METHOD 507

DETERMINATION OF NITROGEN - AND PHOSPHORUS-CONTAINING PESTICIDES IN WATER BY GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

Revision 2.1

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1.0 SCOPE AND APPLICATION

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain nitrogen- and phosphorus-containing pesticides in ground water and finished drinking water. The following compounds can be determined using this method:

Analyte	Chemical Abstract Services Registry Number
Alachlor	15972-60-8
Ametryn	834-12-8
Atraton	1610-17-9
Atrazine	1912-24-9
Bromacil	314-40-9
Butachlor	23184-66-9
Butylate	2008-41-5
Carboxin	5234-68-5
Chlorpropham	101-21-3
Cycloate	1134-23-2
Diazinon[a]*	333-41-5
Dichlorvos	62-73-7
Diphenamid	957-51-7
Disulfoton*	298-04-4
Disulfoton Sulfone*	2497-06-5
Disulfoton Sulfoxide[a]*	2497-07-6
EPTC	759-94-4
Ethoprop	13194-48-4
Fenamiphos	22224-92-6
Fenarimol	60168-88-9
Fluridone	59756-60-4
Hexazinone	51235-04-2
Merphos*	150-50-5
Methyl Paraoxon	950-35-6
Metolachlor	51218-45-2
Metribuzin	21087-64-9
Mevinphos	7786-34-7
MGK 264	113-48-4
Molinate	2212-67-1
Napropamide	15299-99-7

Analyte	Chemical Abstract Services Registry Number
Norflurazon	27314-13-2
Pebulate	1114-71-2
Prometon	1610-18-0
Prometryn	7287-19-6
Pronamide[a]*	23950-58-5
Propazine	139-40-2
Simazine	122-34-9
Simetryn	1014-70-6
Stirofos	22248-79-9
Tebuthiuron	30414-18-1
Terbacil	5902-51-2
Terbufos[a]*	13071-79-9
Terbutryn	886-50-0
Triademefon	43121-43-3
Tricyclazole	41814-78-2
Vernolate	1929-77-7

[a]Compound exhibits aqueous instability. Samples for which this compound is an analyte of interest must be extracted immediately (Sections 11.1 through 11.3).
*These compounds are only qualitatively identified. These compounds are not quantitated because control over precision has not been accomplished.

1.2 This method has been validated in a single laboratory and estimated detection limits (EDLs) and method detection limits (MDLs) have been determined for the analytes above (Section 13.0). Observed detection limits may vary among 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 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 Section 9.0.

1.4 Analytes that are not separated chromatographically, i.e., analytes which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternative technique for identification and quantitation exist (Section 11.5).

1.5 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.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample of approximately 1 L is extracted with methylene chloride by shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL during a solvent exchange to methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by Capillary Column GC with a nitrogen-phosphorus detector (NPD).

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- 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 (SA) -- 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, preserva- tion 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 (PDS) -- 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.

4.0 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 Section 9.2.

4.1.1 Glassware must be scrupulously cleaned[1]. Clean all glass- ware 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 400°C for one 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 may be 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 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 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.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Also, note that all the 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. Further processing of sample extracts may be necessary. Positive identifications should be confirmed (Section 11.5).

4.4 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.

5.0 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[2-4] for the information of the analyst.

Warning: When a solvent is purified, stabilizers added by the manufacturer may be removed thus potentially making the solvent hazardous.

6.0 EQUIPMENT AND SUPPLIES (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. Amber bottles may be used. The container must be washed and dried as described in Section 4.1.1 before use to minimize contamination. Cap liners are cut to fit from sheets (Pierce Catalog No. 012736 or equivalent) and extracted with methanol overnight prior to use.

6.2 Glassware

6.2.1 Separatory Funnel -- 2000 mL, with TFE-fluorocarbon stopcock, ground glass or TFE-fluorocarbon stopper.

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 Flask, Erlenmeyer -- 500 mL.

