between 1 and 5 µg/L, and these data are shown in Table 3.

13.2 With these data, method detection limits were calculated using the formula (2):

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where: $t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses.

14. REFERENCES

1. Alford-Stevens, A., J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/ Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

2. Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol., 15, 1426, 1981.

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

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

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

TABLE 1. MOLECULAR WEIGHTS, RETENTION TIME DATA, AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Retention[b] Time (min:sec)	Primary Quantitation Ions	Secondary Quantitation Ions
Internal standard				
Fluorobenzene	96	16:34	96	77
Surrogates				
4-Bromofluorobenzene	174	26:53	95	174,176
1,2-Dichlorobenzene-d_4	150	35:55	152	115,150
Target Analytes				
Benzene	78	15:31	78	77
Bromobenzene	156	25:12	156	77,158
Bromochloromethane	128	9:20	128	49,130
Bromodichloromethane	162	12:24	83	85,127
Bromoform	250	17:17	173	175,252
Bromomethane	94		94	96
Carbon tetrachloride	152	12:19	117	119
Chlorobenzene	112	22:14	112	77,114
Chloroethane	64		64	66
Chloroform	118	9:41	83	85
Chloromethane	50		50	52
2-Chlorotoluene	126		91	126
4-Chlorotoluene	126		91	126
Dibromochloromethane	206	14:53	129	127
1,2-Dibromo-3-Chloropropane	234	23:55	75	155,157
1,2-Dibromoethane	186	16:10	107	109,188
Dibromomethane	172	10:38	93	95,174
1,2-Dichlorobenzene	146	35:07	146	111,148
1,3-Dichlorobenzene	146	35:55	146	111,148
1,4-Dichlorobenzene	146	35:55	146	111,148
Dichlorodifluoromethane	120	4:14	85	87
1,1-Dichloroethane	98	9:02	63	65,83
1,2-Dichloroethane	98	10:43	62	98
1,1-Dichloroethene	96	7:50	96	61,63
cis-1,2-Dichloroethene	96		96	61,98
trans-1,2-Dichloroethene	96	9:55	96	61,98
1,2-Dichloropropane	112	13:55	63	112
1,3-Dichloropropane	112	16:28	76	78
2,2-Dichloropropane	112		77	97
1,1-Dichloropropene	110		75	110,77
cis-1,3-dichloropropene	110		75	
trans-1,3-dichloropropene	110		75	
Ethylbenzene	106		91	106
p-Isopropyltoluene	134		119	134,91

TABLE 1. (Continued)

Compound	MW[a]	Retention[b] Time (min:sec)	Primary Quantitation Ions	Secondary Quantitation Ions
Methylene chloride	84	5:21	84	86,49
Styrene	104	29:02	104	78
1,1,1,2-Tetrachloroethane	166		131	133,119
1,1,2,2-Tetrachloroethane	166	19:31	83	131,85
Tetrachloroethene	164	20:00	166	168,129
Toluene	92	21:22	92	91
1,1,1-Trichloroethane	132	11:41	97	99,61
1,1,2-Trichloroethane	132		83	97,85
Trichloroethene	130	14:43	95	130,132
Trichlorofluoromethane	136	7:22	101	103
1,2,3-Trichloropropane	146		75	77
Vinyl Chloride	62	4:00	62	64
o-Xylene	106	30:34	106	91
m-Xylene	106	30:48	106	91
p-Xylene	106	30:48	106	91

[a] Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

[b] Retention time measured from the beginning of the thermal desorption step. Compounds with no retention data are known to be amenable to purge and trap extraction (see Method 524.2), and chromatography on the packed gas chromatography column used in this method, but no retention time data is available for this method.

TABLE 2. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 3. ACCURACY AND PRECISION DATA FROM SEVEN TO NINE DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER[a]

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Accuracy (% of True Value)	Method Dect. Limit (µg/L)
Benzene	1.0	0.97	0.036	3.7	97	0.1
Bromobenzene	1.0	0.92	0.042	4.6	92	0.1
Bromodichloromethane	1.0	1.0	0.17	17.	100	0.5
Bromoform	2.5	2.4	0.23	9.6	100	0.7
Carbon tetrachloride	1.0	0.88	0.098	11.	88	0.3
Chlorobenzene	1.0	1.02	0.047	4.6	102	0.1
Chloroform	1.0	1.03	0.086	8.3	103	0.2
Dibromochloromethane	1.0	0.92	0.14	15.	92	0.4
1,2-Dibromo-3-chloropropane	3.5	3.5	0.63	18.	100	2.
1,2-Dibromoethane	1.0	0.93	0.13	14.	93	0.4
Dibromomethane	1.0	0.94	0.11	12.	94	0.3
1,2-Dichlorobenzene	5.0	5.0	0.35	7.0	100	1.
1,4-Dichlorobenzene	5.0	5.6	0.73	13.	112	2.
Dichlorodifluoromethane	1.0	0.96	0.11	12.	96	0.3
1,1-Dichloroethane	1.0	1.05	0.060	5.7	105	0.2
1,2-Dichloroethane	1.0	0.97	0.077	7.9	97	0.2
1,1-Dichloroethene	1.0	1.09	0.066	6.1	109	0.2
trans-1,2-Dichloroethene	1.0	0.98	0.066	6.7	98	0.2
1,2-Dichloropropane	1.0	1.01	0.060	5.9	101	0.2
1,3-Dichloropropane	1.0	1.00	0.033	3.3	100	0.1
Methylene chloride	1.0	0.99	0.45	46.	99	1.
Styrene	1.0	1.2	0.072	6.0	120	0.2
1,1,2,2-Tetrachloroethane	1.0	1.11	0.14	13.	111	0.4
Tetrachloroethene	1.0	0.93	0.10	11.	93	0.3
Toluene	1.0	1.05	0.043	4.1	105	0.1
1,1,1-Trichloroethane	1.0	1.05	0.093	8.9	105	0.3
Trichloroethene	1.0	0.90	0.12	13.	90	0.4
Trichlorofluoromethane	1.0	1.09	0.072	6.6	109	0.2
Vinyl chloride	1.0	0.98	0.11	11.	98	0.3
o-Xylene	1.0	1.02	0.068	6.7	102	0.2
p-Xylene	1.0	1.11	0.047	4.2	111	0.3

[a] Data obtained by Robert W. Slater with a 25-mL sample size and the compounds divided into two groups to minimize coelution.

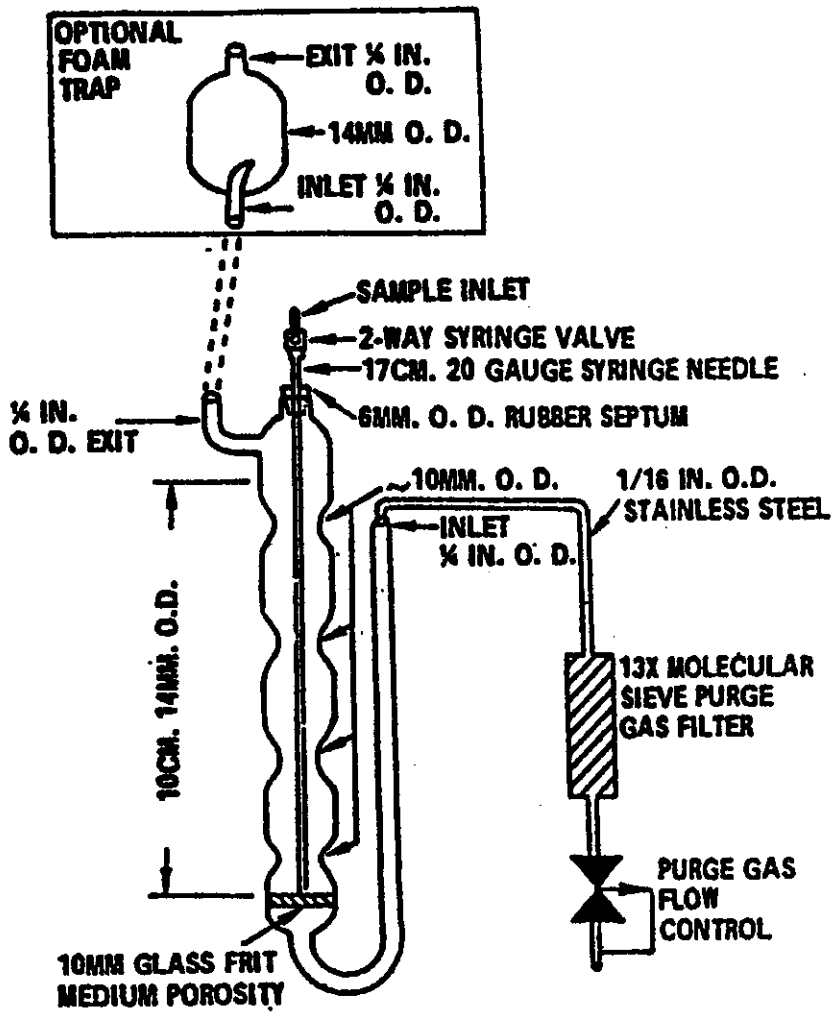

FIGURE 1. PURGING DEVICE

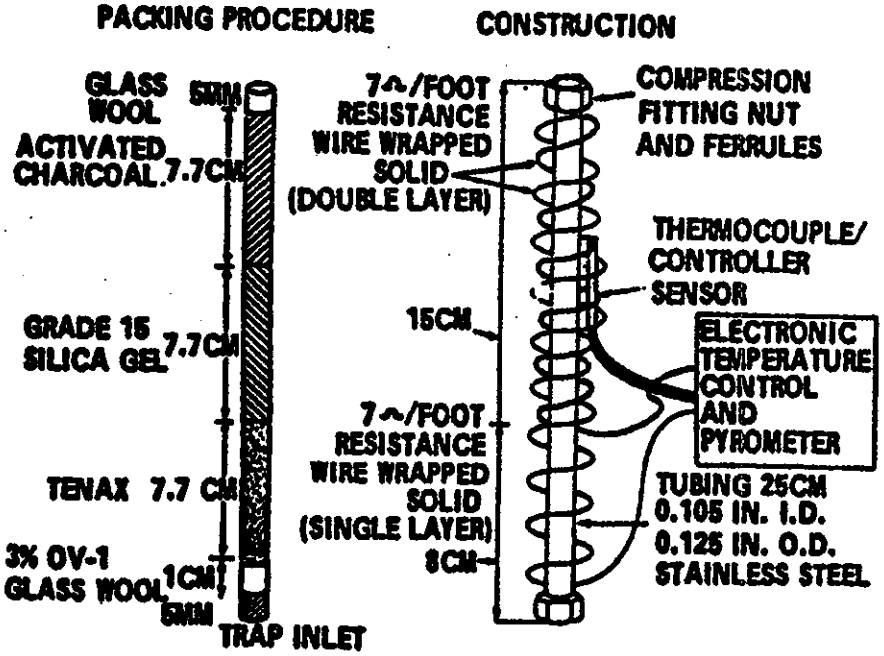

FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

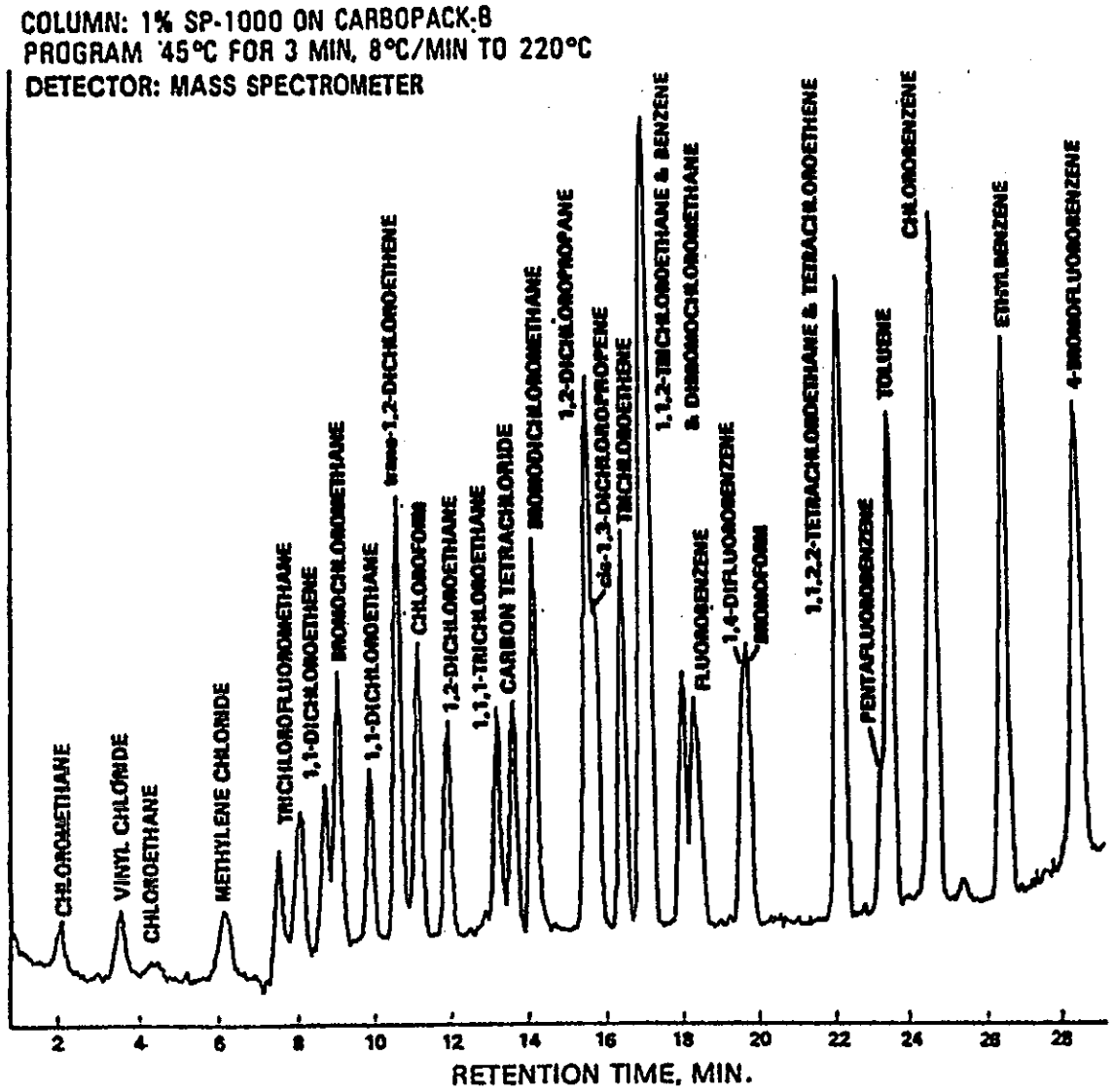

FIGURE 3. GAS CHROMATOGRAM

METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 3.0

A. Alford-Stevens, J. W. Eichelberger, W. L. Budde - Method 524, Revision 1.0 (1983)

R. W. Slater, Jr. - Method 524.2, Revision 2.0 (1986)

J. W. Eichelberger, W. L. Budde - Method 524.2, Revision 3.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
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METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1-2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Compound	Chemical Abstract Service Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5

1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 Method detection limits (MDLs) (3) are compound and instrument dependent and vary from approximately 0.02-0.35 µg/L. The applicable concentration range of this method is primarily column dependent and is approximately 0.02 to 200 µg/L for the wide-bore thick-film columns. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and non-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample (Sect 11.6.2). Analytes which have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect.11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that

may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to separate the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentra-tion.

3.13 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS -- 60-mL to 120-mL screw cap vials (Pierce #19832 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12718 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily

conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven must be cooled to 10°C; therefore, a subambient oven controller is required. If syringe injections of BFB will be used, a split/splitless injection port is required.

6.3.2 Capillary Gas Chromatography Columns. Any gas chromatography column that meets the performance specifications of this method may be used. Separations of the calibration mixture must be equivalent or better than those described in this method. Three useful columns have been identified.

6.3.2.1 Column 1 -- 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 μm film thickness.

Column 2 -- 30 m x 0.53 mm ID DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

Column 3 -- 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 μm film thickness.

