Designation: D 5317 – 98 (Reapproved 2003)ε1

An American National Standard

Standard Test Method for Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector[1]

This standard is issued under the fixed designation D 5317; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Warning notes were editorially moved into the standard text in August 2003.

1. Scope

1.1 This test method covers a gas chromatographic procedure for the quantitative determination of selected chlorinated acids and other acidic herbicides in water. Similar chemicals may also be determined by this test method, but it is the user's responsibility to verify the applicability of this test method to any compounds not listed in this scope. The acid form of the following compounds were interlaboratory tested using this test method, and the results were found acceptable:[2]

Analyte	Chemical Abstract Services Registry Number
Bentazon	25057-89-0
2,4-D	94-75-7
2,4-DB	94-82-6
DCPA acid metabolites [2]	
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
5-Hydroxydicamba	7600-50-2
Pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP (Silvex)	93-72-1

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

1.3 This test method has been validated in an interlaboratory test for reagent water and finished tap water. The analyst should recognize that precision and bias reported in Section 18 may not be applicable to other waters.

1.4 This test method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this test method using the procedure described in 19.3. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.5 Analytes that are not separated chromatographically, that is, 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 exists (16.6, 16.7, and 16.8).

1.6 When this test method is used to analyze unfamiliar samples for any or all of the analytes given in 1.1, analyte identifications must be confirmed by at least one additional qualitative technique.

1.7 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Sections 6, 8, 9, and 10.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] DCPA monoacid and diacid metabolites are included in the scope of this test method; DCPA diacid metabolite is used for validation studies.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data[4]
D 5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[5]
2.2 *EPA Standard:*
Method 515.1, Revision 4.0, Methods for the Determination of Organic Compounds in Drinking Water[6]
2.3 *OSHA Standard:*
29 CFR 1910 OSHA Safety and Health Standards, General Industry[7]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *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.

3.2.1.1 *Discussion*—The internal standard must be an analyte that is not a sample component.

3.2.2 *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.

3.2.2.1 *Discussion*—The purpose of a surrogate analyte is to monitor method performance with each sample.

4. Summary of Test Method

4.1 The compounds listed in 1.1, in water samples, are converted into sodium salts by adjusting the pH to 12 with sodium hydroxide solution (240 g/L) and shaking for 1 h. Extraneous neutral material is removed by extraction with methylene chloride. The sample is acidified, the acids are extracted with ethyl ether and converted to methyl esters using diazomethane. After the excess reagent is removed, the methyl esters are determined by capillary column GC using an electron capture (EC) detector. Other detection systems, such as microcoulometric and electrolytic conductivity, are not as sensitive as EC for measurement of chlorinated acid esters but are more specific and less subject to interferences. A mass spectrometer may also be used as a detector.

4.2 This test method provides a magnesium silicate[8] cleanup procedure to aid in the elimination of interferences that may be present.

5. Significance and Use

5.1 Chlorinated phenoxyacid herbicides, and other organic acids are used extensively for weed control. Esters and salts of 2,4-D and silvex have been used as aquatic herbicides in lakes, streams, and irrigation canals. Phenoxy acid herbicides can be toxic even at low concentrations. For example, the 96 h, TL_m for silvex is 2.4 mg/L for bluegills **(1)**[9]. These reasons make apparent the need for a standard test method for such compounds in water.

6. Interferences

6.1 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 19.2.

6.1.1 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 thoroughly rinsing with dilute acid, tap, and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 1 h. Do not heat volumetric ware. 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. Thermally stable materials such as PCBs may not be eliminated by this treatment.

6.1.2 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.)

6.2 The acid forms of the analytes are strong organic acids that react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with hydrochloric acid (1 + 9) and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte loses due to adsorption.

6.3 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.

6.4 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, which 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.

[4] Discontinued. See 2001 *Annual Book of ASTM Standards*, Vol 11.01.
[5] Discontinued, replaced by D 5847. See 2001 *Annual Book of ASTM Standards*, Vol 11.01.
[6] EPA/600/4-88/039, 1989, available from Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268.
[7] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.
[8] Florisil, a trademark of, and available from, Floridin Co., 2 Gateway Center, Pittsburgh, PA 15222, or its equivalent, has been found satisfactory for this purpose.
[9] The boldface numbers in parentheses refer to the list of references at the end of this test method.

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)**.

6.5 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.

6.6 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all analytes listed in Table 1 are not resolved from each other on any one column, that is, one analyte of interest may be an interferent 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 Section 16 can be used to overcome many of these interferences. Positive identifications should be confirmed. See 16.6, 16.7, and 16.8.

6.7 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.

7. Apparatus and Equipment

7.1 *Sample Bottle*—Borosilicate amber, 1-L volume with graduations, fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. The container must be washed and dried as described in 6.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets and extracted with methanol overnight prior to use.

7.2 *Glassware*.

7.2.1 *Separatory funnel*, 2000-mL, with TFE-fluorocarbon stopcocks, ground glass or TFE-fluorocarbon stoppers.

7.2.2 *Tumbler bottle*, 1.7-L with TFE-fluorocarbon lined screw cap. Cap liners are cut to fit from sheets and extracted with methanol overnight prior to use.

7.2.3 *Concentrator tube*, Kuderna-Danish (K-D), 10 or 25-mL, graduated. Calibration must be checked at the volumes employed in the procedure. Ground-glass stoppers are used to prevent evaporation of extracts.

7.2.4 *Evaporative flask*, K-D, 500-mL. Attach to concentrator tube with springs.

7.2.5 *Snyder column*, K-D, three ball macro.

7.2.6 *Snyder column*, K-D, two ball micro.

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

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

7.3 *Boiling Stone*, TFE-fluorocarbon.

7.4 *Water Bath*, heated, capable of temperature control (±2°C). The bath should be used in a hood.