6.2.4 Concentrator Tube, Kuderna-Danish (K-D) -- 10 mL or 25 mL, graduated (Kontes K-570050-2525 or 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.

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

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

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

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

6.3 Separatory Funnel Shaker (Optional) -- 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. or other suppliers).

6.5 Boiling Stones -- Carborundum, #12 granules (Arthur H. Thomas Co. #1590-033 or equivalent). Heat at 400°C for 30 minutes prior to use. Cool and store in desiccator.

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 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.

6.8.1 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) or equivalent. Helium carrier gas flow is established at 30 cm/sec. linear velocity and oven temperature is programmed from 60-300°C at 4°C/min. Data presented in this method were obtained using this column. The injection volume was 2 µL in splitless mode with a 45 s delay. The injector temperature was 250°C and the detector temperature was 300°C. Alternative columns may be used in accordance with the provisions described in Section 9.4.

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

6.8.3 Detector -- Nitrogen-phosphorus (NPD).

7.0 REAGENTS AND STANDARDS

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 shelflife.

7.1 Acetone, Methylene Chloride, Methyl Tert.-Butyl Ether (MTBE) -- Distilled-in-glass quality or equivalent.

7.2 Phosphate Buffer, pH 7 -- Prepare by mixing 29.6 mL 0.1 N HCl and 50 mL 0.1 M dipotassium phosphate.

7.3 Sodium Chloride (NaCl), Crystal, ACS Grade -- Heat treat in a shallow tray at 400°C for a minimum of four hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.4 Sodium Sulfate, Granular, Anhydrous, ACS Grade -- Heat treat in a shallow tray at 400°C for a minimum of four hours to remove interfering organic substances. Store in a glass bottle (not plastic) to avoid phthalate contamination.

7.5 Sodium Thiosulfate, Granular, Anhydrous, ACS Grade.

7.6 Triphenylphosphate (TPP), 98% purity -- For use as internal standard (available from Aldrich Chemical Co.).

7.7 1,3-Dimethyl-2-nitrobenzene, 98% purity -- For use as surrogate standard (available from Aldrich Chemical Co.).

7.8 Mercuric Chloride, ACS Grade (Aldrich Chemical Co.) -- For use as a bactericide (optional- see Section 8.0).

7.9 Reagent Water -- Reagent water is defined as a 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.

7.10 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:

7.10.1 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. The stock solution for simazine should be prepared in methanol. 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.

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

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

7.11 Internal Standard Solution -- Prepare the internal standard solution by accurately weighing approximately 0.0500 g of pure TPP. Dissolve the TPP in MTBE and dilute to volume in a 100 mL volumetric flask. Transfer the internal standard solution to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Addition of 50 µL of the internal standard solution to 5 mL of sample extract results in a final TPP concentration of 5.0 µg/mL. This solution should be replaced when ongoing QC (Section 9.0) indicates a problem.

Note: TPP has been shown to be an effective internal standard for the method analytes, but other compounds may be used if the quality control requirements in Section 9.0 are met.

7.12 Surrogate Standard Solution -- Prepare the surrogate standard solution by accurately weighing approximately 0.0250 g of pure 1,3-dimethyl-2-nitrobenzene. Dissolve the 1,3-dimethyl-2-nitrobenzene in MTBE and dilute to volume in a 100 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 1,3-dimethyl-2-nitrobenzene concentration in the sample of 12.5 µg/L. Solution should be replaced when ongoing QC (Section 9.0) indicates a problem.

Note: 1,3-dimethyl-2-nitrobenzene has been shown to be an effective surrogate standard for the method analytes, but other compounds may be used if the quality control requirements in Section 9.0 are met.