6.3.3 Interfaces between the GC and MS. The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore columns 1 and 2 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface (7), an all-glass jet separator, or a cryogenic (Sect. 6.3.3.2) device are acceptable interfaces. Any interface can be used if the performance specifications described in this method can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 The narrow bore column 3 cannot accept the thermal desorption gas flow, and a cryogenic interface is required. This interface (Tekmar Model 1000 or equivalent) condenses the desorbed sample components at liquid nitrogen temperature, and allows the helium gas to pass through to an exit. The condensed components are frozen in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed from the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed with a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 260 amu with a complete scan cycle time (including scan overhead) of 2 sec or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of

tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 9.2.6 (or construction of a second or third order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 One 25-μL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

6.4.4 Micro syringes - 10, 100 μL.

6.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers -- 15-mL bottles with PTFE-lined screw caps.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated

carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic acid -- ACS reagent grade, granular.

7.2.6 Sodium thiosulfate -- ACS reagent grade, granular.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-µL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at <0°C; at room temperature, they must be discarded after 1 day.

7.4 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern and the surrogates (but not the internal standard!) in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.4.4 also apply to primary dilution standard solutions.

7.5 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.5.1 A solution containing the internal standard and the surrogates is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each (any appropriate concentration is acceptable). A 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each. A 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each). Additional internal standards and surrogate analytes are optional.

7.5.2 A solution of the internal standard alone is required to prepare calibration standards and laboratory fortified blanks. The internal standard should be in methanol at a concentration of 5 µg/mL (any appropriate concentration is acceptable).

7.6 PREPARATION OF LABORATORY REAGENT BLANK -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject 10 µL of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.7 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard (Sect. 7.8). This is a calibration standard that is treated as a sample.

7.8 PREPARATION OF CALIBRATION STANDARDS

7.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of

concern and each surrogate at a concentration of 2-10 times the method detection limit (Tables 4-6) for that compound. The other CAL standards should contain each analyte of concern and each surrogate at concentrations that define the range of the method. Every CAL solution contains the internal standard at the same concentration (5 µg/L suggested for a 5-mL sample; 1 µg/L for a 25-mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hr unless transferred to a sample bottle and sealed immediately.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid to the sample bottle before filling. If gases are not to be determined, sodium thiosulfate may be used to reduce the residual chlorine. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

8.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

8.1.4 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with

sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

8.2 SAMPLE STORAGE

8.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS

8.3.1 Duplicate field reagent blanks must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION

9.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hr. period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

9.2 INITIAL CALIBRATION

9.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 9.2.2.

9.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 2, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

9.2.3 Purge a medium CAL solution, for example 10-20 μg/L, using the procedure given in Sect. 11.

9.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software. Figure 3 shows an acceptable total ion chromatogram.

9.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are broad, or sensitivity poor, see Sect. 9.3.6 for some possible remedial actions.

9.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 9.3.6.

9.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

9.2.6 Calculate a response factor (RF) for each analyte, surrogate, and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.4), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.
A_{is} = integrated abundance of the quantitation ion of the internal standard.
Q_x = quantity of analyte purged in ng or concentration units.
Q_{is} = quantity of internal standard purged in ng or concentration units.

9.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze

additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Sect. 9.2.7.

9.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a second or third order regression calibration curve.

9.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 8-hr work shift during which analyses are performed using the following procedure.

9.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 2), the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

9.3.2 Purge a medium concentration CAL solution and analyze with the same conditions used during the initial calibration.

9.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 9.2.4.

9.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 9.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

9.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a second or third order regression is used, the point from the continuing calibration check for each analyte and surrogate must fall, within the analyst's judgement, on the curve from the initial calibration. If these conditions do not exist, remedial action must be taken which may require re-initial calibration.

9.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

9.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

9.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

9.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

9.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

9.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

9.3.6.6 Clean the MS ion source and rods (if a quadrupole).

9.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

9.3.6.8 Replace the MS electron multiplier, or any other faulty components.

9.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

9.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

9.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

9.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliters.

10. QUALITY CONTROL

10.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbants, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

10.3 Initial demonstration of laboratory accuracy and precision. Analyze five to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 0.2-5 µg/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte. Calculate the MDL of each analyte using the procedures described in Sect. 13.2 (2).

10.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight

compounds, are measured with less accuracy and precision than other analytes. The method detection limits must be sufficient to detect analytes at the required levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

10.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

10.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks. These should remain reasonably constant over time. A drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected. These integrated areas should also be reasonably constant in laboratory fortified blanks and samples.

10.5 Laboratory reagent blanks. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination. A FRB (Sect. 10.7) may be used in place of a LRB.

10.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in 10.3. If more than 20 samples are included in a batch, analyze one LFB for every 20 samples. Use the procedures described in 10.3.3 to evaluate the accuracy of the measurements, and to estimate whether the method detection limits can be obtained. If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Add these results to the on-going control charts to document data quality.

10.7 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities. If the FRB shows unacceptable contamination, a LRB must be measured to define the source of the impurities.

10.8 At least quarterly, replicates of laboratory fortified blanks should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

10.9 At least quarterly, analyze a quality control sample (QCS) from an external source. If measured analyte concentrations are not of

acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

10.10 Sample matrix effects have not been observed when this method is used with distilled water, reagent water, drinking water, and ground water. Therefore, analysis of a laboratory fortified sample matrix (LFM) is not required. It is recommended that sample matrix effects be evaluated at least quarterly using the QCS described in 10.9.

10.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

11. PROCEDURE

11.1 SAMPLE INTRODUCTION AND PURGING

11.1.1 This method is designed for a 25-mL sample volume, but a smaller (5 mL) sample volume is recommended if the GC/MS system has adequate sensitivity to achieve the required method detection limits. Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device and open the syringe valve on the purging device.

11.1.2 Remove the plungers from two 25-mL (or 5-mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0-mL (or 5-mL). For samples and blanks, add 5-μL (or an appropriate volume) of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. For calibration standards and laboratory fortified blanks, add 5-μL of the fortification solution containing the internal standard only. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

11.1.3 Attach the sample syringe valve to the syringe valve on the purging device. Be sure that the trap is cooler than 25°C, then open the sample syringe valve and inject the sample into the purging chamber. Close both valves and initiate purging. Purge the sample for 11.0 min at ambient temperature.

11.2 SAMPLE DESORPTION

11.2.1 Non-cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode and preheat the trap

to 180°C without a flow of desorption gas. Then simultaneously start the flow of desorption gas at 15-mL/min for about 4 min, begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.2 Cryogenic interface -- After the 11-min purge, place the purge and trap system in the desorb mode, make sure the cryogenic interface is a -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/min for about 5 min. At the end of the 5 min desorption cycle, rapidly heat the cryogenic trap to 250°C, and simultaneously begin the temperature program of the gas chromatograph, and start data acquisition.

11.2.3 While the trapped components are being introduced into the gas chromatograph (or cryogenic interface), empty the purging device using the sample syringe and wash the chamber with two 25-mL flushes of reagent water. After the purging device has been emptied, leave syringe valve open to allow the purge gas to vent through the sample introduction needle.

11.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of 2 sec or less. If water, methanol, or carbon dioxide cause a background problem, start at 47 or 48 m/z. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Several alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide bore columns 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to about 15 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of desorption, then programmed to 160°C at 6°C/min, and held until all components have eluted.

11.3.2 Multi-ramp linear temperature program for wide bore column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced 10°C and held for 6 min from the beginning of desorption, then heated to 70°C at 10°/min, heated to 120°C at 5°/min, heated to 180° at 8°/min, and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow bore column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°C/min for 10 min, then 15°C/min for 5 min to 145°C, and held until all components have eluted.

11.4 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgement when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is

achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12. CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where:
- C_x = concentration of analyte or surrogate in µg/L in the water sample.
- A_x = integrated abundance of the quantitation ion of the analyte in the sample.
- A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
- Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
- V = original water sample volume in mL.
- RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the second or third order regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1- 99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations in µg/L.

13. ACCURACY AND PRECISION

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at concentrations between 1 and 5 µg/L. Four sets of results were obtained using the three columns specified (Sect. 6.3.2) and the open split, cryogenic, and jet separator interfaces (Sect. 6.3.3). These data are shown in Tables 4-6.

13.2 With these data, method detection limits were calculated using the formula (2):

$$MDL = S\, t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. REFERENCES

1. A. Alford-Stevens, J.W. Eichelberger, W.L. Budde, "Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry, Method 524." Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

2. Madding, C., "Volatile Organic Compounds in Water by Purge and Trap Capillary Column GC/MS", Proceedings of the Water Quality Technology Conference, American Water Works Association, Denver, CO, December, 1984.

3. Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters, "Environ. Sci. Technol., 15, 1426, 1981.

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

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

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

7. Arrendale, R.F., R.F. Severson, and O.T. Chortyk, "Open Split Interface for Capillary Gas Chromatography/Mass Spectrometry", Anal. Chem. 1984, 56, 1533.

8. Flesch, J.J., P.S. Fair, "The Analysis of Cyanogen Chloride in Drinking Water," Proceedings of Water Quality Technology Conference, American Water Works Association, St. Louis, MO., November 14-16, 1988.

TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174,176
1,2-Dichlorobenzene-d4	150	152	115,150
Target Analytes			
Benzene	78	78	77
Bromobenzene	156	156	77,158
Bromochloromethane	128	128	49,130
Bromodichloromethane	162	83	85,127
Bromoform	250	173	175,252
Bromomethane	94	94	96
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Carbon tetrachloride	152	117	119
Chlorobenzene	112	112	77,114
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155,157
1,2-Dibromoethane	186	107	109,188
Dibromomethane	172	93	95,174
1,2-Dichlorobenzene	146	146	111,148
1,3-Dichlorobenzene	146	146	111,148
1,4-Dichlorobenzene	146	146	111,148
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65,83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61,63
cis-1,2-Dichloroethene	96	96	61,98
trans-1,2-Dichloroethene	96	96	61,98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97

1,1-Dichloropropene	110	75	110,77

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
cis-1,3-dichloropropene	110	75	110
trans-1,3-dichloropropene	110	75	110
Ethylbenzene	106	91	106
Hexachlorobutadiene	258	225	260
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134,91
Methylene chloride	84	84	86,49
Naphthalene	128	128	
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133,119
1,1,2,2-Tetrachloroethane	166	83	131,85
Tetrachloroethene	164	166	168,129
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99,61
1,1,2-Trichloroethane	132	83	97,85
Trichloroethene	130	95	130,132
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

[a]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SETS OF CONDITIONS[a]

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]
Internal standard				
Fluorobenzene	8:49	6:27	14:06	8:03
Surrogates				
4-Bromofluorobenzene	18:38	15:43	23:38	
1,2-Dichlorobenzene-d4	22:16	19:08	27:25	
Target Analytes				
Benzene	8:14	5:40	13:30	7:25
Bromobenzene	18:57	15:52	24:00	16:25
Bromochloromethane	6:44	4:23	12:22	5:38
Bromodichloromethane	10:35	8:29	15:48	9:20
Bromoform	17:56	14:53	22:46	15:42
Bromomethane	2:01	0:58	4:48	1:17
n-Butylbenzene	22:13	19:29	27:32	17:57
sec-Butylbenzene	20:47	18:05	26:08	17:28
tert-Butylbenzene	20:17	17:34	25:36	17:19
Carbon Tetrachloride	7:37	5:16	13:10	7:25
Chlorobenzene	15:46	13:01	20:40	14:20
Chloroethane	2:05	1:01		1:27
Chloroform	6:24	4:48	12:36	5:33
Chloromethane	1:38	0:44	3:24	0:58
2-Chlorotoluene	19:20	16:25	24:32	16:44
4-Chlorotoluene	19:30	16:43	24:46	16:49
Cyanogen chloride				1:03
Dibromochloromethane	14:23	11:51	19:12	12:48
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02
1,2-Dibromoethane	14:44	11:50	19:24	13:36
Dibromomethane	10:39	7:56	15:26	9:05
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38
Dichlorodifluoromethane	1:33	0:42	3:08	0:53
1,1-Dichloroethane	4:51	2:56	10:48	4:02
1,2-Dichloroethane	8:24	5:50	13:38	7:00
1,1-Dichloroethene	2:53	1:34	7:50	2:20
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32
1,2-Dichloropropane	10:05	7:40	15:12	8:56
1,3-Dichloropropane	14:02	11:19	18:42	12:29
2,2-Dichloropropane	6:01	3:48	11:52	5:19
1,1-Dichloropropene	7:49	5:17	13:06	7:10

TABLE 2. (continued)

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]
cis-1,3-dichloropropene	11.58		16:42	
trans-1,3-dichloropropene	13.46		17:54	
Ethylbenzene	15:59	13:23	21:00	14:44
Hexachlorobutadiene	26:59	23:41	32:04	19:14
Isopropylbenzene	18:04	15:28	23:18	16:25
4-Isopropyltoluene	21:12	18:31	26:30	17:38
Methylene Chloride	3:36	2:04	9:16	2:40
Naphthalene	27:10	23:31	32:12	19:04
n-Propylbenzene	19:04	16:25	24:20	16:49
Styrene	17:19	14:36	22:24	15:47
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47
Tetrachloroethene	13:44	11:09	18:36	13:12
Toluene	12:26	10:00	17:24	11:31
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59
Trichloroethene	9:35	7:16	14:48	9:01
Trichlorofluoromethane	2:16	1:11	6:12	1:46
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59
Vinyl chloride	1:43	0:47	3:56	1:02
o-Xylene	17:07	14:31	22:16	15:47
m-Xylene	16:10	13:41	21:22	15:18
p-Xylene	16:07	13:41	21:18	15:18

[a]Columns 1-3 are those given in Sect. 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (columns 1-2) or from the beginning of thermal release from the cryogenic interface (column 3).
[b]GC conditions given in Sect. 11.3.1.
[c]GC conditions given in Sect. 11.3.2.
[d]GC conditions given in Sect. 11.3.3.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2 Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12
Methylene chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04

TABLE 4. (Continued)

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a]Data obtained by Robert W. Slater using column 1 with a jet separator interface and a quadrupole mass spectrometer (Sect. 11.3.1) with analytes divided among three solutions.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
Benzene	0.1	99	6.2	0.03
Bromobenzene	0.5	97	7.4	0.11
Bromochloromethane	0.5	97	5.8	0.07
Bromodichloromethane	0.1	100	4.6	0.03
Bromoform	0.1	99	5.4	0.20
Bromomethane	0.1	99	7.1	0.06
n-Butylbenzene	0.5	94	6.0	0.03
sec-Butylbenzene	0.5	90	7.1	0.12
tert-Butylbenzene	0.5	90	2.5	0.33
Carbon tetrachloride	0.1	92	6.8	0.08
Chlorobenzene	0.1	91	5.8	0.03
Chloroethane	0.1	100	5.8	0.02
Chloroform	0.1	95	3.2	0.02
Chloromethane	0.1	99	4.7	0.05
2-Chlorotoluene	0.1	99	4.6	0.05
4-Chlorotoluene	0.1	96	7.0	0,05
Cyanogen chloride[b]		92	10.6	0.30
Dibromochloromethane	0.1	99	5.6	0.07
1,2-Dibromo-3-chloropropane	0.1	92	10.0	0.05
1,2-Dibromoethane	0.1	97	5.6	0.02
Dibromomethane	0.1	93	6.9	0.03
1,2-Dichlorobenzene	0.1	97	3.5	0.05
1,3-Dichlorobenzene	0.1	99	6.0	0.05
1,4-Dichlorobenzene	0.1	93	5.7	0.04
Dichlorodifluoromethane	0.1	99	8.8	0.11
1,1-Dichloroethane	0.1	98	6.2	0.03
1,2-Dichloroethane	0.1	100	6.3	0.02
1,1-Dichloroethene	0.1	95	9.0	0.05
cis-1,2 Dichloroethene	0.1	100	3.7	0.06
trans-1,2-Dichloroethene	0.1	98	7.2	0.03
1,2-Dichloropropane	0.1	96	6.0	0.02
1,3-Dichloropropane	0.1	99	5.8	0.04
2,2-Dichloropropane	0.1	99	4.9	0.05
1,1-Dichloropropene	0.1	98	7.4	0.02
cis-1,3-Dichloropropene				
trans-1,3-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04
Isopropylbenzene	0.5	98	6.4	0.10
4-Isopropyltoluene	0.5	87	13.0	0.26
Methylene chloride	0.5	97	13.0	0.09
Naphthalene	0.1	98	7.2	0.04

TABLE 5. (Continued)