TABLE 1 Retention Times and Estimated Method Detection Limits for Method Analytes

Analyte	CAS No.	Retention Time[A] (min)		EDL[B]
		Primary	Confirmation	
3,5-Dichlorobenzoic acid	51-36-5	18.6	17.7	0.061
DCAA (surrogate)	19719-28-9	22.0	14.9	...
Dicamba	1918-00-9	22.1	22.6	0.081
Dichlorprop	120-36-5	25.0	25.6	0.26
2,4-D	94-75-7	25.5	27.0	0.2
DBOB (int. std.)	10386-84-2	27.5	27.6	...
Pentachlorophenol	87-86-5	28.3	27.0	0.076
2,4,5-TP	93-72-1	29.7	29.5	0.075
5-Hydroxydicamba	7600-50-2	30.0	30.7	0.04
2,4,5-T	93-76-5	30.5	30.9	0.08
2,4-DB	94-82-6	32.2	32.2	0.8
Bentazon	25057-89-0	33.3	34.6	0.2
Picloram	1918-02-1	34.4	37.5	0.14
DCPA acid metabolites[C]	...	35.8	37.8	0.02

[A] Columns and analytical conditions are described in 7.7.1 and 7.7.2

[B] Estimated method detection limit, µg/L, determined from 7 replicate analyses of a reagent water fortified with analyte at a concentration level yielding signal-to-noise of 5:1. EDL is defined as the standard deviation × student's t (99 % C.I., n-1 degrees of freedom).

[C] DCPA monoacid and diacid metabolites are included in the scope of this test method; DCPA diacid metabolite is used for validation studies.

7.5 *Diazomethane Generator*—Assemble from two 20- by 155-mm test tubes, two neoprene rubber stoppers, and a source of nitrogen as shown in Fig. 1.

7.6 *Glass Wool*, acid washed and heated at 450°C.

7.7 *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 test method analytes using the columns and analytical conditions described below.

7.7.1 *Column 1 (Primary Column)*, 30-m long by 0.25-mm inside diameter (I.D.) DB-5 bonded fused silica column, 0.25-µm film thickness. Establish helium carrier gas flow at 30

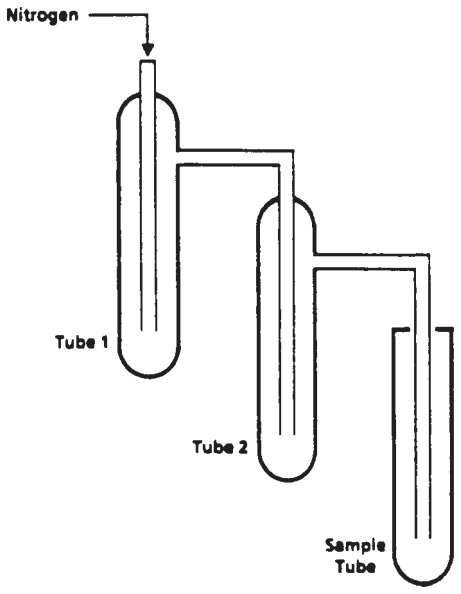

FIG. 1 Gaseous Diazomethane Generator

cm/s linear velocity and program oven temperature from 60°C to 300°C at 4°C/m. Data presented in this test method were obtained using this column (Table 1). The injection volume is 2 µL splitless mode with 45 s delay. The injector temperature is 250°C and the detector is 320°C. Alternative columns may be used in accordance with the provisions described in 19.3.

7.7.2 *Column 2 (Confirmation Column)*, 30-m long by 0.25-mm I.D. DB-1701 bonded fused silica column, 0.25-µm film thickness. Establish helium carrier gas flow at 30 cm/s linear velocity and program oven temperature from 60°C to 300°C at 4°C/m.

7.7.3 *Detector*, electron capture (ECD). 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 test method. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in 19.3.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents to the American Chemical Society, where such specifications are available[10]. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Except as otherwise indicated, references to water shall be understood to mean water conforming to Specification D 1193, Type II. Additionally, the water shall be free of the interferences described in Section 6.

8.3 *Acetone*, pesticide quality.

8.4 *Diazomethane Esterification Reagents*.

8.4.1 *Diethylene Glycol Monoethyl Ether*, reagent grade.[11]

8.4.2 *N-methyl-N-nitroso-paratoluenesulfonamide*, ACS grade.[12]

8.4.3 *N-methyl-N-nitroso-paratoluenesulfonamide solution*—Prepare a solution containing 10 g N-methylN-nitroso-paratoluenesulfonamide in 100 mL of 50:50 by volume mixture of ethyl ether and diethylene glycol monoethyl ether. This solution is stable for one month or longer when stored at 4°C in an amber bottle with a TFE-fluorocarbon-lined screw cap.

8.4.4 *Diethyl Ether*, reagent grade, redistilled in glass after refluxing over granulated sodium-lead alloy for 4 h. (**Warning—**Use immediately, or if stored, test for ether peroxides by test paper,[13] or other suitable means. If present, repeat reflux and distillation.)

8.5 *4,4′′ Dibromooctafluorobiphenyl* (DBOB), 99 % purity, for use as internal standard.

8.6 *2,4 Dichlorophenylacetic Acid* (DCAA), 99 % purity, for use as surrogate standard.

8.7 *Ethyl Acetate*, pesticide quality.

8.8 *Magnesium Silicate*, PR grade (60 to 100 mesh) purchased activated at 1250°F (650°C) and continuously stored at 130°C.

8.9 *Glass Wool*, acid washed.

8.10 *Herbicide Standards*—Acids and methyl esters, analytical reference grade.

8.11 *Hexane*, pesticide quality.

8.12 *Mercuric chloride*.

8.13 *Methyl-t-butyl Ether*, pesticide quality.

8.14 *Methylene Chloride*, pesticide quality.

8.15 *Potassium Hydroxide Solution* (37 g/100 mL)—Dissolve 37 g of potassium hydroxide (KOH) in water, mix and dilute to 100 mL.

8.16 *Silicic Acid*.

8.17 *Sodium Chloride* (NaCl), heat-treated in a shallow tray at 450°C for a minimum of 4 h to remove any potential interfering organic substances.

8.18 *Sodium Hydroxide Solution* (240 g/L)—Dissolve 240 g of sodium hydroxide (NaOH) in water, mix and dilute to 1 L.