7.13 Laboratory Performance Check Solution -- Prepare the laboratory performance check solution by adding 5 µL of the vernolate stock solution, 0.5 mL of the bromacil stock solution, 30 µL of the prometon stock solution, 15 µL of the atrazine stock solution, 1.0 mL of the surrogate solution, and 500 µL of the internal standard solution to a 100 mL volumetric flask. Dilute to volume with MTBE and thoroughly mix the solution. Transfer to a TFE-fluorocarbon-sealed screw cap bottle and store at room temperature. Solution should be replaced when ongoing QC (Section 9.0) indicates a problem.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Grab samples must be collected in glass containers. Conventional sampling practices[5] should be followed; however, the bottle must not be prerinsed with sample before collection.

8.2 Sample Preservation and Storage

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

8.2.2 After the sample is collected in a bottle containing sodium thiosulfate, seal the bottle and shake until dissolved.

8.2.3 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction. Preservation study results indicated that most method analytes present in samples were stable for 14 days when stored under these conditions. The analytes disulfoton sulfoxide, diazinon, pronamide, and terbufos exhibited significant aqueous instability, and samples to be analyzed for these compounds must be extracted immediately. The analytes carboxin, EPTC, fluridone, metolachlor, napropamide, tebuthiuron, and terbacil exhibited recoveries of less than 60% after 14 days. Analyte stability may be affected by the matrix; therefore, the analyst should verify that the preservation technique is applicable to the samples under study.

8.2.4 All performance data presented in this method are from samples preserved with mercuric chloride. No suitable preservation agent (biocide) has been found other than mercuric chloride. However the use of mercuric chloride is not required due to its toxicity and potential harm to the environment.

8.2.5 In some circumstances where biological degradation of target pesticides might be expected, use of mercuric chloride may be appropriate to minimize the possibility of false-negative results. If mercuric chloride is to be used, add it (see Section 7.8) to the sample bottle in amounts to produce a concentration of 10 mg/L. Add 1 mL of a solution containing 10 mg/mL 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.

8.3 Extract Storage -- Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, a 14-day maximum extract storage time is recommended. The analyst should verify appropriate extract holding times applicable to the samples under study.

9.0 QUALITY CONTROL

9.1 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. A method detection limit (MDL) must also be determined for each analyte.

9.2 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 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.

9.3 Initial Demonstration of Capability

9.3.1 Select a representative fortified concentration (about 10 times EDL or at a concentration in the middle of the calibration range established in Section 10.0) for each analyte. Prepare a standard concentrate containing each analyte at 1000 times the selected concentration. With a syringe, add 1 mL of the concentrate to each of four to seven 1 L aliquots of reagent water, and analyze each aliquot according to procedures beginning in Section 11.0.

9.3.2 For each analyte, the mean recovery value for these samples must fall in the range of R ±30% using the values for R for reagent water in Table 2. The RSD for these measurements must be 20% or less. For those compounds that meet the acceptance criteria, performance is considered acceptable. For those compounds that fail these criteria, this procedure must be repeated using fresh replicate samples until satisfactory performance has been demonstrated.

9.3.3 For each analyte, determine the MDL. Prepare a minimum of seven LFBs at a low concentration. The fortification concentration in Table 3 may be used as a guide, or use calibration data obtained in Section 10.0 to estimate a concentration for each analyte that will produce a peak with a three to five times signal to noise response. Extract and analyze each replicate according to Sections 11.0 and 12.0. It is recommended that these LFBs be prepared and analyzed over a period of several days, so that day-to-day variations are reflected in the precision measurement. Calculate mean recovery and standard deviation for each analyte. Use the equation given in Table 3 to calculate the MDL.

9.3.3 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.

9.4 The analyst is permitted to modify GC columns, GC conditions, 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 9.3.

9.5 Assessing Surrogate Recovery

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

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

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

9.6 Assessing the Internal Standard

9.6.1 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%.

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

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

9.6.2.2 If a deviation of greater than 30% is obtained for the reinjected extract, analysis of the sample should be repeated beginning with Section 11.0, provided the sample is still available. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

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

9.6.3.1 If the check standard provides a response factor (RF) within 20% of the predicted value, then follow procedures itemized in Section 9.6.2 for each sample failing the IS response criterion.