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
n-Propylbenzene	0.1	99	6.6	0.06
Styrene	0.1	96	19.0	0.06
1,1,1,2-Tetrachloroethane	0.1	100	4.7	0.04
1,1,2,2-Tetrachloroethane	0.5	100	12.0	0.20
Tetrachloroethene	0.1	96	5.0	0.05
Toluene	0.1	100	5.9	0.08
1,2,3-Trichlorobenzene	0.1	98	8.9	0.04
1,2,4-Trichlorobenzene	0.1	91	16.0	0.20
1,1,1-Trichloroethane	0.1	100	4.0	0.04
1,1,2-Trichloroethane	0.1	98	4.9	0.03
Trichloroethene	0.1	96	2.0	0.02
Trichlorofluoromethane	0.1	97	4.6	0.07
1,2,3-Trichloropropane	0.1	96	6.5	0.03
1,2,4-Trimethylbenzene	0.1	96	6.5	0.04
1,3,5-Trimethylbenzene	0.1	99	4.2	0.02
Vinyl chloride	0.1	96	0.2	0.04
o-Xylene	0.1	94	7.5	0.06
m-Xylene	0.1	94	4.6	0.03
p-Xylene	0.1	97	6.1	0.06

[a]Data obtained by Caroline A. Madding using column 3 with a cryogenic interface and a quadrupole mass spectrometer (Sect 11.3.3).
[b]Reference 8.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	-	-	-	-
Surrogates					
4-Bromofluorobenzene	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d_4	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	d	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	d	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3

TABLE 6. (Continued)

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,3-Dichloropropene[c]					
trans-1,3-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene chloride	27	e		e	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl chloride	36	104	3.5	115	14.
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	f		f	
p-Xylene	61	98	2.3	103	1.4

[a]Data obtained by James W. Eichelberger using column 2 with the open split interface and an ion trap mass spectrometer (Sect. 11.3.2) with all method analytes in the same reagent water solution.
[b]Designation in Figures 1 and 2.
[c]Not measured; authentic standards were not available.
[d]Not found at 0.2 µg/L.
[e]Not measured; methylene chloride was in the laboratory reagent blank.
[f]m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

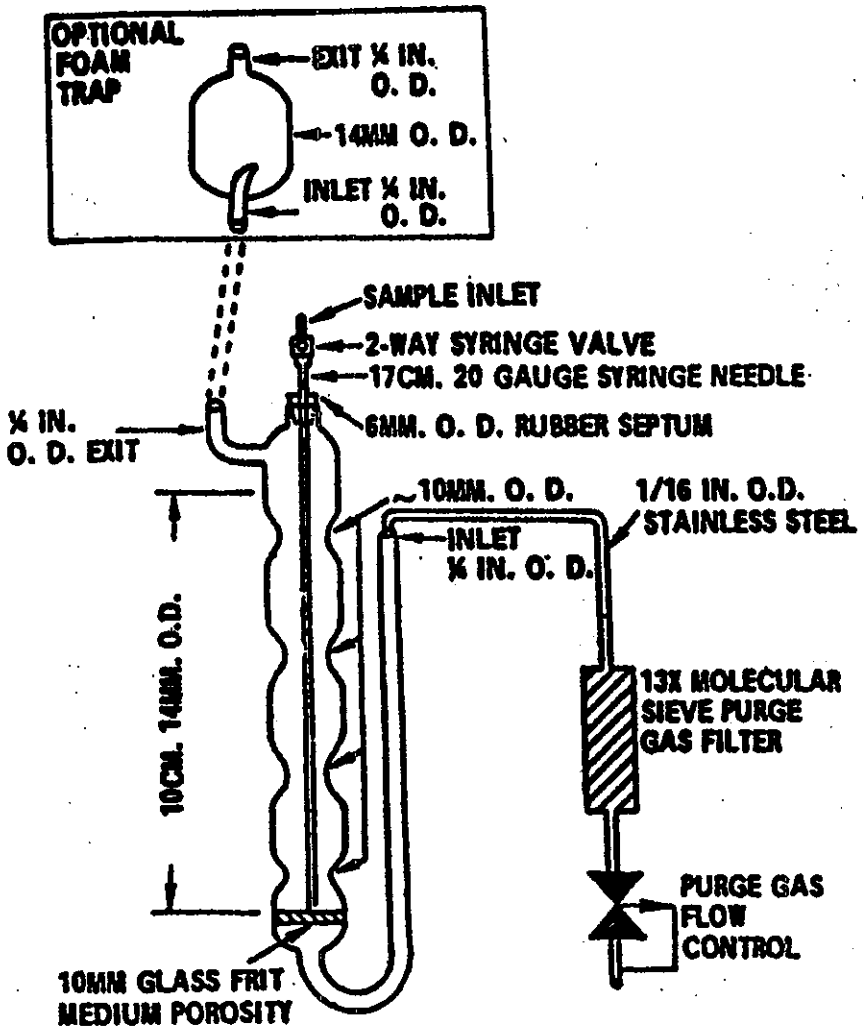


FIGURE 1. PURGING DEVICE

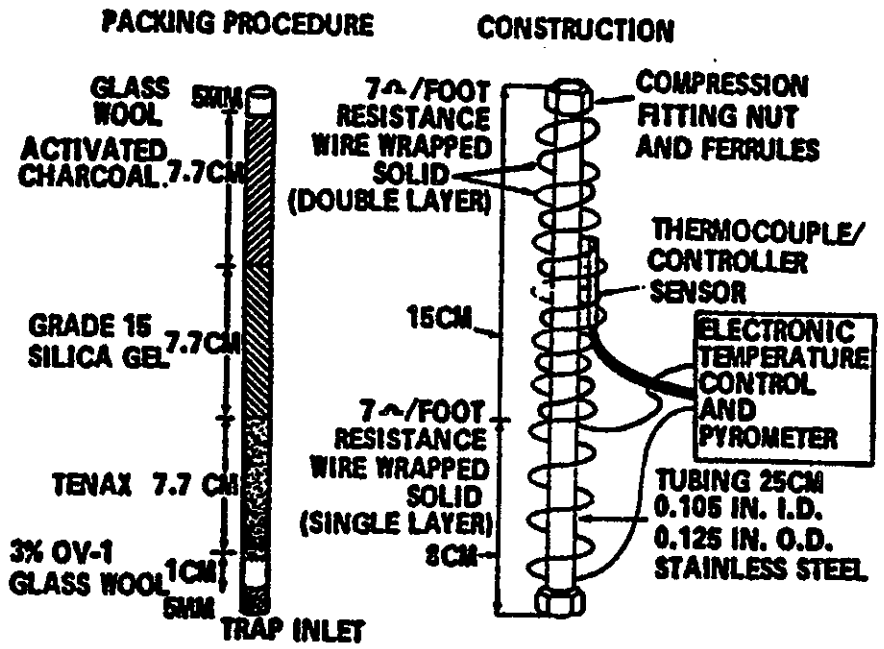


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

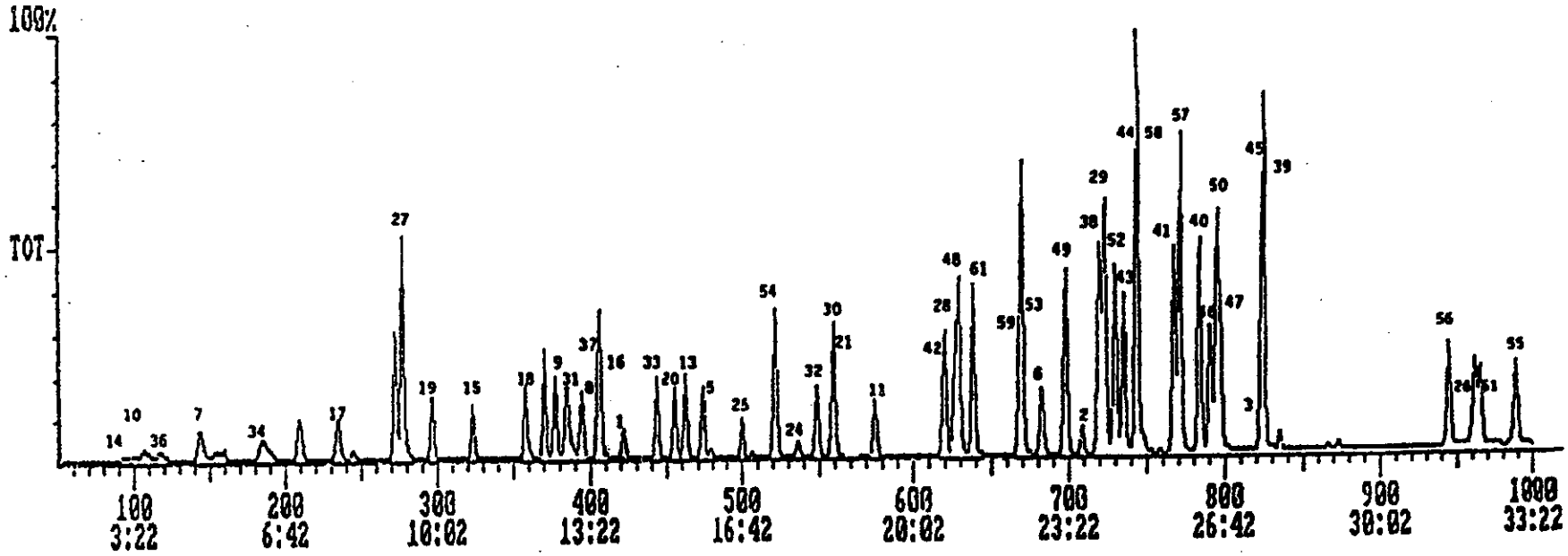
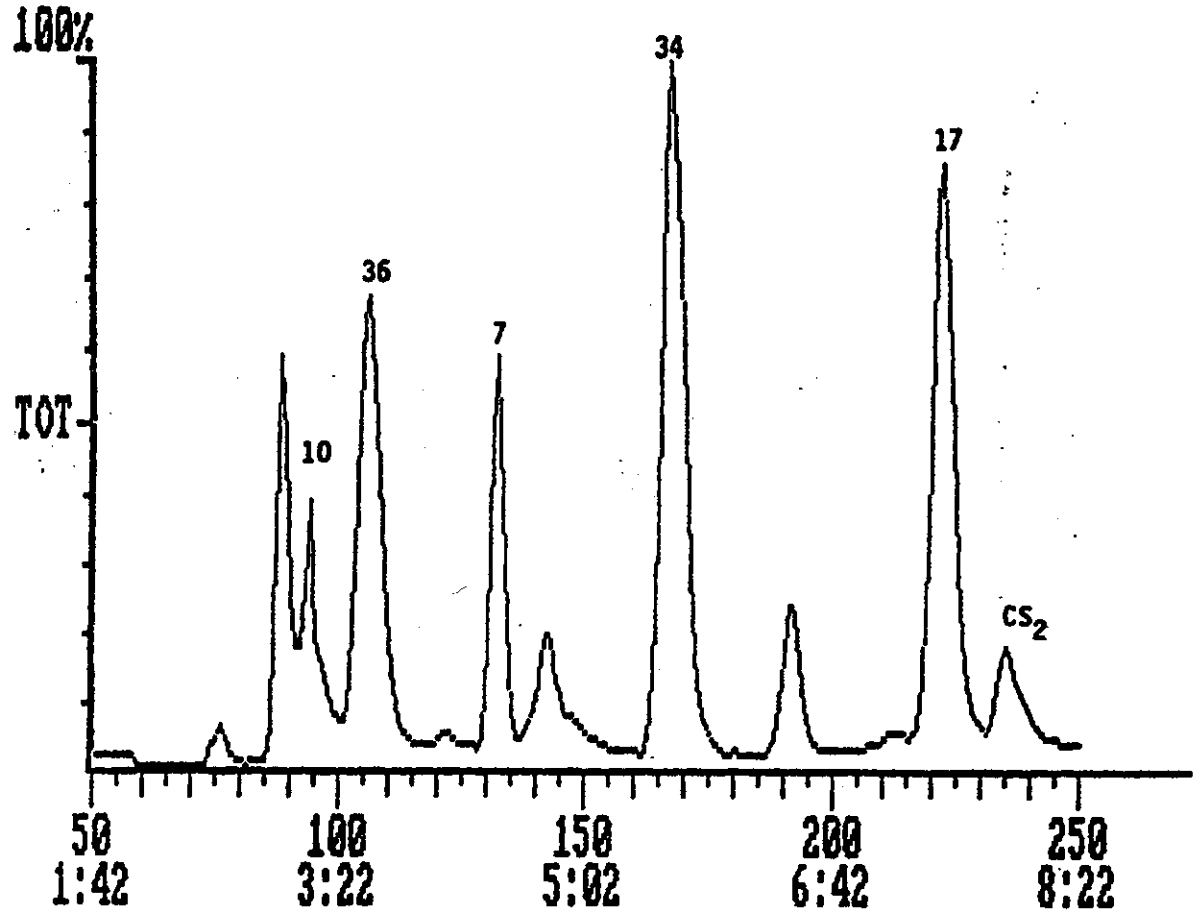


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



METHOD 525.1 DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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METHOD 525.1

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid silica matrix in a cartridge or disk, and sufficiently volatile and thermally stable for gas chromatography. Single-laboratory accuracy and precision data have been determined at two concentrations with two instrument systems for the following compounds:

Compound	MW[1]	Chemical Abstracts Service Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Anthracene	178	120-12-7
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Butylbenzylphthalate	312	85-68-7
Chlordane components		
Alpha-chlordane	406	5103-71-9
Gamma-chlordane	406	5103-74-2
Trans nonachlor	440	39765-80-5
2-Chlorobiphenyl	188	2051-60-7
Chrysene	228	218-01-9
Dibenz[a,h]anthracene	278	53-70-3
Di-n-butylphthalate	278	84-72-2
2,3-Dichlorobiphenyl	222	16605-91-7
Diethylphthalate	222	84-66-2
Bis(2-ethylhexyl)adipate	222	103-23-1
Bis(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
Endrin	378	72-20-8
Fluorene	166	86-73-7
Heptachlor	370	76-44-8

Compound	MW[1]	Chemical Abstracts Service Registry Number
Heptachlor epoxide	386	1024-57-3
2,2',3,3',4,4',6-Heptachlorobiphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2',4,4',5,6'-Hexachlorobiphenyl	358	60145-22-4
Hexachlorocyclopentadiene	270	77-47-4
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Lindane	288	58-89-9
Methoxychlor	344	72-43-5
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	426	40186-71-8
2,2',3',4,6-Pentachlorobiphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
Pyrene	202	129-00-0
Simazine	201	122-34-9
2,2',4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene mixture		8001-35-2
2,4,5-Trichlorobiphenyl	256	15862-07-4

[1]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

A laboratory may use this method to identify and measure additional analytes after the laboratory obtains acceptable (defined in Sect. 10) accuracy and precision data for each added analyte.

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero (1). The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. For the listed analytes, MDLs vary from 0.01 to 15 µg/L. The concentration calibration range of this method is 0.1 µg/L to 10 µg/L.

2. SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 liter of sample water through a cartridge or disk containing a solid inorganic matrix coated with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with a small quantity of methylene chloride, and concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated methylene

chloride extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the

FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- a solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- a sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and liquid-solid extraction columns. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited (2-4).

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6. Apparatus and Equipment

6.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in an oven. Volumetric glassware is never heated.

6.2 Sample containers. 1-liter or 1-quart amber glass bottles fitted with a Teflon-lined screw cap. (Bottles in which high purity solvents were received can be used as sample containers without additional cleaning if they have been handled carefully to avoid contamination during use and after use of original contents.)

6.3 Separatory funnels. 2-liter and 100-mL with a Teflon stopcock.

6.4 Liquid chromatography column reservoirs. Pear-shaped 100- or 125-mL vessels without a stopcock but with a ground glass outlet joint sized to fit the liquid-solid extraction column. (Lab Glass, Inc. part no. ML-700-706S, with a 24/40 top outer joint and a 14/35 bottom inner joint, or equivalent). A 14/35 outlet joint fits some commercial cartridges.

6.5 Syringe needles. No. 18 or 20 stainless steel.

6.6 Vacuum flasks. 1- or 2-liter with solid rubber stoppers.

6.7 Volumetric flasks, various sizes.

6.8 Laboratory or aspirator vacuum system. Sufficient capacity to maintain a slight vacuum of 13 cm (5 in.) of mercury in the vacuum flask.

6.9 Micro syringes, various sizes.

6.10 Vials. Various sizes of amber vials with Teflon-lined screw caps.

6.11 Drying column. Approximately 1.2 cm x 40 cm with 10 mL graduated collection vial.

6.12 Analytical balance. Capable of weighing 0.0001 g accurately.

6.13 Fused silica capillary gas chromatography column. Any capillary column that provides adequate resolution, capacity, accuracy, and precision (Sect. 10) can be used. A 30 m X 0.25 mm id fused silica capillary column coated with a 0.25 μm bonded film of polyphenylmethylsilicone is recommended (J&W DB-5 or equivalent).