8.19 *Sodium Sulfate, Acidified*—Slurry 100 g of the sodium sulfate that has been heat treated in a shallow tray at 450°C for a minimum of 4 h with sufficient diethyl ether to just cover the solid. Add 0.1 mL of concentrated sulfuric acid (sp gr 1.84) and mix thoroughly. Remove the ether with vacuum. Ensure that a pH below 4 can be obtained from mixing 1 g of the solid with 5 mL of water. Store continuously at 130°C.

8.20 *Sodium Thiosulfate*, anhydrous ($Na_2S_2O_3$), reagent grade.

8.21 *Standard Solution, Stock* (1.00 µg/µL)—Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

8.21.1 Prepare stock standard solutions by weighing approximately 0.0100 g of pure material to three significant figures. Dissolve the material in MTBE and dilute to volume in a 10-mL volumetric flask. Larger volumes may be prepared 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.

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

8.21.3 Replace stock standard solutions after two months or sooner if comparison with laboratory fortified blanks, or quality control sample indicates a problem.

[10] "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society (ACS), Washington, DC. For suggestions on the testing of reagents not listed by the ACS, see "Analar Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

[11] Carbitol, a registered trademark of and available from Sigma Chemical Co., P.O. Box 14508, St Louis, MO 63178-9916, or its equivalent, has been found suitable for this purpose.

[12] Diazald, a registered trademark, is available from Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, WI 53233, and has been found satisfactory for this purpose.

[13] EM Quant, a trademark of, and available from, EM Laboratories, Inc., 500 Executive Blvd., Elmsford, NY 10523, or its equivalent, has been found satisfactory for this purpose.

8.22 *Standard Solution, Internal*—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 quality control in Section 19 indicates a problem. Note that DBOB has been shown to be an effective internal standard for the test method analytes **(4)**, but other compounds may be used if the quality control requirements in Section 19 are met.

8.23 *Surrogate Standard Solution*—Prepare a surrogate standard solution by weighing approximately 0.0010 g of pure DCAA to three significant figures. 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 quality control described in Section 19 indicates a problem.

NOTE 1—DCAA has been shown to be an effective surrogate standard for the method analytes **(4)**, but other compounds may be used if the quality control requirements in 19.4 are met.

8.24 *Sulfuric Acid Solution* (335 + 665)—Carefully add, with constant mixing, 335 mL of concentrated sulfuric acid to 665 mL of water.

8.25 *Toluene*, pesticide quality.

8.26 *Hydrochloric Acid* (HCl) (1 + 9)—Carefully add, with constant mixing, 100 mL of concentrated HCl to 900 mL of water.

9. Hazards

9.1 The toxicity or carcinogenicity of each reagent used in this test 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 test 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 (29 CFR 1910) **(5, 6)** for the information of the analyst.

9.2 *Diazomethane*—A toxic carcinogen that can explode under certain conditions. The following precautions must be followed:

9.2.1 Use only a well ventilated hood—do not breathe vapors.

9.2.2 Use a safety screen.

9.2.3 Use mechanical pipetting aids.

9.2.4 Do not heat above 90°C—Explosion may result.

9.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers—Explosion may result.

9.2.6 Store away from alkali metals—Explosion may result.

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

9.2.8 The diazomethane generation apparatus used in the esterification procedures 13.2 produces micromolar amounts of diazomethane to minimize safety hazards.

9.3 *Ethyl ether*, pesticide quality, redistilled in glass, if necessary.

9.3.1 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.

9.3.2 Must be free of peroxides as indicated by test strips.[13] (**Warning—**When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.)

10. Sample Collection, Preservation, and Storage

10.1 Collect the sample in accordance with Practice D 3370 in an amber glass bottle. Do not prerinse the bottle with sample before collection.

10.2 Add mercuric chloride to the sample bottle in an amount to produce a concentration of 10 mg HgCl by adding 1 mL of a 10 mg HgCl/mL solution to the sample bottle at the sampling site, or in the laboratory before shipping to the sampling site. (**Warning—**Mercuric chloride is highly toxic. If the use of another bacteriacide can be shown to be equivalent to $HgCl_2$, it can be used provided all quality control criteria in Sections 18 and 19 are met.)

10.3 Test for the presence of chlorine with potassium iodide-starch test paper previously moistened with dilute acid. Darkening of the test paper indicates the presence of chlorine (and a few other oxidizing materials). Add 80 mg $Na_2S_2O_3$ to the bottle before adding the sample.

10.4 After the sample is collected in the bottle containing preservative, seal the bottle and shake vigorously for 1 min.

10.5 Immediately store the sample at 4°C away from light 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 **(4)**. 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.

11. Calibration

11.1 Establish GC operating parameters equivalent to those indicated in 7.7. The GC system may be calibrated using either the internal standard technique (11.2) or the external standard technique (11.3).

NOTE 2—Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

11.2 *Internal Standard Calibration Procedure*—Select one or more internal standards compatible in analytical behavior to the compounds of interest. Demonstrate that the measurement

of the internal standard is not affected by test method or matrix interferences. DBOB has been identified as a suitable internal standard.

11.2.1 Prepare calibration standards at a minimum of three (five are recommended) 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 13.2 or 13.3. The lowest standard should represent analyte concentrations near, but above, the respective estimated detection levels (EDLs). The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector (Table 1).

11.2.2 Analyze each calibration standard according to the procedure (Section 16). 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 the following equation:

$$RF = \frac{(A_s)\,(C_{is})}{(A_{is})\,(C_s)} \quad (1)$$

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, and
C_s = concentration of the analyte to be measured, µg/L.

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

11.2.4 Verify the working calibration curve or *RF* 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 %, repeat the test using a fresh calibration standard. If the repetition also fails, generate a new calibration curve for that analyte using freshly prepared standards.

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

11.2.6 Verify calibration standards periodically, at least quarterly is recommended, 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.

11.3 *External Standard Calibration Procedure*:

11.3.1 Prepare calibration standards at a minimum of three (five are recommended) 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 (13.2 or 13.3). The lowest standard should represent analyte concentrations near, but above, the respective EDL (Table 1). The remaining standards should bracket the analyte concentrations expected in the sample extracts, or should define the working range of the detector.

11.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Section 16 and tabulate response (peak height or area) versus the concentration 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), assume linearity through the origin and put the average ratio or calibration factor in place of a calibration curve.