9.6.3.2 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 9.0.

9.7 Assessing Laboratory Performance -- Laboratory Fortified Blank (LFB)

9.7.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period) whichever is greater. Ideally, the fortified concentration of each analyte in the LFB should be the same concentration selected in Section 9.3.1. Calculate accuracy as percent recovery (X_i). If the recovery of any analyte falls outside the control limits (see Section 9.7.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.7.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20-30 analyses, the laboratory should assess laboratory performance against the control limits in Section 9.3.2 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:

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

After each five to 10 new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points. These calculated control limits must <u>not</u> exceed the fixed limits listed in Section 9.3.2.

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

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

9.8 Assessing Analyte Recovery -- Laboratory Fortified Sample Matrix

9.8.1 The laboratory must add a known concentration to a minimum of 5% of the routine samples or one sample per set, whichever is greater. The fortified 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 (Section 9.7). Over time, samples from all routine sample sources should be fortified.

9.8.2 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 reagent water recoveries listed in Table 2. The calculated value of P must fall in the range of R ±35%. If P exceeds this control limit the results for that analyte in the unfortified matrix must be listed as suspect due to matrix interference.

9.9 Assessing Instrument System -- Laboratory Performance Check (LPC)

9.9.1 After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. LPC sample components and performance criteria are listed in Table 4. 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. The purpose of the sensitivity requirement is to monitor the stability of instrument sensitivity, not as an absolute sensitivity requirement. If laboratory EDLs differ from those listed in this method, concentrations of the LPC standard compounds must be adjusted to be compatible with the laboratory EDLs.

9.10 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.

10.0 CALIBRATION

10.1 Establish GC operating parameters equivalent to those indicated in Section 6.8. The GC system may be calibrated using either the internal standard technique (Section 10.2) or the external standard technique (Section 10.3). Be aware that NPDs may exhibit instability (i.e., fail to hold calibration curves over time). The analyst may, when analyzing samples for target analytes which are very rarely found, prefer to analyze on a daily basis a low level (e.g. five to 10 times detection limit or ½ times the regulatory limit, whichever is less), sample (containing all analytes of interest) and require some minimum sensitivity (e.g., ½ full scale deflection) to show that if the analyte were present it would be detected. The analyst may then quantitate using single point calibration (Section 10.2.5 or 10.3.4).

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

10.2 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. TPP has been identified as a suitable internal standard.

10.2.1 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. Guidance on the number of standards is as follows: A minimum of three calibration standards are 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. 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. If Merphos is to be determined, calibrate with DEF (S,S,S-tributylphosphoro-trithioate). Merphos is converted to S,S,S-tributylphosphoro-trithioate (DEF) in the hot GC injection port; DEF is actually detected using the analysis conditions in this method. To each calibration standard, add a known constant amount of one or more of the internal standards, and dilute to volume with MTBE.

10.2.2 Analyze each calibration standard according to the procedure described in Section 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 the following equation. RF is a unitless value.

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

where: A_s = Response for the analyte
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

10.2.3 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.

10.2.4 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 eight hours), 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. For those analytes that failed the calibration verification, results from field samples analyzed since the last passing calibration should be considered suspect. Reanalyze sample extracts for these analytes after acceptable calibration is restored.

10.2.5 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

10.3 External Standard Calibration Procedure

10.3.1 Prepare calibration standards as in Section 10.2.1, omitting the use of the internal standard.

10.3.2 Starting with the standard of lowest concentration, analyze each calibration standard according to Section 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.

10.3.3 The working calibration curve or calibration factor must be verified on each working day by the procedures described in Section 10.2.4.

10.3.4 Verify calibration standards periodically (at least quarterly), by analyzing a QCS.

11.0 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 (Section 11.1.6). Add preservative (Section 8.0) to LRBs and LFBs. Fortify the sample with 50 µL of the surrogate standard 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 acid or base if necessary to obtain pH 7.