6.14 Gas chromatograph/mass spectrometer/data system (GC/MS/DS)

6.14.1 The GC must be capable of temperature programming and be equipped for splitless/split or on-column capillary injection. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.

6.14.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity (see Sect. 9 for calibration requirements).

6.14.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 45 to 450 amu with a complete scan cycle time (including scan overhead) of 1.5 sec or less. (Scan cycle time = Total MS data acquisition time in sec divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when 5 ng or less of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance.

6.14.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Sect. 9.2.6 (or construction of a second or third order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.15 Millipore Standard Filter Apparatus, ALL GLASS. This will be used if the disks are to be used to carry out the extraction instead of the cartridges.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Helium carrier gas, as contaminant free as possible.

7.2 Liquid-solid extraction (LSE) cartridges. Cartridges are inert non- leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into methylene chloride. The cartridges are packed with about 1 gram of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into methylene chloride. One liter of water should pass through the cartridge in about 2 hrs with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. Sect. 10 provides criteria for acceptable LSE cartridges which are available from several commercial suppliers.

The extraction disks contain approximately 0.5 grams of 8 um octadecyl bonded silica uniformly enmeshed in a matrix of inert PFTE fibrils. The size of the disks is 47mm x 0.5mm. As with cartridges, the disks should not contain any organic compounds, either from the PFTE or the bonded silica, which will leach into the methylene chloride eluant. One liter of reagent water should pass through the disks in 5-20 minutes using a vacuum of about 66cm (26 in.) of mercury. Section 10 provides criteria for acceptable LSE disks which are available commercially.

7.3 Solvents

7.3.1 Methylene chloride, acetone, toluene and methanol. High purity pesticide quality or equivalent.

7.3.2 Reagent water. Water in which an interferent is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with Teflon-lined septa and screw caps.

7.4 Hydrochloric acid. 6N.

7.5 Sodium sulfate, anhydrous. (Soxhlet extracted with methylene chloride for a minimum of 4 hrs.)

7.6 Stock standard solutions. Individual solutions of analytes, surrogates, and internal standards may be purchased as certified solutions or prepared from pure materials. To prepare, add 10 mg (weighed on an analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol or acetone in a 2-mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the analytical standard is available only in quantities smaller than 10 mg, reduce the volume of solvent accordingly. Some polycyclic aromatic hydrocarbons are not soluble in methanol or acetone, and their stock standard solutions are prepared in toluene. Methylene chloride should be avoided as a solvent for standards because its high vapor pressure leads to rapid evaporation and concentration changes. Methanol and acetone are not as volatile as methylene chloride, but their solutions must also be handled with care to avoid evaporation. Compounds 10, 11, and 35 in Table 2 are soluble in acetone. Compounds 12, 13, and 20 in Table 2 are soluble in toluene. If compound purity is certified by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 μg/μL). Store the amber vials in a dark cool place.

7.7 Primary dilution standard solution. The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple analytes. The recommended solvent for this dilution is acetone. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 10 ng/μL. Store the primary dilution standard solution in an amber vial in a dark cool place, and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions.

7.8 Fortification solution of internal standards and surrogates. Prepare a solution of acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12}, and perylene-D_{12} in methanol or acetone at a concentration of 500 μg/mL of each. This solution is used in the preparation of the calibration solutions. Dilute a portion of this solution by 10 to 50 μg/mL and use this solution to fortify the

actual water samples (see Sect. 11.2). Other surrogates, for example, caffeine-$^{15}N_2$ and pyrene-D_{10} may be included in this solution as needed (a 100-µL aliquot of this 50 µg/mL solution added to 1 liter of water gives a concentration of 5 µg/L of each internal standard or surrogate). Store this solution in an amber vial in a dark cool place.

7.9 MS performance check solution. Prepare a 5 ng/µL solution of DFTPP in methylene chloride. Store this solution in an amber vial in a dark cool place.

7.10 Calibration solutions (CAL1 through CAL6). Prepare a series of six concentration calibration solutions in acetone which contain all analytes except pentachlorophenol and toxaphene at concentrations of 10, 5, 2, 1, 0.5, and 0.1 ng/µL, with a constant concentration of 5 ng/µL of each internal standard and surrogate in each CAL solution. CAL1 through CAL6 are prepared by combining appropriate aliquots of the primary dilution standard solution (7.7) and the fortification solution (500 µg/mL) of internal standards and surrogates (7.8). Pentachlorophenol is included in this solution at a concentration four times the other analytes. Toxaphene CAL solutions should be prepared as separate solutions at concentrations of 250, 200, 100, 50, 25, and 10 ng/µL. Store these solutions in amber vials in a dark cool place. Check these solutions regularly for signs of deterioration, for example, the appearance of anthraquinone from the oxidation of anthracene.

7.11 Reducing agents. Sodium sulfite or sodium arsenite. Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.

7.12 Fortification solution for optional recovery standard. Prepare a solution of terphenyl-D_{14} in methylene chloride at a concentration of 500 µg/mL. An aliquot of this solution may be added (optional) to the extract of the LSE cartridge to check on the recovery of the internal standards in the extraction process.

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Sample collection. When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2-5 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach analytes into water. Automatic samplers that composite samples over time must use refrigerated glass sample containers.

8.2 Sample dechlorination and preservation. All samples should be iced or refrigerated at 4°C from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of a reducing agent. Add 40-50 mg of sodium sulfite or sodium arsenite (these may be added as solids with stirring until dissolved) to each liter of water. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in unchlorinated water. The sample pH is adjusted to <2 with 6 N hydrochloric acid. This is the same pH used in the extraction, and is required to support the recovery of pentachlorophenol.

8.3 Holding time. Samples must be extracted within 7 days and the extracts analyzed within 30 days of sample collection.

8.4 Field blanks.

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal, and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with filled sample bottles.

8.4.2 When hydrochloric acid is added to samples, use the same procedures to add the same amount to the FRB.

9. CALIBRATION

9.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hr. period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

9.2 INITIAL CALIBRATION

9.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 9.2.2.

9.2.2 Inject into the GC a 1-μL aliquot of the 5 ng/μL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak. If the spectrum does not meet all criteria (Table 1), the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

9.2.3 Inject a 1-μL aliquot of a medium concentration calibration solution, for example 0.5-2 μg/L, and acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.5 sec or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak.

9.2.3.1 Multi-ramp temperature program GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 45°C and hold in splitless mode for 1 min. Heat rapidly to 130°C. At 3 min start the temperature program: 130-180°C at 12°/min; 180-240°C at 7°/min; 240-320°C at 12°/min. Start data acquisition at 5 min.

9.2.3.2 Single ramp linear temperature program. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 40°C and hold in splitless mode for 1 min. Heat rapidly to 160°C. At 3 min start the temperature program: 160-320°C at 6°/min; hold at 320° for 2 min. Start data acquisition at 3 min.

9.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software. Figure 1 shows an acceptable total ion chromatogram.

9.2.4.1 GC performance. Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance. See Sect. 9.3.6.

9.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Sect. 9.3.6.

9.2.4.3 Lack of degradation of endrin. Examine a plot of the abundance of m/z 67 in the region of 1.05-1.3 of the retention time of endrin. This is the region of elution of endrin aldehyde, a product of the thermal isomerization of endrin. Confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% of the abundance of m/z 67 produced by endrin. If more than 10% endrin aldehyde is observed, system maintenance is required to correct the problem. See Sect. 9.3.6.

9.2.5 If all performance criteria are met, inject a 1-μL aliquot of each of the other CAL solutions using the same GC/MS conditions.

9.2.6 Calculate a response factor (RF) for each analyte and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 2 contains suggested internal standards for each analyte and surrogate, and quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.14.4), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

A_x = integrated abundance of the quantitation ion of the analyte.
A_{is} = integrated abundance of the quantitation ion internal standard.
Q_x = quantity of analyte injected in ng or concentration units.
Q_{is} = quantity of internal standard injected in ng or concentration units.

9.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Sect. 9.2.7.

9.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a linear, second, or third order regression calibration curve.

9.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 8 hr. work shift during which analyses are performed using the following procedure.

9.3.1 Inject a 1-μL aliquot of the 5ng/μL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria

(Table 1), the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

9.3.2 Inject a 1-μL aliquot of a medium concentration calibration solution and analyze with the same conditions used during the initial calibration.

9.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 9.2.4.

9.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 9.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

9.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a second or third order regression is used, the point from the continuing calibration check for each analyte and surrogate must fall, within the analyst's judgement, on the curve from the initial calibration. If these conditions do not exist, remedial action must be taken which may require reinitial calibration.

9.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

9.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

9.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

9.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

9.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

9.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

9.3.6.6 Clean the MS ion source and rods (if a quadrupole).

9.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

9.3.6.8 Replace the MS electron multiplier, or any other faulty components.

10. QUALITY CONTROL

10.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 Initial demonstration of low system background and acceptable particle size and packing. Before any samples are analyzed, or any time a new supply of cartridges or disks is received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it must be demonstrated that the particle size and packing of the LSE cartridge or disk are acceptable. Consistent flow rate is an indication of acceptable particle size distribution and packing.

10.2.1 A major source of potential contamination is the liquid-solid extraction (LSE) cartridge which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes (5). Although disks are made of a teflon matrix, they may still contain phthalate materials. Generally, phthalate esters will be leached from the cartridges into methylene chloride and produce a variable background that is equivalent to <2 µg/L in the water sample. If the background contamination is sufficient to prevent accurate and precise analyses, the condition must be corrected before proceeding with the initial demonstration. Figure 2 shows unacceptable background contamination from a poor quality commercial LSE cartridge. The background contamination is the large broad peak, and the small peaks are method analytes present at a concentration equivalent to 2 µg/L. Several sources of LSE cartridges may be evaluated before an acceptable supply is identified.

10.2.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with

the next section. In general, background from method analytes should be below the method detection limit.

10.2.3 One liter of water should pass through a cartridge in about 2 hrs with a partial vacuum of about 13 cm (5 in.) of mercury. The flow rate through a disk should be about 5-20 minutes for a liter of drinking water, using full aspirator or pump vacuum. The extraction time should not vary unreasonably among a set of LSE cartridges or disks.

10.3 Initial demonstration of laboratory accuracy and precision. Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 2-5 μg/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of the primary dilution standard solution, or another certified quality control sample, to reagent water. Analyze each replicate according to the procedures described in Sect. 11 and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte. Calculate the MDL of each analyte using the procedures described in Sect. 13.1.2 (1).

10.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be <30%. Some analytes, particularly the polycyclic aromatic hydrocarbons with molecular weights >250, are measured at concentrations below 2 μg/L, with a mean accuracy of 35-130% of true value. The MDLs should be sufficient to detect analytes at the regulatory levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

10.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

10.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Sect. 9.3.4). In laboratory fortified blanks or

samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in laboratory fortified blanks and samples. The addition of 10 µL of the recovery standard, terphenyl-D_{14} (500 µg/mL), to the extract is optional, and may be used to monitor the recovery of internal standards and surrogates in laboratory fortified blanks and samples. Internal standard recovery should be in excess of 70%.

10.5 Laboratory reagent blanks. With each batch of samples processed as a group within a work shift, analyze a laboratory reagent blank to determine the background system contamination. Any time a new batch of LSE cartridges or disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in 10.2.

10.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in 10.3. If more than 20 samples are included in a batch, analyze a LFB for every 20 samples. Use the procedures described in 10.3.3 to evaluate the accuracy of the measurements, and to estimate whether the method detection limits can be obtained. If acceptable accuracy and method detection limits cannot be achieved, the problem must be located and corrected before further samples are analyzed. Add these results to the on-going control charts to document data quality.

10.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. A laboratory fortified sample matrix should be analyzed for every 20 samples processed in the same batch.

10.8 With each set of field samples a field reagent blank (FRB) should be analyzed. The results of these analyses will help define contamination resulting from field sampling and transportation activities.

10.9 At least quarterly, replicates of laboratory fortified blanks should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality (as in Sect. 10.3).

10.10 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Sect. 10.3.3), check the entire analytical procedure to locate and correct the problem source.

10.11 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

11. PROCEDURE

11.1 CARTRIDGE EXTRACTION

11.1.1 Setup the extraction apparatus shown in Figure 3A. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of 13 cm (5 in.) of mercury is used during all operations with the apparatus. The pressure used is critical as a vacuum > than 13 cm may result in poor precision. About 2 hrs is required to draw a liter of water through the system.

11.1.2 Pour the water sample into the 2-L separatory funnel with the stopcock closed, add 5 mL methanol, and mix well. Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid. Add a 100-μL aliquot of the fortification solution (50 μg/mL) for internal standards and surrogates, and mix immediately until homogeneous. The concentration of these compounds in the water should be 5 μg/L.

11.1.3 Flush each cartridge with two 10 mL aliquots of methylene chloride, followed by two 10 mL aliquots of methanol, letting the cartridge drain dry after each flush. These solvent flushes may be accomplished by adding the solvents directly to the solvent reservoir in Figure 3A. Add 10 mL of reagent water to the solvent reservoir, but before the reagent water level drops below the top edge of the packing in the LSE cartridge, open the stopcock of the separatory funnel and begin adding sample water to the solvent reservoir. Close the stopcock when an adequate amount of sample is in the reservoir.

11.1.4 Periodically open the stopcock and drain a portion of the sample water into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, wash the separatory funnel and cartridge with 10 mL of reagent water, and draw air through the cartridge for 10 min.

11.1.5 Transfer the 125-mL solvent reservoir and LSE cartridge (from Figure 3A) to the elution apparatus (Figure 3B).

The same 125-mL solvent reservoir is used for both apparatus. Wash the 2-liter separatory funnel with 5 mL of methylene chloride and collect the washings. Close the stopcock on the 100-mL separatory funnel of the elution apparatus, add the washings to the reservoir and enough additional methylene chloride to bring the volume back up to 5 mL and elute the LSE cartridge. Elute the LSE cartridge with an additional 5 mL of methylene chloride (10-mL total). A small amount of nitrogen positive pressure may be used to elute the cartridge. Small amounts of residual water from the LSE cartridge will form an immiscible layer with the methylene chloride in the 100-mL separatory funnel. Open the stopcock and allow the methylene chloride to pass through the drying column packed with anhydrous sodium sulfate (1-in) and into the collection vial. Do not allow the water layer to enter the drying column. Remove the 100 mL separatory funnel and wash the drying column with 2 mL of methylene chloride. Add this to the extract. Concentrate the extract to 1 mL under a gentle stream of nitrogen. If desired, gently warm the extract in a water bath to evaporate to between 0.5 - 1.0 mL (without gas flow). Do not concentrate the extract to less than 0.5 mL (or dryness) as this will result in losses of analytes. If desired, add an aliquot of the recovery standard to the concentrated extract to check the recovery of the internal standards (see Sect. 10.4).

11.2 DISK EXTRACTION (This may be manual or automatic)

11.2.1 Preparation of Disks

11.2.1.1 Insert the disk into the 47mm filter apparatus as shown in Figure 4. Wash the disk with 5mL methylene chloride (MeCl2) by adding the MeCl2 to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining MeCl2 through the disk.

11.2.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.2.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.2.2 Add 5 mL MeOH per liter of water sample. Mix well.

11.2.3 Add the water sample to the reservoir and turn on the vacuum to begin the extraction. Full aspirator vacuum may be used. Particulate-free water may pass through the disk in as little as ten minutes or less. Extract the entire sample, draining as much water from the sample container as possible.

11.2.4 Remove the filtration top from the vacuum flask, but do not disassemble the reservoir and fritted base. Empty the water from the flask, and insert a suitable sample tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.5 Add 5 mL methylene chloride to the sample bottle, and rinse the inside walls thoroughly. Allow the methylene chloride to settle to the bottom of the bottle, and transfer to the disk with a pipet or syringe, rinsing the sides of the glass filtration reservoir in the process. Draw about half of the methylene chloride through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining methylene chloride through the disk.

11.2.6 Repeat the above step twice. Pour the combined eluates through a small funnel with filter paper containing three grams of anhydrous sulfate. Rinse the test tube and sodium sulfate with two 5 mL portions of methylene chloride. Collect all the extract and washings in a concentrator tube.