11.3.3 Verify the working calibration curve or calibration factor 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 h), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response is by more than ±20 %, repeat the test 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 11.3.4.

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

11.3.5 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.

12. Procedure

12.1 *Manual Hydrolysis, Preparation, and Extraction*:

12.1.1 Add preservative to every blank sample and quality-control check the standard. Mark the water meniscus on the side of the sample bottle for later determination of sample volume (12.1.9). Pour the entire sample into a 2-L separatory funnel. Fortify sample with 50 µL of the surrogate standard solution.

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

12.1.3 Add 17 mL of NaOH solution (240 g/L) 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 NaOH (240 g/L). Let the sample sit at room temperature for 1 h, and shake the separatory funnel and contents periodically.

12.1.4 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.

12.1.5 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.

12.1.6 Add 17 mL of H_2SO_4 solution (335 + 665) 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 H_2SO_4 solution (335 + 665).

12.1.7 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 either a 500-mL round-bottom flask or a 500-mL Erlenmeyer flask containing approximately 10 g of acidified anydrous sodium sulfate. Periodically, vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for approximately 2 h.

12.1.8 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 round-bottom or Erlenmeyer flask. Perform a third extraction with 60 mL of ethyl ether in the same manner.

12.1.9 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.

12.2 *Automated Hydrolysis, Preparation, and Extraction*:

12.2.1 Follow the fortification and preservation procedures given in 12.1.1. 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.

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

12.2.3 Add 17 mL of NaOH solution (240 g/L) 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 NaOH (240 g/L). Shake sample for 1 h using the appropriate mechanical mixing device.

12.2.4 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 h. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

12.2.5 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.

12.2.6 Add 17 mL of H_2SO_4 solution (335 + 665) 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 H_2SO_4 solution (335 + 665).

12.2.7 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 h. Complete and thorough mixing of the organic and aqueous phases should be observed at least 2 min after starting the mixing device.

12.2.8 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 Erlenmeyer or 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 h.

12.2.9 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.

12.3 *Extract Concentration*:

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

12.3.2 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 flask and funnel with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

12.3.3 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 the 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.

12.3.4 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 concentration 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. If the gaseous diazomethane procedure (13.2) is to be used for esterification, rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. If diazomethane solution is to be used (13.3) rinse the walls of the concentrator tube while adjusting the volume to 4.5 mL with MTBE.

13. Esterification

13.1 Two methods are described for using deazomethane as the esterifications reagent.

13.2 *Gaseous Diazomethane Procedure*:

13.2.1 Assemble the diazomethane generator (Fig. 1) in a hood.

13.2.2 Add 5 mL of ethyl ether to Tube 1. Add 1 mL of ethyl ether, 1 mL of carbitol, 1.5 mL of aqueous KOH solution (37 g/100 mL), and 0.2 g N-methyl-N-nitroso-paratoluenesulfonamide 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. The presence of color or particulates can obscure the yellow color in some samples. Evolution of N_2 gas in 13.3.5 will indicate that sufficient diazomethane was present to complete the reaction. Repeat methylation procedure if necessary.

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

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

13.3 *Diazomethane Solution Procedure*:

13.3.1 Assemble the diazomethane generator (Fig. 2) in a hood. The collection vessel is a 10 or 15-mL vial, equipped with a TFE-fluorocarbon-lined screw cap and maintained at 0 to 5°C.

13.3.2 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 to 10 mL/min. Add 2 mL N-methyl-N-nitroso-paratoluenesulfonamide solution (8.4.3) and 1.5 mL of KOH (37 g/100 mL) 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. The vial should be sealed with PTFE-lined cap and the vial stored inside a sealed glass vessel. When stored at 0 to 5°C, this diazomethane solution may be used over a period of 48 h.

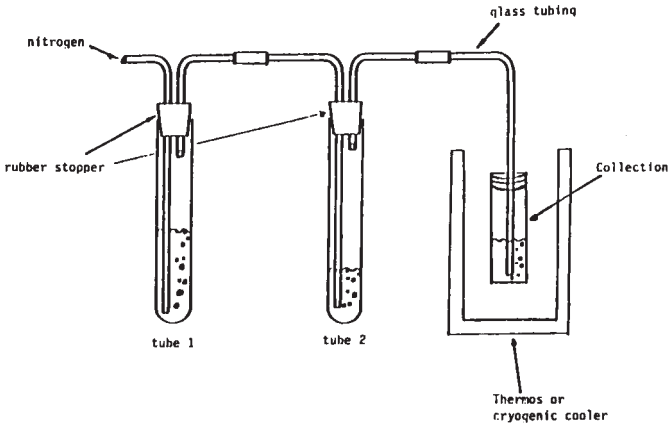

FIG. 2 Diazomethane Solution Generator

13.3.3 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, no more than once.

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

13.3.5 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 has stopped (approximately 20 min). Adjust the sample volume to 5.0 mL with MTBE.

14. Magnesium Silicate Separation

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

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

14.3 Apply 5 mL methylated sample to the magnesium silicate leaving silicic acid in the tube. Collect eluate in K-D tube.

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

14.5 If necessary, diluate eluate to 10 mL with 5 % methanol in MTBE.

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

15. Extract Storage

15.1 Store extracts at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days **(7)**; however, the analyst should verify appropriate extract holding times applicable to the samples under study.

16. Chromatography

16.1 The recommended operating conditions for the GC are summarized in 7.7. Included in Table 1 are retention times observed using this test method. Other GC columns, chromatographic conditions, or detectors may be used if the requirements of 19.3 are met.

16.2 Calibrate the system daily as described in Section 11. The standards and extracts must be in MTBE.

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

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

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

16.6 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.

16.7 Base the width of the retention time window used to make identifications upon measurements of actual retention time variations of standards over the course of a day. Use three times the standard deviation of a retention time to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

16.8 Identification requires expert judgment when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (that is, 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) employ appropriate alternative techniques to help confirm peak identification. For example, more positive identification may be made by the use of an alternative detector that operates on a chemical/physical principle different from that originally used, for example, mass spectrometry, or the use of a second chromatography column. A suggested alternative column is described in 7.7.2.

17. Calculation

17.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Section 11.

17.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the response factor (RF) determined in 11.2.2 and Eq 2, or determine sample concentration from the calibration curve.

$$C\ (\mu g/L) = \frac{(A_s)\ (I_{is})}{(A_{is})\ (RF)\ (V_o)} \quad (2)$$

where:

A_s = response for the parameter to be measured,
A_{is} = response for the internal standard,
I_{is} = amount of internal standard added to each extract, µg, and
V_o = volume of water extracted, L.

17.3 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 11.3. The concentration (C) in the sample can be calculated from Eq 3.

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

where:

A = amount of material injected, ng,
V_i = volume of extract injected, µL,
V_t = volume of total extract, µL, and
V_s = volume of water extracted, µL.

18. Precision and Bias [14]

18.1 The collaborative study for performance evaluation of this test method was conducted in accordance with Practice D 2777 – 86. EPA Method 515.1 was used to generate precision and bias data shown in Table 2 and Table 3

[14] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19–1150.

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TABLE 2 Summary Statistics and Regression Equations for the 12 Quantitative Analytes Tested in the Collaborative Study

Analyte	C [A]	Reagent Water				Finished Drinking Water			
		X [B]	s_R [C]	s_r [D]	Regr. Equations	X	s_R	s_r	Regr. Equations
Bentazon	0.40 [E]	0.40	0.01	0.09	X = 0.758C + 0.094	0.52	0.25	0.12	X = 0.849C + 0.172
	0.60	0.55	0.10	...	s_R = 0.196X − 0.049	0.67	0.15	...	s_R = 0.226X + 0.008
	2.39 [E]	2.03	0.10	0.22	s_r = 0.115X + 0.035	1.91	0.87	0.88	s_r = 0.079X + 0.331 [F]
	2.98	1.79	0.50	...	...	2.98	0.55	...	...
	7.97	6.51	0.94	0.98	...	7.31	1.48	0.95	...
	9.96	8.38	1.98	...	...	8.49	2.35	...	...
2,4-D	0.40 [E]	0.38	0.13	0.09	X = 0.913C + 0.007	0.61	0.33	0.11	X = 0.955C + 0.244
	0.60	0.53	0.08	...	s_R = 0.106X + 0.070	0.83	0.23	...	s_R = 0.056X + 0.254
	2.39	2.18	0.07	0.33	s_r = 0.104X + 0.050	2.85	0.33	0.42	s_r = 0.094X + 0.048
	2.98	2.89	0.38	...	...	3.28	0.70	...	...
	7.95	7.45	1.46	0.82	...	7.20	0.77	0.56	...
	9.94	8.50	1.28	...	...	8.64	0.64	...	...
2,4-DB	8.00	8.17	1.21	1.61	X = 0.988C + 0.152	7.78	1.99	1.42	X = 0.884C + 1.128
	12.00	11.54	1.98	...	s_R = 0.161X − 0.050	12.15	2.33	...	s_R = 0.214X + 0.215
	20.00	20.33	2.96	1.39	s_r = 0.073X + 0.770	20.22	6.55	4.36	s_r = 0.206X − 0.560
	24.00	23.63	3.56	...	...	24.57	3.24	...	...
	32.00	33.81	3.91	4.58	...	28.56	5.70	5.41	...
	40.00	37.56	4.46	...	...	31.63	8.46	...	...
3,5 Dichlorobenzoic acid	0.12	0.10	0.06	0.02	X = 0.910C − 0.008	0.14	0.06	0.09	X = 0.891C + 0.046
	0.18	0.16	0.08	...	s_R = 0.273X + 0.036	0.24	0.12	...	s_R = 0.200X + 0.048 [G]
	0.49	0.44	0.18	0.04	s_r = 0.070X + 0.012	0.44	0.18	0.09	s_r = 0.007X + 0.080
	0.61	0.54	0.23	...	...	0.62	0.16	...	...
	1.22	1.05	0.16	0.09	...	1.12	0.18	0.08	...
	1.58	1.50	0.45	...	...	1.42	0.26	...	...
DCPA-diacid	0.40	0.28	0.11	0.13	X = 0.871C − 0.084	0.34 [E]	0.06	0.06	X = 0.737C + 0.046
	0.60	0.43	0.20	...	s_R = 0.158X + 0.075	0.50 [E]	0.23	...	s_R = 0.210X + 0.022
	1.00	0.72 [E]	0.06	0.05	s_r = 0.12 [F]	0.54 [E H]	0.27 [H]	0.16	s_r = 0.259X − 0.039
	1.20	0.91	0.24	...	...	0.84 [E]	0.10	...	...
	1.60	1.35	0.29	0.18	...	1.30 [E]	0.30	0.29	...
	2.00	1.83	0.46	...	...	1.54 [E]	0.34	...	...
Dicamba	0.16	0.14	0.05	0.03	X = 0.998C − 0.020	0.19	0.02	0.03	X = 0.946C + 0.038
	0.24	0.25	0.03	...	s_R = 0.055X + 0.037 [G]	0.26	0.05	...	s_R = 0.142X − 0.001
	0.96	0.95	0.11	0.08	s_r = 0.045X + 0.022	0.97	0.10	0.12	s_r = 0.100X + 0.008
	1.21	1.18	0.13	...	...	1.25	0.15	...	...
	3.22	3.09	0.27	0.15	...	3.15	0.50	0.34	...
	4.02	4.02	0.12	...	...	3.46	0.56	...	...
Dichlorprop	0.80	0.84	0.09	0.13	X = 0.956C + 0.082	1.12	0.42	0.28	X = 0.905C + 0.424
	1.19	1.17	0.22	...	s_R = 0.144X − 0.016	1.57	0.42	...	s_R = 0.022X + 0.393 [G]
	2.00	2.20	0.11	0.29	s_r = 0.084X + 0.060	2.13	0.61	0.33	s_r = 0.063X + 0.200
	2.40	2.44	0.34	...	...	2.69	0.06	...	...
	3.19	3.08	0.48	0.28	...	3.51	0.46	0.46	...
	3.99	3.60	0.61	...	...	3.71	0.75	...	...
5-Hydroxydicamba	0.08 [E]	0.11	0.03	0.02	X = 0.957C + 0.038	0.30 [E]	0.26	0.08	X = 1.038C + 0.189
	0.12 [E]	0.16	0.03	...	s_R = 0.308X − 0.011	0.26	0.22	...	s_R = 0.223X + 0.180
	0.32 [E]	0.32	0.08	0.06	s_r = 0.187X − 0.007	0.39	0.25	0.20	s_r = 0.271X + 0.010 [G]
	0.40 [E]	0.44	0.11	...	...	0.63 [E]	0.32	...	...
	0.80 [E]	0.85	0.24	0.17	...	1.16 [E]	0.40	0.23	...
	1.04 [E]	0.91	0.37	...	...	1.54 [E]	0.68	...	...
Pentachlorophenol	0.20	0.20	0.01	0.03	X = 0.827C + 0.040	0.19	0.04	0.04	X = 0.832C + 0.019
	0.30	0.29	0.05	...	s_R = 0.239X − 0.036	0.24	0.06	...	s_R = 0.113X + 0.022
	0.50	0.47	0.06	0.07	s_r = 0.05 [F]	0.45	0.02	0.03	s_r = 0.04 [C]
	0.60	0.57	0.11	...	...	0.58	0.04	...	...
	0.80	0.67	0.13	0.04	...	0.67	0.13	0.04	...
	1.00	0.81	0.17	...	...	0.78	0.16	...	...
Picloram	0.27	0.23	0.07	0.02	X = 1.079C − 0.064	0.38	0.07	0.11	X = 1.132C + 0.087
	0.40	0.35	0.07	...	s_R = 0.352X − 0.020	0.57	0.19	...	s_R = 0.399X − 0.068
	1.06	1.17	0.37	0.28	s_r = 0.181X − 0.030	1.26	0.59	0.26	s_r = 0.145X + 0.042
	1.33	1.45	0.69	...	...	1.66	0.36	...	...
	2.66	2.83	0.96	0.38	...	3.03	1.02	0.54	...
	3.46	3.33	0.85	...	...	3.93	1.71	...	...
2,4,5-T	0.16	0.19	0.06	0.03	X = 0.902C + 0.033	0.18	0.04	0.03	X = 0.897C + 0.048
	0.24	0.22	0.04	...	s_R = 0.067X + 0.035 [G]	0.28	0.01	...	s_R = 0.190X − 0.008
	0.97	0.89	0.04	0.09	s_r = 0.084X + 0.020	0.98	0.26	0.23	s_r = 0.204X − 0.018
	1.21	1.20	0.10	...	...	1.25	0.20	...	...
	3.23	2.97	0.18	0.33	...	2.84	0.45	0.57	...
	4.04	3.66	0.18	...	...	3.04	0.70	...	...
2,4,5-TP (Silvex)	0.38	0.42	0.07	0.06	X = 0.961C + 0.056	0.50	0.09	0.23	X = 0.935C + 0.180
	0.58	0.59	0.10	...	s_R = 0.137X + 0.015	0.79	0.28	...	s_R = 0.195X + 0.034
	1.54	1.64	0.22	0.13	s_r = 0.061X + 0.028	1.56	0.52	0.32	s_r = 0.027 [F]
	1.92	2.03	0.28	...	...	2.06	0.17	...	...