11.2.7 Concentrate the extract to 1 mL under a gentle stream of nitrogen. If desired, gently warm the extract in a water bath or heating block to concentrate to between 05. and 1 mL. Do not concentrate the extract to less than 0.5 mL, since this will result in losses of analytes.

11.3 Analyze a 1-2 µL aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Sect. 9.2.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram. If any ion abundance exceeds the system working range, dilute the sample aliquot and analyze the diluted aliquot.

11.5 Identification of analytes. Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within 10 sec of the time observed for that same compound when a calibration solution was analyzed.

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.5.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. See Sect. 9.2.4.1. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Benzo[b] and benzo[k]fluoranthene are measured as an isomeric pair.

11.5.4 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentration of the background in the blank is highly variable.

12. CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. For example, although two listed analytes, dibenz[a,h]anthracene and indeno[1,2,3,c,d]pyrene, were not resolved with the GC conditions used, and produced mass spectra containing common ions, concentrations (Tables 3-6) were calculated by measuring appropriate characteristic ions.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)(Q_{is})}{(A_{is})\ RF\ V}$$

where:

C_x = concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in liters.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the second or third order regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainity). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

13. METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data (Tables 3-7) for each listed analyte was obtained at two concentrations with the same extracts analyzed on more than two different instrument systems. Seven 1-liter aliquots of reagent water containing 2 µg/L of each analyte, and five to seven 1-liter aliquots of reagent water containing 0.2 µg/L of each analyte were analyzed with this procedure. Tables 8-10 list data gathered using C-18 disks. These data were results from different extracts generated by a volunteer laboratory, Environmental Health Laboratories.

13.1.2 With these data, method detection limits (MDL) were calculated using the formula:

$$MDL = S\ t_{(n-1,1-alpha = 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates
S = standard deviation of replicate analyses.

13.2 PROBLEM COMPOUNDS

13.2.1 The common phthalate and adipate esters (compounds 14, 21, and 23-26), which are widely used commercially, appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately or precisely measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentrations of the background in blanks is highly variable.

13.2.2 Some polycyclic aromatic hydrocarbons are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore residual chlorine must be reduced before analysis.

13.2.3 In water free of residual chlorine, some polycyclic aromatic hydrocarbons (for example, compounds 9, 12, 13, 20, and 35) are not accurately measured because of low recoveries in the extraction process.

13.2.4 Pentachlorophenol No. 40 and hexachlorocyclopentadiene No. 34 may not be accurately measured. Pentachlorophenol is a strong acid and elutes as a broad weak peak. Hexachlorocyclopentadiene is susceptible to photochemical and thermal decomposition.

14. REFERENCES

1. Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave, and W. L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol. 1981 15, 1426-1435.

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

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

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

5. Junk, G.A., M. J. Avery, J. J. Richard, "Interferences in Solid-Phase Extraction Using C-18 Bonded Porous Silica Cartridges," Anal. Chem. 1988, 60, 1347.

TABLE 1. ION ABUNDANCE CRITERIA FOR BIS(PERFLUOROPHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYLPHOSPHINE, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	Present and < mass 443	high mass resolution
442	base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

[1]All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES.

Compound	Compound Number	Retention Time(min:sec) A[a]	Retention Time(min:sec) B[b]	Quantitation Ion (m/z)	Internal Standard Reference
Internal standards					
acenaphthene-D_{10}	1	4:49	7:45	164	-
phenanthrene-D_{10}	2	8:26	11:08	188	-
chrysene-D_{12}	3	18:14	19:20	240	-
Surrogate					
perylene-D_{12}	4	23:37	22:55	264	3
Target analytes					
acenaphthylene	5	4:37	7:25	152	1
aldrin	6	11:21	13:36	66	2
anthracene	7	8:44	11:20	178	2
atrazine	8	7:56	10:42	200/215	1/2
benz[a]anthracene	9	18:06	19:14	228	3
benzo[b]fluoranthene	10	22:23	22:07	252	3
benzo[k]fluoranthene	11	22:28	22:07	252	3
benzo[a]pyrene	12	23:28	22:47	252	3
benzo[g,h,i]perylene	13	27:56	26:44	276	3
butylbenzylphthalate	14	16:40	18:09	149	2/3
chlordane components					
alpha-chlordane	15	13:44	15:42	375	2/3
gamma-chlordane	16	13:16	15:18	375	2/3
trans nonachlor	17	13:54	15:50	409	2/3
2-chlorobiphenyl	18	4:56	7:55	188	1
chrysene	19	18:24	19:23	228	3
dibenz[a,h]anthracene	20	27:15	25:57	278	3
di-n-butylphthalate	21	10:58	13:20	149	2
2,3-dichlorobiphenyl	22	7:20	10:12	222	1
diethylphthalate	23	5:52	8:50	149	1
di(2-ethylhexyl) phthalate	24	19:19	20:01	149	2/3
di(2-ethylhexyl)adipate	25	17:17	18:33	129	2/3
dimethylphthalate	26	4:26	7:21	163	1
endrin	27	15:52	16:53	81	2/3
fluorene	28	6:00	8:53	166	1
heptachlor	29	10:20	12:45	100/160	2
heptachlor epoxide	30	12:33	14:40	81/353	2

TABLE 2. (Continued)

Compound	Compound Number	Retention Time(min:sec) A[a]	B[b]	Quantitation Ion (m/z)	Internal Standard Reference
2,2',3,3',4,4',6-hepta-chlorobiphenyl	31	18:25	19:25	394/396	3
hexachlorobenzene	32	7:37	10:20	284/286	1/2
2,2',4,4',5,6'-hexa-chlorobiphenyl	33	14:34	16:30	360	2
hexachlorocyclo-pentadiene	34	3:36	6:15	237	1
indeno[1,2,3,c,d]pyrene	35	27:09	25:50	276	3
lindane	36	8:17	10:57	181/183	1/2
methoxychlor	37	18:34	19:30	227	3
2,2',3,3',4,5',6,6'-octachlorobiphenyl	38	18:38	19:33	430	3
2,2',3',4,6-penta chlorobiphenyl	39	12:50	15:00	326	2
pentachlorophenol	40	8:11	10:51	266	2
phenanthrene	41	8:35	11:13	178	2
pyrene	42	13:30	15:29	202	2/3
simazine	43	7:47	10:35	201	1/2
2,2',4,4'-tetrachloro-biphenyl	44	11:01	13:25	292	2
toxaphene	45	11:30-23:30	13:00-21:30	159	2
2,4,5-trichlorobiphenyl	46	9:23	11:59	256	2
alachlor	47	--	13:19	160	2

[a]Single ramp linear temperature program conditions (Sect. 9.2.3.2).
[b]Multi-ramp linear temperature program conditions (Sect. 9.2.3.1).

TABLE 3. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES AT 2 µG/L WITH LIQUID-SOLID EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound Number (Table 2)	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Method Accuracy (% of True Conc.)	Method Detection Limit (MDL) (µg/L)
4	5	5.0	0.3	6.0	100	a
5	2	1.9	0.2	11.	95	a
6	2	1.6	0.2	13.	80	a
7	2	1.7	0.1	5.9	85	a
8	2	2.2	0.3	14.	110	a
9	2	1.8	0.2	11.	90	a
10	2	not separated from No. 11; measured with No. 11				
11	2	4.2	0.3	7.1	105	a
12	2	0.8	0.2	25.	40	a
13	2	0.7	0.1	14.	35	a
14	2	2.0	0.3	15.	100	a
15	2	2.0	0.2	10.	100	a
16	2	2.2	0.3	14.	110	a
17	2	2.7	1.0	37.	135	a
18	2	1.9	0.1	5.2	95	a
19	2	2.2	0.1	4.5	110	a
20	2	0.3	0.3	100.	15	a
21	2	2.2	0.3	14.	110	a
22	2	2.3	0.1	4.3	115	a
23	2	2.0	0.3	15.	100	a
24	2	1.9	0.2	11.	95	a
25	2	1.6	0.3	19.	80	a
26	2	1.9	0.2	11.	95	a
27	2	1.8	0.1	5.5	90	a
28	2	2.2	0.2	9.1	110	a
29	2	2.2	0.3	14.	110	a
30	2	2.3	0.2	8.7	115	a
31	2	1.4	0.2	14.	70	a
32	2	1.7	0.2	12.	85	a
33	2	1.6	0.4	25.	80	a
34	2	1.1	0.1	9.1	55	a
35	2	0.4	0.2	50.	20	a
36	2	2.1	0.2	9.5	105	a
37	2	1.8	0.2	11.	90	a
38	2	1.8	0.2	11.	90	a
39	2	1.9	0.1	5.3	95	a
40	8	8.2	1.2	15.	102	a
41	2	2.4	0.1	4.2	120	a
42	2	1.9	0.1	5.3	95	a
43	2	2.1	0.2	9.5	105	a
44	2	1.5	0.1	6.7	75	a
45	25	28.	4.7	17.	112	15.
46	2	1.7	0.1	5.9	85	a
Mean[b]	2	1.8	0.2	15.	91	0.6

[a]See Table 4. [b]Compounds 4, 40, and 45 excluded from the means.

TABLE 4. ACCURACY AND PRECISION DATA FROM FIVE TO SEVEN DETERMINATIONS OF THE METHOD ANALYTES AT 0.2 µG/L WITH LIQUID-SOLID EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound Number (Table 2)	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Method Accuracy (% of True Conc.)	Method Detection Limit (MDL) (µg/L)
4	0.5	0.45	0.6	13.	90	0.1
5	0.2	0.13	0.03	23.	65	0.1
6	0.2	0.13	0.03	23.	65	0.1
7	0.2	0.13	0.01	7.7	65	0.04
8	0.2	0.24	0.03	13.	120	0.1
9	0.2	0.14	0.01	7.1	70	0.04
10	0.2	not separated from No. 11; measured with No. 11				
11	0.2	0.25	0.04	16.	62	0.2
12	0.2	0.03	0.01	33.	15	0.04
13	0.2	0.03	0.02	67.	15	0.1
14	0.2	0.32	0.07	22.	160	0.3
15	0.2	0.17	0.04	24.	85	0.2
16	0.2	0.19	0.03	16.	95	0.1
17	0.2	0.17	0.08	47.	85	0.3
18	0.2	0.19	0.03	16.	95	0.1
19	0.2	0.21	0.01	4.8	105	0.04
20	0.2	0.03	0.02	67.	150	0.1
21	0.2	0.48	0.09	19.	240	0.3
22	0.2	0.20	0.03	15.	100	0.1
23	0.2	0.45	0.21	47.	225	0.8
24	0.2	0.39	0.16	41.	195	0.6
25	0.2	0.31	0.16	52.	155	0.6
26	0.2	0.21	0.01	4.8	105	0.04
27	0.2	0.12	0.12	100.	60	0.5
28	0.2	0.21	0.05	24.	105	0.2
29	0.2	0.22	0.01	4.5	110	0.04
30	0.2	0.19	0.04	21.	95	0.2
31	0.2	0.19	0.03	16.	95	0.1
32	0.2	0.16	0.04	25.	80	0.1
33	0.2	0.19	0.03	16.	95	0.1
34	0.2	0.04	0.01	25.	20	0.03
35	0.2	0.04	0.03	75.	20	0.1
36	0.2	0.22	0.02	9.1	110	0.1
37	0.2	0.11	0.01	9.1	55	0.04
38	0.2	0.19	0.05	26.	95	0.2
39	0.2	0.13	0.02	15.	65	0.1
40	0.8	0.78	0.08	10.	97	0.3
41	0.2	0.20	0.004	2.0	100	0.01
42	0.2	0.18	0.005	2.8	90	0.02
43	0.2	0.25	0.04	16.	125	0.2
44	0.2	0.14	0.04	29.	70	0.1
45		not measured at this level				
46	0.2	0.13	0.02	15.	65	0.06
Mean[a]	0.2	0.18	0.04	25.	95	0.16

[a]Compounds 4, 40, and 45 excluded from the means.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES AT 2 μG/L WITH LIQUID-SOLID EXTRACTION AND A MAGNETIC SECTOR MASS SPECTROMETER

Compound Number (Table 2)	True Conc. (μg/L)	Mean Observed Conc. (μg/L)	Std. Dev. (μg/L)	Rel. Std. Dev. (%)	Mean Method Accuracy (% of True Conc.)	Method Detection Limit (MDL) (μg/L)
4	5	5.7	0.34	6.0	114	a
5	2	1.9	0.22	12.	95	a
6	2	1.6	0.18	11.	80	a
7	2	2.2	0.67	30.	110	a
8	2	2.4	0.46	19.	120	a
9	2	2.2	0.87	40	110	a
10	2	not separated from No. 11; measured with No. 11				
11	2	4.0	0.37	9.3	100	a
12	2	0.85	0.15	18.	43	a
13	2	0.69	0.12	17.	35	a
14	2	2.0	0.20	10.	100	a
15	2	2.2	0.41	19.	110	a
16	2	2.1	0.38	18.	105	a
17	2	1.9	0.10	5.2	95	a
18	2	2.0	0.29	14.	100	a
19	2	2.1	0.32	15.	105	a
20	2	0.75	0.18	24.	38	a
21	2	2.5	0.32	13.	125	a
22	2	2.0	0.23	12.	100	a
23	2	3.5	1.8	51.	175	a
24	2	2.0	0.28	14.	100	a
25	2	1.4	0.16	11.	70	a
26	2	2.9	0.70	24.	145	a
27	2	1.7	0.45	26.	85	a
28	2	2.6	1.0	38.	130	a
29	2	1.2	0.10	8.3	60	a
30	2	2.6	0.42	16.	130	a
31	2	1.5	0.19	13.	75	a
32	2	1.5	0.35	23.	75	a
33	2	1.9	0.17	8.9	95	a
34	2	0.89	0.11	12.	45	a
35	2	0.83	0.072	8.7	42	a
36	2	2.2	0.10	4.5	110	a
37	2	2.0	0.88	44.	100	a
38	2	1.5	0.11	7.3	75	a
39	2	1.6	0.14	8.8	80	a
40	8	12.	2.6	22.	150	a
41	2	2.3	0.18	7.8	115	a
42	2	2.0	0.26	13.	100	a
43	2	2.5	0.34	14.	125	a
44	2	1.6	0.17	11.	80	a
45	25	28.	2.7	10.	112	9.
46	2	1.9	0.073	3.8	95	a
Mean[b]	2	1.8	0.32	16.	88	1.

[a]See Table 6. [b]Compounds 4, 40, and 45 excluded from the means.

TABLE 6. ACCURACY AND PRECISION DATA FROM SIX OR SEVEN DETERMINATIONS OF THE METHOD ANALYTES AT 0.2 µG/L WITH LIQUID-SOLID EXTRACTION AND A MAGNETIC SECTOR MASS SPECTROMETER.