TABLE 2 *Continued*

Analyte	C [A]	Reagent Water				Finished Drinking Water			
		X [B]	s_R [C]	s_r [D]	Regr. Equations	X	s_R	s_r	Regr. Equations
	3.84	3.64	0.46	0.30	...	3.65	0.66	0.25	...
	4.99	4.42	0.71	...	...	4.71	0.87	...	...

[A] Spike concentration, µg/L.
[B] Mean recovery, µg/L.
[C] Overall standard deviation, µg/L.
[D] Single analyst standard deviation, µg/L.
[E] Data set contains 5 or less data points.
[F] Coefficient of determination of weighted equation was poor ($COD_w \leq 0.00$). Average standard deviation or unweighted linear regression as reported.
[G] Coefficient of determination of weighted equation was weak ($COD_w < 0.50$).
[H] Data set not used in calculation of weighted linear regression equations.

18.2 Eight laboratories participated in the study. The study design was based on Youden's nonreplicate plan for collaborative tests of analytical methods. Reagent and finished drinking water were spiked with the 12 analytes, each at six concentration levels, prepared as three Youden pairs. Analyses of the spiked reagent water evaluated the proficiency of the test method on a sample free of interferences. Analyses of the spiked finished drinking water demonstrated the suitability of the test method on a regulated matrix and served to compare the results with those of reagent water as shown in Table 2 and Table 3. Mean percent recoveries at 10 to 15 times the method detection limits ranged from 79 % to 105 % in reagent water and from 75 % to 123 % in finished drinking water. In reagent water, overall precision, RSD_R ranged from 9.6 % to 34.2 %. In finished drinking water, the RSD_R ranged from 11.9 % to 37 %. Single analyst precision RSD_r ranged from 5.8 % to 17.7 % in reagent water and 4.6 % to 27.9 % in drinking water.

19. Quality Control

19.1 As specified by Practice D 5789, the minimum quality control requirements for the analysis of organic compounds in water are verification of system calibration, verification of control at zero analyte concentration, initial demonstration of proficiency, verification of control at representative analyte concentration, assessment of precision, assessment of bias, and maintenance of interlaboratory traceability. Also, specific to this test method are the 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 used), and daily assessment of instrument performance.

19.2 *Verification of System Calibration*—These requirements are satisfied by the calibration procedure in Section 11.

19.3 *Verification of Control at Zero Analyte Concentration*—Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control by the analysis of a reagent water blank through the entire test method. Each time a set of samples is extracted, reagents are changed, or at the beginning of each day, whichever occurs first, a reagent water blank must be analyzed. If a peak is detected within the retention window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

19.4 *Initial Demonstration of Proficiency*—This demonstration is a requirement for the new test method user to confirm their ability to use the test method to generate meaningful data. It is required at least once per analyst for each compound of interest.