Compound Number (Table 2)	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Std. Dev. (µg/L)	Rel. Std. Dev. (%)	Mean Method Accuracy (% of True Conc.)	Method Detection Limit (MDL) (µg/L)
4	0.5	0.67	0.07	9.4	134	0.2
5	0.2	0.11	0.03	24.	55	0.1
6	0.2	0.11	0.02	21.	56	0.1
7	0.2	0.14	0.02	17.	70	0.1
8	0.2	0.26	0.08	31.	130	0.3
9	0.2	0.24	0.06	26.	120	0.2
10	0.2	not separated from No. 11; measured with No. 11				
11	0.2	0.40	0.10	25.	100	0.3
12	0.2	0.08	0.02	27.	38	0.1
13	0.2	0.07	0.01	22.	33	0.1
14	0.2	0.33	0.16	48.	160	0.5
15	0.2	0.19	0.02	13.	95	0.1
16	0.2	0.17	0.08	45.	85	0.3
17	0.2	0.19	0.04	18.	95	0.1
18	0.2	0.17	0.02	13.	85	0.1
19	0.2	0.27	0.08	28.	135	0.3
20	0.2	0.09	0.01	15.	46	0.1
21	0.2	1.1	1.2	109.	550	4.
22	0.2	0.18	0.05	30.	90	0.2
23	0.2	0.29	0.17	59.	145	0.6
24	0.2	0.42	0.23	55.	210	0.8
25	0.2	0.32	0.16	50.	160	0.5
26	0.2	0.20	0.09	47.	100	0.3
27	0.2	0.53	0.30	57.	265	1.
28	0.2	0.18	0.03	15.	90	0.1
29	0.2	0.11	0.05	42.	55	0.2
30	0.2	0.33	0.08	26.	165	0.3
31	0.2	0.17	0.01	7.1	85	0.04
32	0.2	0.11	0.04	40.	55	0.2
33	0.2	0.17	0.03	15.	85	0.1
34	0.2	0.05	0.02	35.	24	0.1
35	0.2	0.08	0.06	8.1	40	0.02
36	0.2	0.27	0.03	11.	135	0.1
37	0.2	0.24	0.09	39.	120	0.3
38	0.2	0.15	0.02	12.	75	0.1
39	0.2	0.13	0.02	13.	65	0.1
40	0.8	1.8	0.82	46.	225	3.
41	0.2	0.21	0.07	33.	105	0.2
42	0.2	0.19	0.04	23.	95	0.1
43	0.2	0.27	0.07	27.	135	0.2
44	0.2	0.13	0.03	22.	65	0.1
45		not measured at this level				
46	0.2	0.16	0.04	23.	80	0.12
Mean[a]	0.2	0.21	0.09	28.	102	0.3

[a]Compounds 4, 40, and 45 excluded from the means.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS AT 2 μG/L WITH LIQUID-SOLID EXTRACTION AND A QUADRUPOLE MASS SPECTROMETER

Compound Number (Table 2)	True Conc. (μg/L)	Mean Observed Conc. (μg/L)	Std. Dev. (μg/L)	Rel. Std. Dev. (%)	Mean Method Accuracy (% of True Conc.)	Method Detection Limit (MDL) (μg/L)
47	2	2.4	0.4	16.	122	1.0

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN REPLICATES AT 0.2 µG/L WITH LIQUID-SOLID C-18 DISK EXTRACTION AND AN ION TRAP MASS SPECTROMETER

Compound Number (Table 2)	Target Concentration (µg/L)	Standard Deviation (µg/L)	Relative Deviation (%)	Mean (µg/L)	Accuracy (% of target)
1	0.2	0.01	5.3	0.22	110
4	5.0	0.37	7.4	5.55	111
6	0.2	0.03	13.2	0.26	130
7	0.2	0.03	13.7	0.22	108
8	0.2	0.04	22.4	0.21	105
9	0.2	0.07	33.2	0.29	147
10	0.2	0.16	77.6	0.40	199
11	0.2	0.03	13.7	0.21	107
12	0.2	0.04	21.7	0.26	128
13	0.2	0.03	14.9	0.23	115
14	0.2	0.07	32.5	0.37	183
15	0.2	0.12	61.1	0.19	95
16	0.2	0.06	31.9	0.19	93
17	0.2	0.18	91.3	0.55	276
18	0.2	0.01	7.2	0.16	78
19	0.2	0.02	10.9	0.27	136
20	0.2	0.05	22.9	0.18	90
21	0.2	0.08	40.3	0.47	233
22	0.2	0.02	9.7	0.17	87
23	0.2	0.02	11.9	0.27	133
24	0.2	0.50	252.0	1.54	771
25	0.2	0.04	20.8	0.36	180
26	0.2	0.02	7.6	0.23	117
27	0.2	0.05	25.4	0.23	117
28	0.2	0.01	7.3	0.20	101
29	0.2	0.05	22.9	0.28	139
30	0.2	0.08	38.9	0.36	181
31	0.2	0.08	38.0	0.28	141
32	0.2	0.04	17.7	0.22	109
33	0.2	0.06	31.9	0.19	96
34	0.2	0.01	5.2	0.34	170
35	0.2	0.05	27.0	0.29	143
36	0.2	0.01	6.5	0.22	110
37	0.2	0.03	13.4	0.20	100
38	0.2	0.04	21.1	0.20	99
39	0.2	0.03	15.1	0.17	84
40	2.0				
41	0.2	0.02	12.2	0.20	102
42	0.2	0.02	10.2	0.24	121
43	0.2	0.04	18.8	0.19	94
44	0.2	0.06	28.1	0.21	107
45	20.0	2.47	12.3	24.80	123
46	0.2	0.04	21.4	0.19	95
47	0.2	0.03	14.7	0.11	55

TABLE 9. ACCURACY AND PRECISION DATA FROM SEVEN REPLICATES AT 2.0 µG/L WITH LIQUID-SOLID C-18 DISK EXTRACTION AND AN ION TRAP MASS SPECTROMETER

Compound Number (Table 2)	Target Concentration (µg/L)	Standard Deviation (µg/L)	Relative Deviation (%)	Mean (µg/L)	Accuracy (% of target)
1	2	0.18	9.2	2.00	100
4	5	0.45	9.1	5.22	104
6	2	0.30	14.8	2.14	107
7	2	0.17	8.6	2.25	112
8	2	0.47	23.5	2.78	139
9	2	0.21	10.4	2.21	111
10	2	0.62	30.9	2.84	142
11	2	0.57	28.7	2.30	115
12	2	0.31	15.6	2.61	130
13	2	0.28	13.9	2.28	114
14	2	0.33	16.7	2.92	146
15	2	0.62	31.1	1.21	61
16	2	1.02	51.2	1.92	96
17	2	1.39	69.3	3.29	164
18	2	0.22	11.2	2.52	126
19	2	0.23	11.6	1.99	100
20	2	0.27	13.4	2.25	113
21	2	0.23	11.3	2.45	123
22	2	0.38	18.9	2.35	117
23	2	0.22	11.1	2.23	111
24	2	0.38	19.1	3.25	163
25	2	0.26	12.8	2.49	124
26	2	0.69	34.6	1.80	90
27	2	0.12	6.1	1.97	98
28	2	0.19	9.7	2.15	108
29	2	0.30	15.0	2.10	105
30	2	0.15	7.4	2.41	121
31	2	0.64	32.2	2.46	123
32	2	0.85	42.3	1.96	98
33	2	0.52	25.9	2.05	102
34	2	0.22	11.0	1.42	71
35	2	0.37	18.3	2.31	115
36	2	0.42	21.2	2.69	134
37	2	0.34	16.8	2.34	117
38	2	0.77	38.5	0.97	49
39	2	0.29	14.7	2.11	106
40	20	15.16	75.8	19.51	98
41	2	0.20	9.9	2.20	110
42	2	0.17	8.3	2.34	117
43	2	0.27	13.3	2.37	119
44	2	0.15	7.4	2.11	106
45	100	3.36	3.4	98.33	98
46	2	0.58	28.8	1.65	82
47	2	0.07	3.5	1.55	77

TABLE 10. MINIMUM DETECTION LIMITS FROM SEVEN REPLICATES USING LIQUID-SOLID EXTRACTION C-18 DISKS AND AN ION TRAP MASS SPECTROMETER

Chemical Name	Minimum Detection Limits
Acenaphtyiene	0.033
Alachlor	0.092
Aldrin	0.083
Anthracene	0.086
Atrazine	0.140
Benz[a]anthracene	0.224
Benzo[b]fluoranthene	0.488
Benzo[k]fluoranthene	0.086
Benzo[a]pyrene	0.137
Benzo[ghi]perylene	0.094
Butylbenzylphthalate	0.204
Chlordane-alpha	0.384
Chlordane-gamma	0.200
Chlordane (transnonachlor)	0.574
Chrysene	0.068
Dibenz[ah]anthracene	0.144
Di-n-butylphthalate	0.253
Diethylphthalate	0.075
Di(2-ethylhexyl)phthalate	1.584
Di(2-ethlyhexyl)adipate	0.131
Dimethylphthalate	0.048
Endrin	0.160
Fluorene	0.046
Heptachlor	0.144
Heptachlorepoxide	0.244
Hexachlorobenzene	0.111
Hexachlorocyclopentadiene	0.039
Indeno[123cd]pyrene	0.170
Lindane	0.041
Methoxychlor	0.084
PCB-mono-Cl-isomer	0.045
PCB-di-Cl-isomer	0.061
PCB-tri-Cl-ISOMER	0.135
PCB-tetra-Cl-isomer	0.177
PCB-penta-Cl-isomer	0.095
PCB-hexa-Cl-isomer	0.200
PCB-hepta-Cl-isomer	0.239
PCB-octa-Cl-isomer	0.133
Pentachlorophenol	47.648
Phenanthrene	0.076
Pyrene	0.064
Simazine	0.118
Toxaphene	7.763

FIGURE 1. TOTAL ION CHROMATOGRAM OF TWO NANOGRAMS OF ANALYTES AND FIVE NANOGRAMS OF SURROGATES AND INTERNAL STANDARD

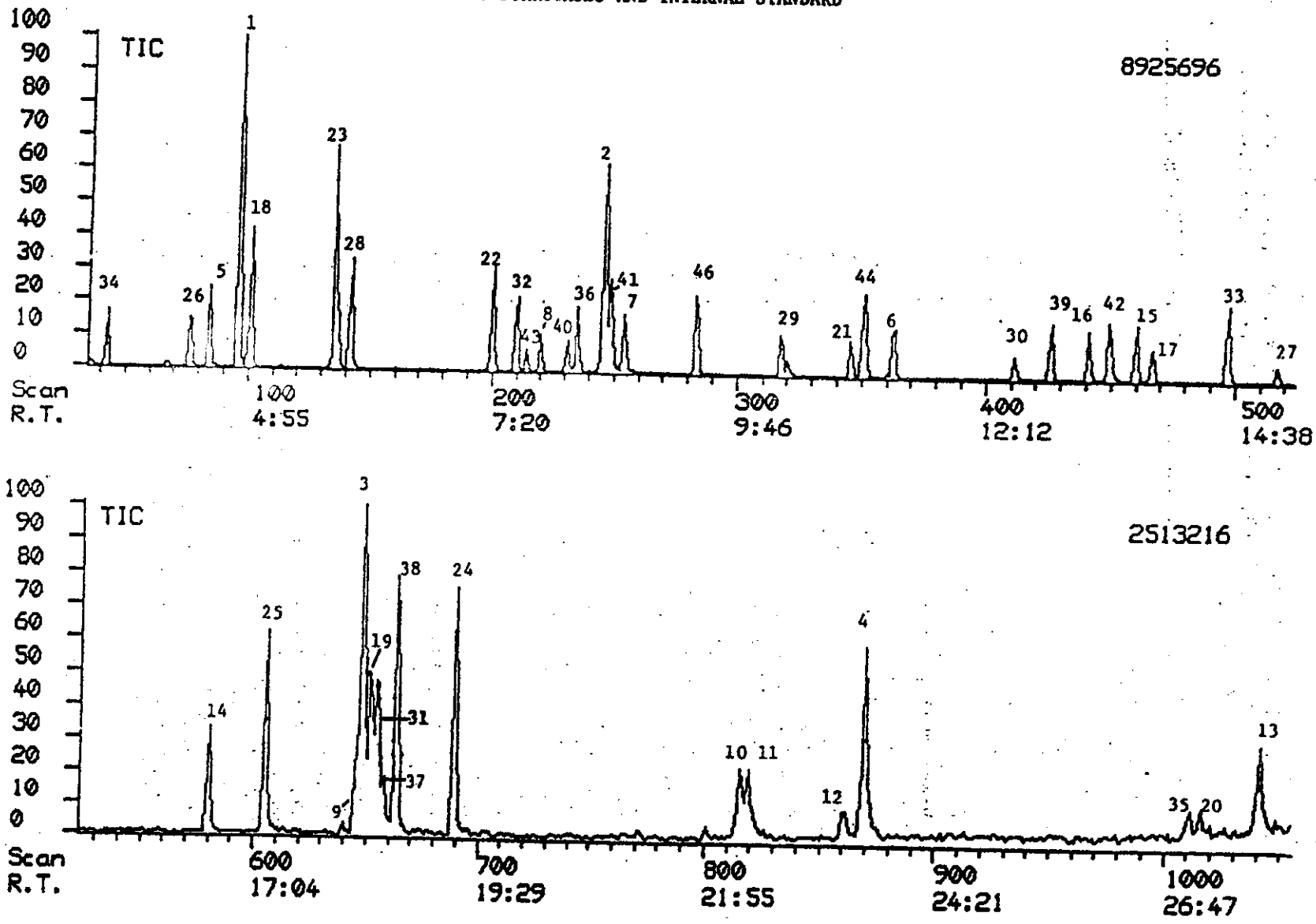
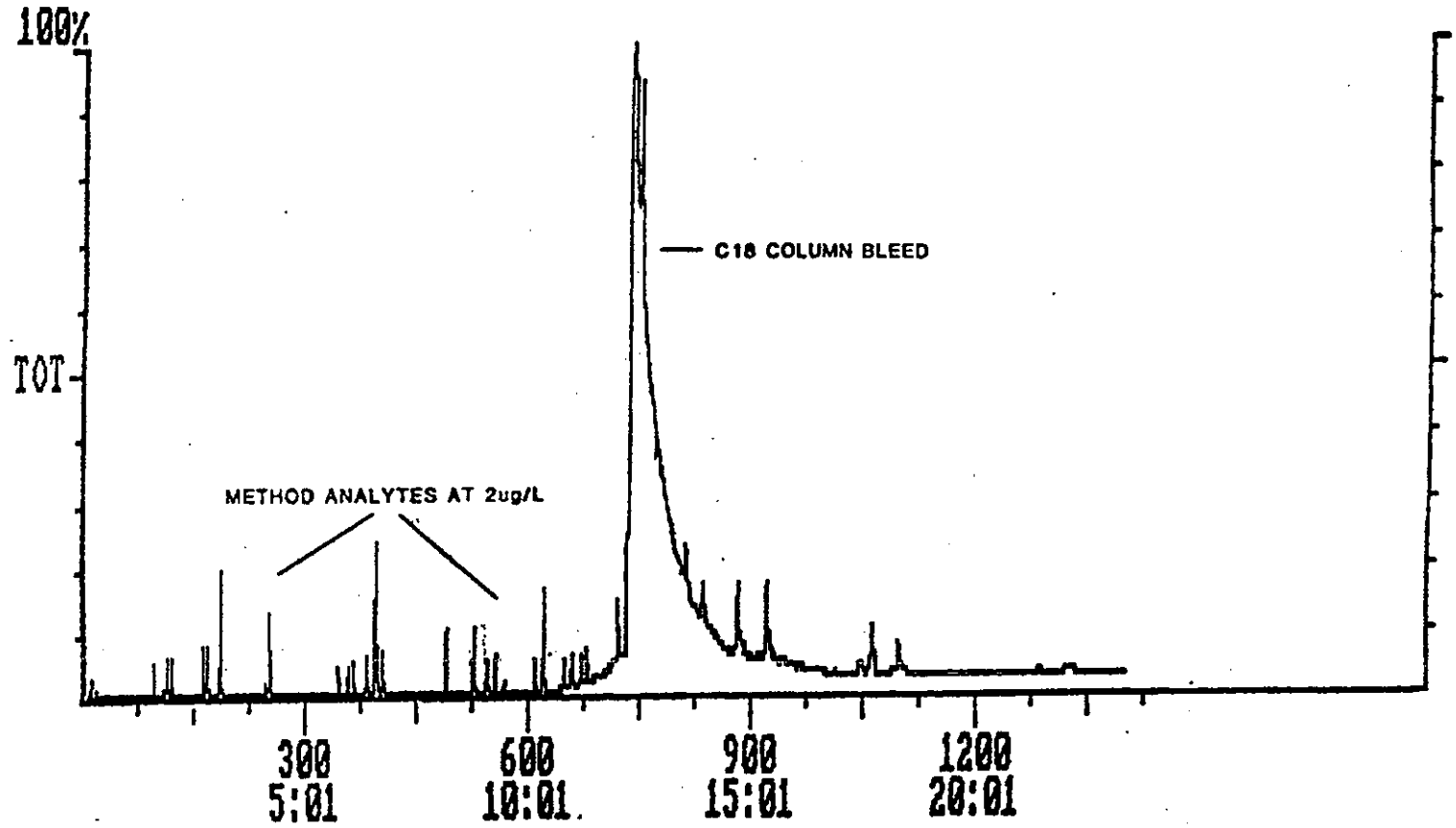
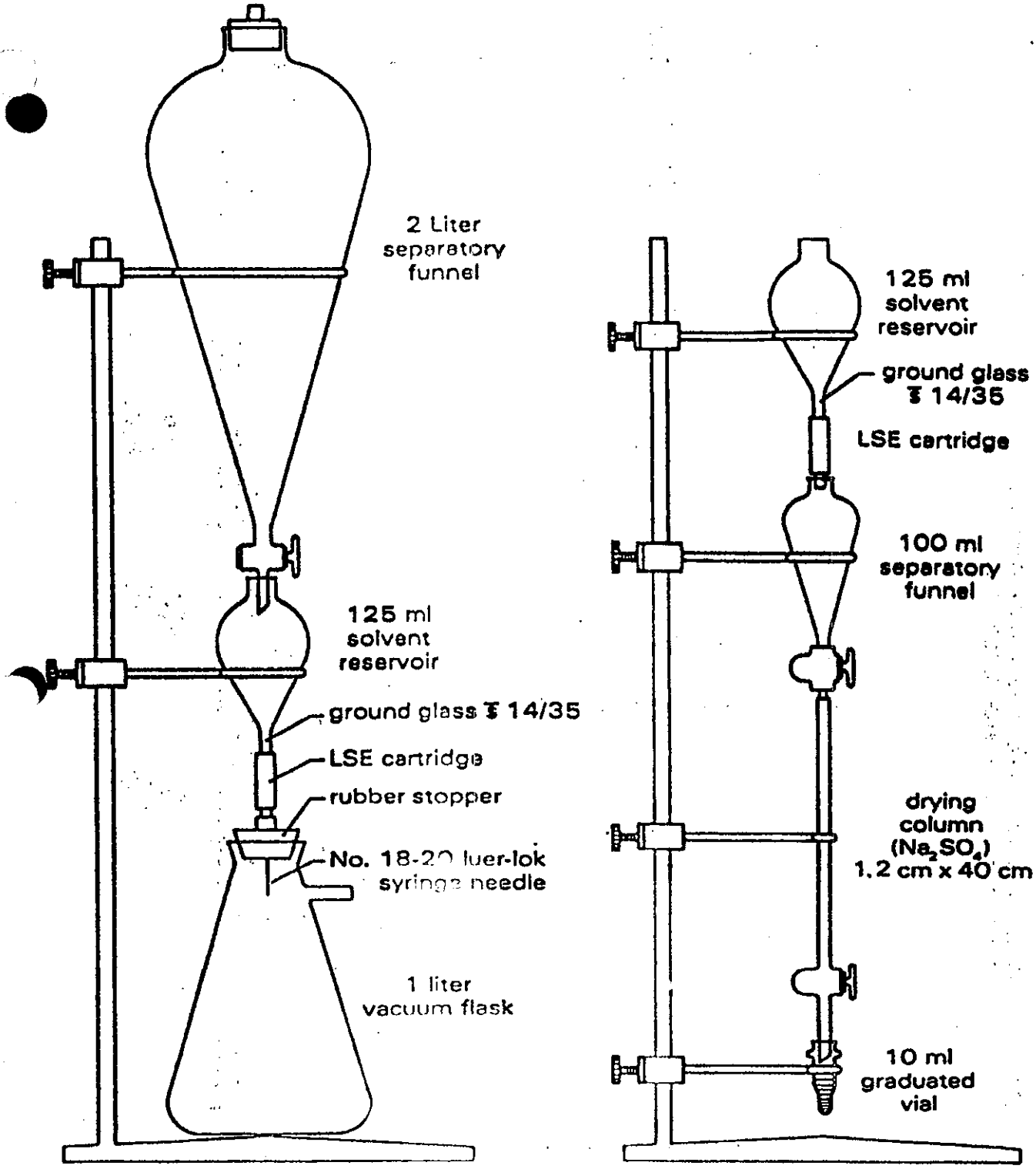


FIGURE 2. TOTAL ION CHROMATOGRAM FROM A LABORATORY BLANK WITH AN UNACCEPTABLY HIGH BACKGROUND

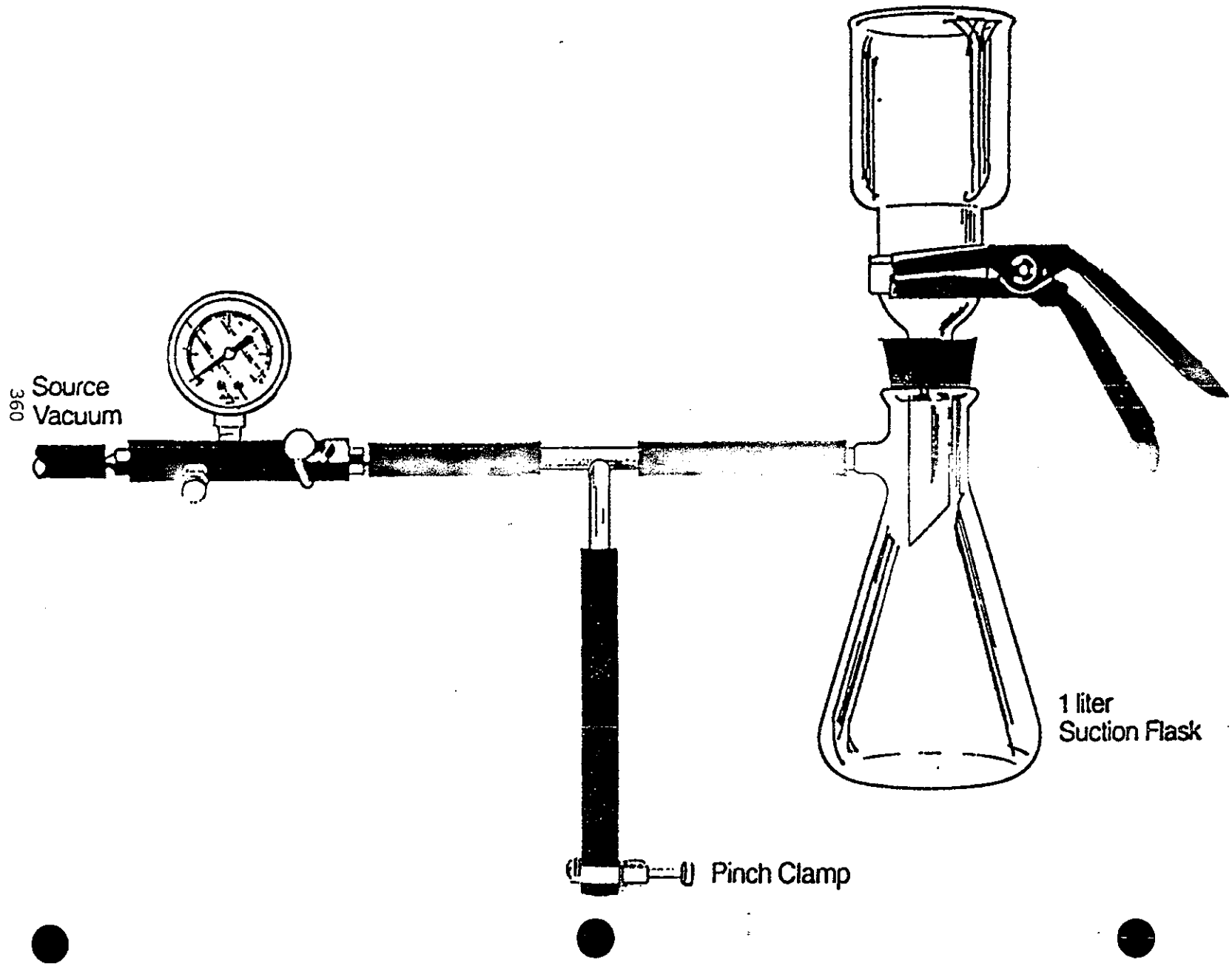




A. Extraction apparatus **B. Elution apparatus**

FIGURE 3

FIGURE 4. DISK EXTRACTION APPARATUS



METHOD 531.1. MEASUREMENT OF N-METHYLCARBAMOYLOXIMES AND N-METHYLCARBAMATES IN WATER BY DIRECT AQUEOUS INJECTION HPLC WITH POST COLUMN DERIVATIZATION

Revision 3.0

D. L. Foerst - Method 531, Revision 1.0 (1985)

T. Engels (Battelle Columbus Laboratories) - National Pesticide Survey Method 5, Revision 2.0 (1987)

R. L. Graves - Method 531.1, Revision 3.0 (1989)

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METHOD 531.1

MEASUREMENT OF N-METHYLCARBAMOYLOXIMES AND N-METHYLCARBAMATES IN WATER BY DIRECT AQUEOUS INJECTION HPLC WITH POST COLUMN DERIVATIZATION

1. SCOPE AND APPLICATION

1.1 This is a high performance liquid chromatographic (HPLC) method applicable to the determinations of certain N-methylcarbamoyloximes and N-methylcarbamates in ground water and finished drinking water(1). The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number
Aldicarb	116-06-3
Aldicarb sulfone	1646-88-4
Aldicarb sulfoxide	1646-87-3
Baygon	114-26-1
Carbaryl	63-25-2
Carbofuran	1563-66-2
3-Hydroxycarbofuran	16655-82-6
Methiocarb	2032-65-7
Methomyl	16752-77-5
Oxamyl	23135-22-0

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for the analytes above (Sect.12). Observed detection limits may vary between ground waters, depending upon the nature of interferences in the sample matrix and the specific instrumentation used.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of liquid chromatography and in the interpretation of liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Sect. 10.3.

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications should be confirmed by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 The water sample is filtered and a 400-µL aliquot is injected into a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05 N sodium hydroxide (NaOH) at 95°C. The methyl amine formed during hydrolysis is

reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative which is detected by a fluorescence detector (2).

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in liquid chromatograms. Specific sources of contamination have not been identified. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Sect. 10.2.

4.1.1 Glassware must be scrupulously cleaned.(2) Clean all glassware as soon as possible after use by thoroughly

rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 450°C for 1 hour. Do not heat volumetric ware. Thermally stable materials might not be eliminated by this treatment. Thorough rinsing with acetone may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the mamufacturer are removed, thus potentially reducing the shelf-life.

4.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. A preventive technique is between-sample rinsing of the sample syringe and filter holder with two portions of reagent water. After analysis of a sample containing high concentrations of analytes, one or more laboratory method blanks should be analyzed.

4.3 Matrix interference may be caused by contaminants that are present in the sample. The extent of matrix interference will vary considerably from source to source, depending upon the water sampled. Positive identifications must be confirmed.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must 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 material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (4-6) for the information of the analyst.

5.2 WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6. APPARATUS AND EQUIPMENT (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 SAMPLING EQUIPMENT

6.1.1 Grab sample bottle -- 60-mL screw cap vials (Pierce No. 13075 or equivalent) and caps equipped with a PTFE-faced silicone septa (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa as described in Sect. 3.1.1.

6.2 BALANCE -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.3 FILTRATION APPARATUS

6.3.1 Macrofiltration -- To filter derivatization solutions and mobile phases used in HPLC. Recommend using 47 mm filters (Millipore Type HA, 0.45 μm for water and Millipore Type FH, 0.5 μm for organics or equivalent).

6.3.2 Microfiltration -- To filter samples prior to HPLC analysis. Use 13 mm filter holder (Millipore stainless steel XX300/200 or equivalent), and 13 mm diameter 0.2 μm polyester filters (Nuclepore 180406 or equivalent).

6.4 SYRINGES AND SYRINGE VALVES

6.4.1 Hypodermic syringe -- 10-mL glass, with Luer-Lok tip.

6.4.2 Syringe valve -- 3-way (Hamilton HV3-3 or equivalent).

6.4.3 Syringe needle -- 7 to 10-cm long, 17-gauge, blunt tip.

6.4.4 Micro syringes -- various sizes.

6.5 MISCELLANEOUS

6.5.1 Solution storage bottles -- Amber glass, 10- to 15-mL capacity with TFE-fluorocarbon-lined screw cap.

6.5.2 Helium, for degassing solutions and solvents.

6.6 HIGH PERFORMANCE LIQUID CHROMATOGRAPH (HPLC)

6.6.1 HPLC system capable of injecting 200- to 400-μL aliquots, and performing binary linear gradients at a constant flow rate. A data system is recommended for measuring peak areas. Table 1 lists retention times observed for method analytes using the columns and analytical conditions described below.

6.6.2 Column 1 (Primary column) -- 150 mm long x 3.9 mm I.D. stainless steel packed with 4 μm NovaPak C18. Mobil Phase is established at 10:90 methanol: water, hold 2 min., then program as a linear gradient to 80:20 methanol: water in 25 min. Alternative columns may be used in accordance with the provisions described in Sect. 10.4.

6.6.3 Column 2 (Alternative column)* -- 250 mm long x 4.6 mm I.D. stainless steel packed with 5 μm Beckman Ultrasphere ODS. Mobile phase is established at 1.0 mL/min as a linear gradient from 15:85 methanol: water to methanol in 32 min. Data presented in this method were obtained using this column. * Newer manufactured columns have not been able to resolve aldicarb sulfone from oxamyl.

6.6.4 Column 3 (Alternative column) -- 250 mm long x 4.6 mm I.D. stainless steel packed with 5 μm Supelco LC-1. Mobile phase is established at 1.0 mL/min as a linear gradient from 15:85 methanol: water to methanol in 32 min.

6.6.5 Post column reactor -- Capable of mixing reagents into the mobile phase. Reactor should be constructed using PTFE tubing and equipped with pumps to deliver 0.1 to 1.0 mL/min of each reagent; mixing tees; and two 1.0-mL delay coils, one thermostated at 95°C (ABI URS 051 and URA 100 or equivalent).

6.6.6 Fluorescence detector -- Capable of excitation at 330 nm (nominal) and detection of emission energies greater than 418 nm. A Schoffel Model 970 fluorescence detector was used to generate the validation data presented in this method.

7. <u>REAGENTS AND CONSUMABLE MATERIALS</u> -- WARNING: When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous. Also, when a solvent is purified, preservatives added by the manufacturer are removed, thus potentially reducing the shelf-life.

7.1 REAGENT WATER -- Reagent water is defined as water that is reasonably free of contamination that would prevent the determination of any analyte of interest. Reagent water used to generate the validation data in this method was distilled water obtained from the Magnetic Springs Water Co., 1801 Lone Eagle St., Columbus, Ohio 43228.

7.2 METHANOL -- Distilled-in-glass quality or equivalent.

7.3 HPLC MOBILE PHASE

7.3.1 Water -- HPLC grade (available from Burdick and Jackson).

7.3.2 Methanol -- HPLC grade. Filter and degas with helium before use.

7.4 POST COLUMN DERIVATIZATION SOLUTIONS

7.4.1 Sodium hydroxide, 0.05 N -- Dissolve 2.0 g of sodium hydroxide (NaOH) in reagent water. Dilute to 1.0 L with reagent water. Filter and degas with helium just before use.

7.4.2 2-Mercaptoethanol (1+1) -- Mix 10.0 mL of 2-mercapto-ethanol and 10.0 mL of acetonitrile. Cap. Store in hood (CAUTION -- stench).

7.4.3 Sodium borate (0.05 N) -- Dissolve 19.1 g of sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) in reagent water. Dilute to 1.0 L with reagent water. The sodium borate will completely dissolve at room temperature if prepared a day before use.

7.4.4 OPA reaction solution -- Dissolve 100 ± 10 mg of o-phthaldehyde (mp 55-58°C) in 10 mL of methanol. Add to 1.0 L of 0.05 N sodium borate. Mix, filter, and degas with helium. Add 100 µL of 2-mercaptoethanol (1+1) and mix. Make up fresh solution daily.

7.5 MONOCHLOROACETIC ACID BUFFER (pH3) -- Prepare by mixing 156 mL of 2.5 M monochloroacetic acid and 100 mL 2.5 M potassium acetate.

7.6 4-BROMO-3,5-DIMETHYLPHENYL N-METHYLCARBAMATE (BDMC) -- 98% purity, for use as internal standard (available from Aldrich Chemical Co.).

7.7 STOCK STANDARD SOLUTIONS (1.00 µg/µL) -- Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.7.1 Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in HPLC quality methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.7.2 Transfer the stock standard solutions into TFE-fluorocarbon-sealed screw cap vials. Store at room temperature and protect from light.

7.7.3 Stock standard solutions should be replaced after two months or sooner if comparison with laboratory fortified blanks, or QC samples indicate a problem.

7.8 INTERNAL STANDARD SOLUTION -- Prepare an internal standard fortification solution by accurately weighing approximately 0.0010 g of pure BDMC. Dissolve the BDMC in pesticide-quality methanol and dilute to volume in a 10-mL volumetric flask. Transfer the internal standard fortification solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 5 µL of the internal standard fortification solution to 50 mL of sample results in a final internal standard concentration of 10 µg/L. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem. Note: BDMC has been shown to be an effective internal standard for the method analytes (1), but other compounds may be used, if the quality control requirements in Sect. 9 are met.