19.4.1 Select a representative concentration for each analyte. Concentrations in Table 3 are recommended. Prepare a sample concentrate (in methanol) containing each analyte at 1000 times the selected concentration. With a syringe, add 1-mL of the concentrate to each of at least seven 1-L aliquots

TABLE 3 Precision Statistics Calculated from Regression Equations by Compound and by Water Type [A]

Analyte	µg/L [B]	Concn. % Recov [C]	Reagent Water				Finished Drinking Water				
			s_r	s_R	RSD_r	RSD_R	% Recov	s_r	s_R	RSD_r	RSD_R
Bentazon	3.0	78.8	0.30	0.41	12.8	17.5	90.5	0.65	0.71	27.5	26.2
2,4-D	3.0	91.6	0.34	0.36	12.2	13.1	103.6	0.34	0.43	11.0	14.0
2,4-DB	40.0	99.2	3.66	6.34	9.2	16.0	91.2	6.95	8.02	19.1	22.0
3,5-Dichlorobenzoic acid	1.0	90.0	0.07	0.28	8.1	30.6	98.7	0.09	0.24	9.2	25.3
DCPA-diacid	2.0	83.1	0.12	0.34	7.2	20.6	76.0	0.33	0.38	23.1	26.8
Dicamba	1.0	97.8	0.06	0.09	6.5	9.6	98.4	0.11	0.14	11.0	13.9
Dichlorprop	4.0	97.6	0.39	0.54	9.9	13.9	101.1	0.45	0.48	11.3	11.9
5-Hydroxydicamba	1.0	98.7	0.17	0.29	17.7	29.8	122.7	0.34	0.45	27.9	37.0
Pentachlorophenol	1.0	86.7	0.05	0.18	5.8	20.4	85.1	0.04	0.12	4.6	13.7
Picloram	2.0	104.7	0.35	0.72	16.7	34.2	117.6	0.38	0.87	16.2	36.9
2,4,5-T	1.0	93.2	0.10	0.10	10.5	11.0	94.5	0.18	0.17	19.3	17.9
2,4,5-TP (Silvex)	3.0	97.8	0.21	0.41	7.1	14.0	99.5	0.27	0.61	9.2	20.5
Average					10.3	19.2				15.8	22.2

[A] s_r and s_R = single-analyst and overall standard deviations, respectively. Calculated using weighted linear regression equations found in Table 2. RSD_r and RSD_R = corresponding percent relative standard deviations.
[B] Concentration value is ca. 10 to 15 times estimated MDL.
[C] Percent recovery calculated using weighted linear regression equations found in Table 2.

of reagent water and analyze each aliquot according to procedures beginning in Section 12. Calculate the mean and standard deviation of the measured concentrations and compare to the acceptable range of precision and bias found in Table 4.

19.5 *Verification of Control at Representative Analyte Concentration*:

19.5.1 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 h period), whichever is greater. The concentration of each analyte in the LFB should be 10 times the EDL (Table 1) or the MCL, whichever is less. Calculate accuracy as percent recovery (X). If the recovery of any analyte falls outside the control limits (19.5.2), that analyte is judged out of control and the source of the problem should be identified and resolved before continuing analyses.

19.5.2 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 Table 5. 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:

$$\text{upper control limit} = X + 3S \quad (4)$$

$$\text{lower control limit} = X - 3S \quad (5)$$

After each five to ten new recovery measurements, calculate new control limits using only the most recent 20 to 30 data points. These calculated control limits should never exceed those established in Table 5.

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

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

19.5.5 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 the U.S. Environmental Protection Agency. Performance evaluation studies serve as independent checks on the analyst's performance.

TABLE 5 Acceptance Limits for the Analysis of a Laboratory Quality Control Sample, as Percent of Spiked Value, %

Analyte	Spike Level [A]	Mean Recovery [B]	Overall Std. Dev. [B]	Acceptance Limits, % [C]
Bentazon	3	2.37	0.41	37–120
2,4-D	3	2.75	0.36	55–128
2,4-DB	40	39.7	6.34	52–147
3,5-Dichlorobenzoic acid	1	0.90	0.28	7–173
DCPA-diacid	2	1.66	0.34	32–134
Dicamba	1	0.98	0.09	70–126
Dichlorprop	4	3.91	0.54	57–138
5-Hydroxydicamba	1	0.99	0.29	11–187
Pentachlorophenol	1	0.87	0.18	34–140
Picloram	2	2.10	0.72	0–213
2,4,5-T	1	0.93	0.10	62–124
2,4,5-TP (Silvex)	3	2.94	0.41	57–139

[A] Spike level is 10 to 15 times the estimated method detection limit, µg/L.
[B] Derived from the regression equations for mean recovery and overall standard deviation for reagent water matrix reported in the collaborative study.
[C] Acceptance limits, as %, defined as 100 (mean recovery ±3 overall standard deviations)/spike level.

19.6 *Assessment of Precision*—The replicate analyses of samples is for the laboratory to ensure that the test method is performing the job for which it was intended and to demonstrate that provisions in the test method to address matrix effects, including subsampling procedures in the laboratory, are being properly implemented.

19.6.1 *Frequency*—The assessment of precision in a sample matrix should be conducted with a frequency equivalent to 5 % of the sample workload and samples should be selected in a manner that will evaluate all representative matrices in a reasonable time period.

19.6.2 When a high frequency of nondetects are expected, spiked replicates should be used to assess precision.

19.6.3 Calculate relative standard deviation estimates from duplicate results using the following formula:

$$\text{relative standard deviation, \%} = \left(\frac{R}{\bar{X}}\right)\left(\frac{100}{\sqrt{2}}\right) \quad (6)$$

where:
R = range of duplicates, and
X = average of duplicates.