7.9 LABORATORY PERFORMANCE CHECK SOLUTION -- Prepare concentrate by adding 20 µL of the 3-hydroxycarbofuran stock standard solution, 1.0 mL of the aldicarb sulfoxide stock standard solution, 200 µL of the methiocarb stock standard solution, and 1 mL of the internal standard fortification solution to a 10-mL volumetric flask. Dilute to volume with methanol. Thoroughly mix concentrate. Prepare check solution by placing 100 µL of the concentrate solution into a 100-mL volumetric flask. Dilute to volume with buffered reagent water. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Sect. 10) indicates a problem.

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Grab samples must be collected in glass containers. Conventional sampling practices (8) should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 SAMPLE PRESERVATION/PH ADJUSTMENT -- Oxamyl, 3-hydroxycarbofuran, aldicarb sulfoxide, and carbaryl can all degrade quickly in neutral and basic waters held at room temperature. (6,7) This short term degradation is of concern during the time samples are being shipped and the time processed samples are held at room temperature in autosampler trays. Samples targeted for the analysis of these three analytes must be preserved at pH 3. The pH adjustment also minimizes analyte biodegradation.

8.2.1 Add 1.8 mL of monochloroacetic acid buffer to the 60-mL sample bottle. Add buffer to the sample bottle at the sampling site or in the laboratory before shipping to the sampling site.

8.2.2 If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.2.3 After sample is collected in bottle containing buffer, seal the sample bottle and shake vigorously for 1 min.

8.2.4 Samples must be iced or refrigerated at 4°C from the time of collection until storage. Samples must be stored at -10°C until analyzed. Preservation study results indicate that method analytes are stable in water samples for at least 28 days when adjusted to pH 3 and stored at -10°C. However, analyte stability may be effected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

9. CALIBRATION

9.1 Establish HPLC operating parameters equivalent to those indicated in Sect. 6.6. The HPLC system may be calibrated using either the internal standard technique (Sect. 9.2) or the external standard technique (Sect. 9.3).

9.2 INTERNAL STANDARD CALIBRATION PROCEDURE. The analyst must select one or more internal standards similar in analytical behavior to the analytes of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. BDMC has been identified as a suitable internal standard.

9.2.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or of the more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with buffered reagent water. To prepare buffered reagent water, add 10 mL of 1.0 M monochloroacetic acid buffer to 1 L of reagent water. The lowest standard should represent analyte concentrations near, but above, their respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

9.2.2 Analyze each calibration standard according to the procedure (Sect. 11.2). Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each analyte, surrogate and internal standard using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)} \qquad \text{Equation 1}$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard µg/L).
C_s = Concentration of the analyte to be measured µg/L).

9.2.3 If the RF value over the working range is constant (20% RSD or less) the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios (A_s/A_{is}) vs. C_s.

9.2.4 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the repetition also fails, a new calibration curve must be generated for that analyte using freshly prepared standards.

9.2.5 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards. The single point standards should be prepared at a concentration that deviates from the sample extract response by no more than 20%.

9.2.6 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

9.3 EXTERNAL STANDARD CALIBRATION PROCEDURE

9.3.1 Prepare calibration standards at a minimum of three (recommend five) concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. Dilute to volume with buffered reagent water. The lowest standard should represent analyte concentrations near, but above, the respective EDLs. The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

9.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Sect. 11.2 and tabulate responses (peak height or area) versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range <20% relative standard deviation), linearity through the

origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

9.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the concentration curve. For extended periods of analysis (greater than 8 hr), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for any analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve or use a single point calibration standard as described in Sect. 9.3.3.

9.3.4 Single point calibration is a viable alternative to a calibration curve. Prepare single point standards from the secondary dilution standards. The single point standards should be prepared at a concentration that deviates from the sample extract response by no more than 20%.

9.3.5 Verify calibration standards periodically, recommend at least quarterly, by analyzing a standard prepared from reference material obtained from an independent source. Results from these analyses must be within the limits used to routinely check calibration.

10. QUALITY CONTROL

10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks and QC samples.

10.2 LABORATORY REAGENT BLANKS. Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a laboratory reagent blank (LRB) must be analyzed. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 INITIAL DEMONSTRATION OF CAPABILITY.

10.3.1 Select a representative concentration (about 10 times EDL) for each analyte. Prepare a sample concentrate (in methanol) containing each analyte at 1000 times selected concentration. With a syringe, add 50 μL of the concentrate to each of at least four 50-mL aliquots of reagent water, and analyze each aliquot according to procedures beginning in Sect. 11.

10.3.2 For each analyte the recovery value for all four of these samples must fall in the range of R ± 30% (or within R ± $3S_R$ if broader) using the values for R and S_R for reagent water in Table 2. For those compounds that meet the acceptance criteria, performance is judged acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

10.4 The analyst is permitted to modify HPLC columns, HPLC conditions, internal standards or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 10.3.

10.5 ASSESSING THE INTERNAL STANDARD

10.5.1 When using the internal standard calibration procedure, the analyst is expected to monitor the IS response (peak area or peak height) of all samples during each analysis day. The IS response for any sample chromatogram should not deviate from the daily calibration check standard's IS response by more than 30%.

10.5.2 If >30% deviation occurs with an individual extract, optimize instrument performance and inject a second aliquot.

10.5.2.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

10.5.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the sample should be repeated beginning with Sect. 11,

provided the samples is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

10.5.3 If consecutive samples fail the IS response acceptance criterion, immediately analyze a calibration check standard.

10.5.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Sect. 10.5.2 for each sample failing the IS response criterion.

10.5.3.2 If the check standard provides a response factor which deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Sect. 9.

10.6 ASSESSING LABORATORY PERFORMANCE - LABORATORY FORTIFIED BLANKS

10.6.1 The laboratory must analyze at least one laboratory fortified blank (LFB) sample with every 20 samples or one per sample set (all samples analyzed within a 24-h period) whichever is greater. The fortification concentration of each analyte in the LFB should be 10 times EDL or the MCL, whichever is less. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Sect. 10.7.2), that analyte is judged out of control, and the source of the problem must be identified and resolved before continuing analyses.

10.6.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20 to 30 analyses, the laboratory should assess laboratory performance against the control limits in Sect. 10.3.2 that are derived from the data in Table 2. When sufficient internal performance data becomes available, develop control limits from the mean percent recovery (X) and standard deviation (S) of the percent recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = X + 3S$$
$$\text{LOWER CONTROL LIMIT} = X - 3S$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits should never exceed those established in Sect. 10.3.2.

10.6.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for analytes of interest.

10.6.4 At least quarterly, analyze a QC sample from an outside source.

10.6.5 Laboratories are encouraged to participate in external performance evaluation studies such as the laboratory certification programs offered by many states or the studies conducted by U.S. EPA. Performance evaluation studies serve as independent checks on the analyst's performance.

10.7 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.7.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample concentration per set, whichever is greater. The concentration should not be less then the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Sect. 10.6). Over time, samples from all routine sample sources should be fortified.

10.7.2 Calculate the percent recovery, P of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample, i.e.,:

$$P = 100\ (X - b) \ /\ \text{fortifying concentration},$$

and compare these values to control limits appropriate for reagent water data collected in the same fashion. If the analyzed unfortified sample is found to contain NO background concentrations, and the added concentrations are those specified in Sect. 10.7, then the appropriate control limits would be the acceptance limits in Sect. 10.7. If, on the other hand, the analyzed unfortified sample is found to contain background concentration, b, estimate the standard deviation at the background concentration, s_b, using regressions or comparable background data and, similarly, estimate the mean, X_a, and standard deviation, s_a, of analytical results at the total concentration after fortifying. Then the appropriate percentage control limits would be $\bar{P} \pm 3s_p$, where:

$$\bar{P} = 100\ \bar{X}\ /\ (b + \text{fortifying concentration})$$

$$\text{and } s_P = 100\ (s_a^2 + s_b^2)^{1/2} /\text{fortifying concentration}$$

would be (1.6 μg/L minus 1.0 μg/L)/1 μg/L or 60%. This calculated P is compared to control limits derived from prior reagent water data. Assume it is known that analysis of an interference free sample at 1 μg/L yields an_s of 0.12 μg/L and similar analysis at 2.0 μg/L yields X and s of 2.01 μg/L and 0.20 μg/L, respectively. The appropriate limits to judge the reasonableness of the percent recovery, 60%, obtained on the fortified matrix sample is computed as follows:

[100 (2.01 μg/L) / 2.0 μg/L]

$$\pm 3\ (100)\ \left[(0.12\ \mu g/L)^2 + (0.20\ \mu g/L)^2\right]^{1/2} / 1.0\ \mu g/L =$$

100.5% ± 300 (0.233) =

100.5% ± 70% or 30% to 170% recovery of the added analyte.

10.7.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sect. 10.6), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.8 ASSESSING INSTRUMENT SYSTEM - LABORATORY PERFORMANCE CHECK SAMPLE - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 3. Inability to demonstrate acceptable instrument performance indicates the need for reevaluation of the instrument system. The sensitivity requirements are set based on the EDLs published in this method. If laboratory EDLs differ from those listed in this method, concentrations of the instrument QC standard compounds must be adjusted to be compatible with the laboratory EDLs.

10.9 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11. PROCEDURE

11.1 PH ADJUSTMENT AND FILTRATION

11.1.1 Add preservative to any samples not previously preserved (Sect. 8). Adjust the pH of the sample or standard to pH 3 ± 0.2 by adding 1.5 mL of 2.5 M monochloroacetic acid buffer to each 50 mL of sample. This step should not be necessary if sample pH was adjusted during sample collection as a preservation precaution. Fill a 50-mL volumetric flask to the mark with the sample. Add 5 µL of the internal standard fortification solution (if the internal standard calibration procedure is being employed) and mix by inverting the flask several times.

11.1.2 Affix the three-way valve to a 10-mL syringe. Place a clean filter in the filter holder and affix the filter holder and the 7- to 10-cm syringe needle to the syringe valve. Rinse the needle and syringe with reagent water. Prewet the filter by passing 5 mL of reagent water through the filter. Empty the syringe and check for leaks. Draw 10 mL of sample into the syringe and expel through the filter. Draw another 10 mL of sample into the syringe, expel through the filter, and collect the last 5 mL for analysis. Rinse the syringe with reagent water. Discard the filter.

11.2 LIQUID CHROMATOGRAPHY

11.2.1 Sect. 6.6 summarizes the recommended operating conditions for the liquid chromatograph. Table 1 lists retention times observed using this method. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 10.4 are met.

11.2.2 Calibrate the system daily as described in Sect. 10. The standards and samples must be in pH 3 buffered water.

11.2.3 Inject 400 µL of the sample. Record the volume injected and the resulting peak size in area units.

11.2.4 If the response for the peak exceeds the working range of the system, dilute the sample with pH 3 buffered reagent water and reanalyze.

11.3 IDENTIFICATION OF ANALYTES

11.3.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then identification is considered positive.

11.3.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.3.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry, or the use of a second chromatography column. A suggested alternative column is described in Sect. 6.6.3.

12. CALCULATIONS

Determine the concentration of individual compounds in the sample using the following equation:

$$C_x = \frac{A_x \cdot Q_s}{A_s \cdot RF},$$

where: C_x = analyte concentration in micrograms per liter;
A_x = response of the sample analyte;
A_s = response of the standard (either internal or external), in units consistent with those used for the analyte response;
RF = response factor (with an external standard, RF = 1, because the standard is the same compound as the measured analyte);

Q_s = concentration of internal standard present or concentration of external standard that produced As, in micrograms per liter.

13. PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were determined at five concentration levels. Results were used to determine analyte EDLs and demonstrate method range.(1) Analyte

recoveries and standard deviation about the percent recoveries at one concentration are given in Table 2.

13.2 In a single laboratory, analyte recoveries from two standard synthetic ground waters were determined at one concentration level. Results were used to demonstrate applicability of the method to different ground water matrices.(1) Analyte recoveries from the two synthetic matrices are given in Table 2.

14. REFERENCES

1. National Pesticide Survey Method No. 5., "Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Groundwater by HPL with Post Column Derivatization."

2. Moye, H.A., S.J. Sherrer, and P. A. St. John, "Dynamic Labeling of Pesticides for High Performance Liquid Chromatography: Detection of N-Methylcarbamates and o-Phthalaldehyde," Anal. Lett, 10, 1049, 1977.

3. ASTM Annual Book of Standards, Part 11, Volume 11.02, D3694-82, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 86, 1986.

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

5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

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

7. Foerst, D. L. and H. A. Moye, "Aldicarb in Drinking Water via Direct Aqueous Injection HPLC with Post Column Derivatization," Proceedings of the 12th annual AWWA Water Quality Technology Conference, 1984.

8. Hill, K. M., R.H. Hollowell, and L. A. DalCortevo, "Determination of N-Methylcarbamate Pesticides in Well Water by Liquid Chromatography and Post Column Fluorescence Derivatization," Anal. Chem, 56, 2465 (1984).

9. ASTM Annual Book of Standards, Part 11, Volume 11.01, D3370-82, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 130, 1986.

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] (minutes) Primary[1]	Alternative[2]	Alternative[3]
Aldicarb sulfoxide	6.80	15.0	17.5
Aldicarb sulfone	7.77	15.2	12.2
Oxamyl	8.20	17.4	14.6
Methomyl	8.94	18.4	14.8
3-Hydroxycarbofuran	13.65	23.3	19
Aldicarb	16.35	27.0	21.4
Baygon	18.86	29.3	24.4
Carbofuran	19.17	29.6	23.4
Carbaryl	20.29	30.8	25.4
Methiocarb	24.74	34.9	28.6
BDMC	25.28	35.5	

[a] Columns and analytical conditions are described in Sect. 6.6.2 and 6.6.3.

(1) Waters NovaPak C18

(2) Beckman Ultrasphere ODS

(3) Supelco LC-1

TABLE 2. SINGLE LABORATORY ACCURACY, PRECISION AND ESTIMATED DETECTION LIMITS (EDLS) FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUND WATERS[a]

Analyte	Water 2[f] EDL µg/L[b]	Concentration Level µg/L	Reagent Water R[c]	Reagent Water S_R[d]	Synthetic Water 1[e] R	Synthetic Water 1[e] S_R	Synthetic R	Synthetic S_R
Aldicarb	1.0	5	115	3.5	106	3.2	102	8.2
Aldicarb sulfone	2.0	10	101	4.0	98	3.9	95	9.5
Aldicarb sulfoxide	2.0	10	97	4.9	105	4.2	94	10.3
Baygon	1.0	5	106	3.2	96	4.8	97	5.8
Carbaryl	2.0	10	97	5.8	94	4.7	104	10.4
Carbofuran	1.5	7.5	102	5.1	102	3.1	100	7.0
3-Hydroxycarbofuran	2.0	10	102	4.1	98	4.9	101	10.1
Methiocarb	4.0	20	94	1.9	102	4.1	112	3.4
Methomyl	0.5	2.5	105	4.2	98	3.9	105	9.5
Oxamyl	2.0	10	100	4.0	97	2.9	102	10.2

[a] Data corrected for amount detected in blank and represent the mean of 7-8 samples.

[b] EDL = Estimated detection limit; defined as either MDL (Appendix B to 40 CFR Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher. The concentration level used in determining the EDL is not the same as the concentration level presented in this table.

[c] R = Average percent recovery.

[d] S_R = Standard deviation of the percent recovery.

[e] Corrected for amount found in blank; Absopure Nature Artesian Spring Water Obtained from the Absopure Water Company in Plymouth, Michigan.

[f] Corrected for amount found in blank; reagent water fortified with fulvic acid at the 1 mg/L concentration level. A well-characterized fulvic acid, available from the International Humic Substances Society (associated with the United States Geological Survey in Denver, Colorado) was used.

TABLE 3. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc, µg/mL	Requirements
Sensitivity	3-Hydroxycarbofuran	2	Detection of analyte; S/N > 3
Chromatographic performance	Aldicarb sulfoxide	100	0.90 <PGF<1.1[a]
Column performance	Methiocarb	20	Resolution >1.0[c]
	4-Bromo-3,5-dimethylphenyl N-methylcarbamate (IS)	10	

[a] PGF = peak Gaussian factor. Calculated using the equation:

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where W(1/2) is the peak width at half height and W(1/10) is the peak width at tenth height.

[b] Resolution between the two peaks as defined by the equation:

$$R = \frac{t}{W}$$

where t is the difference in elution times between the two peaks and W is the average peak width, at the baseline, of the two peaks.

*U.S. Government Printing Office: 1991 — 648-187/40638