19.6.4 Initially the relative standard deviation estimate calculated in 19.6.3 should be compared to S_r estimates from the collaborative study. Strict acceptance criteria for the first few replicates are difficult to develop due to the lack of sufficient

TABLE 4 Acceptance Criteria for Initial Demonstration of Proficiency

Analyte	Spike Concentration ug/L	Proficiency Demonstration		
		Max Acceptable Standard Deviation	Acceptance Range for Mean Recovery	Acceptance Range % Recovery
Bentazon	3.0	0.893	1.14 - 3.58	38.2 - 119.4
2,4-D	3.0	0.901	2.07 - 3.43	69.0 - 114.2
2,4-DB	40.0	9.841	19.84 - 59.52	49.6 - 148.8
3,5-Dichlorobenzoic acid	1.0	0.201	0.00 - 1.91	0.0 - 191.3
DCPA-diacid	2.0	0.349	0.38 - 2.94	19.0 - 147.2
Dicamba	1.0	0.167	0.74 - 1.21	74.3 - 121.3
Dichlorprop	4.0	1.129	2.25 - 5.56	56.2 - 139.0
5-Hydroxydicamba	1.0	0.585	0.00 - 2.11	0.0 - 211.1
Pentachlorophenol	1.0	0.134	0.26 - 1.48	25.7 - 147.7
Picloram	2.0	0.936	0.00 - 4.47	0.0 - 223.3
2,4,5-T	1.0	0.264	0.80 - 1.06	80.3 - 106.1
2,4,5-TP (Silvex)	3.0	0.555	1.56 - 4.31	51.9 - 143.7

degrees of freedom for a critical assessment. As soon as sufficient data are available, the analyst should construct control charts as described in Guide D 3856 and Practice D 4210.

19.7 *Assessment of Bias*:

19.7.1 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 than the background concentration of the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (19.5). Over time, samples from all routine sample sources should be fortified.

19.7.2 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, that is:

$$P = 100\,(X - b)/\text{fortifying concentration} \quad (7)$$

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 19.5, then the appropriate control limits would be the acceptance limits in 19.5. 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. The appropriate percentage control limits would be $P \pm 3\text{sp}$, where:

$$P = 100X/(b + \text{fortifying concentration}), \text{ and} \quad (8)$$

$$\text{sp} = 1 - (s_a^2 + s_b^2)^{1/2}/\text{fortifying concentration} \quad (9)$$

For example, if the background concentration for Analyte A is found to be 1 µg/L and the added amount is 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 µ/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:

$$[100\,(2.01\ \mu\text{g/L})/2.0\ \mu\text{g/L}] \pm 3\,(100)\,[(0.12\ \mu\text{/L})^2 + (0.20\ \mu\text{g/L})^2]^{1/2}/1\ \mu\text{g/L} = 100.5\ \% \pm 300\,(0.233) \quad (10)$$

$$= 100.5\ \% \pm 70\ \%\ \text{or}\ 30\ \%\ \text{to}\ 170\ \%\ \text{recovery of the added analyte.} \quad (11)$$

19.7.3 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 (19.5), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The results for that analyte in the unfortified sample are labeled suspect/matrix to inform that data user that the results are suspect due to matrix effects.

19.8 *Maintenance of Interlaboratory Traceability*—The periodic analysis of a certified reference material (CRM) or participation in interlaboratory proficiency studies, or both, are used to provide an independent verification of calibration and quantification practices.

19.8.1 The laboratory should analyze a CRM or participate in an interlaboratory proficiency study for the compounds of interest at least once a quarter.

19.8.2 Certified reference materials from the National Institute of Standards and Technology (NIST), or similar reference material from other agencies or reputable commercial sources may be used. Results from analysis of the independent reference material must be within the control limits specified by the outside source if available; otherwise either the criteria in 6.4 or 8.4 as appropriate. Refer to Guide D 3856 for further information on external calibration checks.

19.9 *Assessing Surrogate Recovery*:

19.9.1 When surrogate recovery from a sample or test method blank is <70 % or >130 %, check: calculations to locate possible errors; spiking solutions for degradation; contamination; and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

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

19.9.3 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.

19.10 *Assessing the Internal Standard (IS)*:

19.10.1 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 %.

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

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

19.10.2.2 If a deviation of greater than 30 % is obtained for the reinjected extract, repeat analysis of the samples beginning with Section 12, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

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

19.10.3.1 If the check standard provides a response factor (RF) within 20 % of the predicted value, then follow procedures itemized in 19.10.2 for each sample failing the IS response criterion.

19.10.3.2 If the check standard provides a response factor that deviates more than 20 % of the predicted value, recalibrate as specified in Section 12.

19.11 *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. 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 test method. If laboratory EDLs differ from those listed in this test method, concentrations of the instrument quality control standard compounds must be adjusted to be compatible with the laboratory EDLs.

19.12 The laboratory may adopt additional quality control practices for use with this test 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.

20. Keywords

20.1 electron capture; gas chromatography; herbicides; organic acid

APPENDIX

(Nonmandatory Information)

X1. Example Calculation Of Acceptance Criteria for Initial Demonstration Of Proficiency

X1.1 Maximum Acceptable Standard Deviation (S_m):

From Practice D 5789:

$$S_m = (S_o)\ (F_{0.99})^{0.5}$$

For bentazon at 3.0 ug/L in reagent water:

$$S_o = 0.115\ (0.758\ (3.0) + 0.094) + 0.035$$
$$S_o = 0.307$$

Degrees of freedom from initial demonstration of Proficiency = $n - 1 = 6$.
Degrees of freedom form interlab study = number of labs upon which S_o is based
For bentazon, two of eight labs were rejected, therefore $df = 6$.

$F_{0.99}$ = 8.47 from Table 1 in D 5789.

$$S_m = (0.307)\ (8.47)^{0.5}$$
$$S_m = 0.893$$

X1.2 Acceptance Range for Mean Recovery:

From Practice D 5789:

acceptance recovery = $X \pm t_{0.99}(S_t^2 - ((n-1)\ S_o^2)/n)^{0.5}$

For bentazon at 3.0 ug/L in reagent water:

$$S_t = 0.196\ (0.758\ (3.0) + 0.094) - 0.049$$
$$S_t = 0.415$$

$t_{0.99}$ = 4.032 from Table 2 in Practice D 5789 for six labs

acceptable recovery = $2.36 \pm 4.032\ (0.415^2 - ((6)0.307^2)/7)^{0.5}$
acceptable recovery = 2.36 ± 1.22
acceptable recovery = 1.14 – 3.58

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