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 seconds to rinse the inner walls. Transfer the solvent to the separatory funnel and extract the sample by vigorously shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. 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 Extraction (Automated 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 (Section 11.2.6). Add preservative to LRBs and LFBs. Fortify the 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 Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Check pH. Add acid or base if necessary to obtain pH 7.

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 seconds to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 seconds, venting periodically. Repeat shaking and venting until pressure release is not observed. Reseal and place sample container in appropriate mechanical mixing device (separatory funnel shaker or tumbler). Shake or tumble the sample for one hour. Complete mixing of the organic and aqueous phases should be observed within about two minutes 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 minutes. 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 Section 9.3 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 minutes. 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 one to two 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, 65-70°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 15-20 minutes. 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 minutes.

11.3.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 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 five to 10 minutes. 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.

Note: If methylene chloride is not completely removed from the final extract, it may cause detector problems. If the internal standard calibration procedure is used, add 50 µL of the internal standard solution to the sample extract, seal, and shake to distribute the internal standard.

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 Section 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 or chromatographic conditions may be used if the requirements of Section 9.0 are met.

11.4.2 Verify the calibration the system daily as described in Section 10.2.4 or 10.3.3. The standards and extracts must be in MTBE.

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

11.4.4 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If using IS calibration, add an appropriate amount of IS so that the extract concentration will match the calibration standards.

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 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 alternative techniques to help confirm peak identification, need 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[6], or the use of a second chromatography column. A suggested alternative column is described in Section 6.8.

12.0 CALCULATIONS

12.1 Calculate analyte concentrations in the sample from the response for the analyte using the procedure for multi-point calibration described in Section 10.0. Do not use the daily calibration verification standard to calculate analye amounts in samples.

12.2 If the internal standard calibration procedure is used, calculate the concentration (C) in the sample using the response factor (RF) determined in Section 10.2.2 and the equation, or determine sample concentration from the calibration curve.

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

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 10.3.2. The concentration (C) in the sample can be calculated from the following equation.

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

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)

13.0 PRECISION AND ACCURACY

13.1 In a single laboratory, analyte recoveries from reagent water were used to determine analyte MDLs, EDLs (Table 3) and demonstrate method range. Analytes were divided into five groups for recovery studies. 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. Analyte recoveries from the two synthetic matrices are given in Table 2.

14.0 POLLUTION PREVENTION

14.1 This method uses significant volumes of organic solvents. It is highly recommended that laboratories use solvent recovery systems to recover used solvent as sample extracts are being concentrated. Recovered solvents should be recycled or properly disposed of.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", also available from the American Chemical Society at the address in Section 14.2.

16.0 REFERENCES

1. 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.

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, August 1977.

3. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), 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. 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.

6. Munch, J. W. "Method 525.2-Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Chromatography/Mass Spectrometry" in Methods for the Determination of Organic Compounds in Drinking Water; Supplement 3 (1995). USEPA, National Exposure Research Laboratory, Cincinnati, Ohio 45268.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] Column 1	Column 2
1,3-Dimethyl-2-Nitrobenzene (surrogate)	14.48	–[b]
Dichlorvos	16.54	15.35
Disulfoton Sulfoxide	19.08	–[b]
EPTC	20.07	16.57
Butylate	22.47	18.47
Mevinphos	22.51	21.92
Vernolate	22.94	19.25
Pebulate	23.41	19.73
Tebuthiuron	25.15	42.77
Molinate	25.66	22.47
Ethoprop	28.58	26.42
Cycloate	28.58	29.67
Chlorpropham	29.09	–[b]
Atraton	31.26	29.97
Simazine	31.49	31.32
Prometon	31.58	30.00
Atrazine	31.77	31.23
Propazine	32.01	31.13
Terbufos	32.57	–[b]
Pronamide	32.76	32.63
Diazinon	33.23	–[b]
Disulfoton	33.42	30.90
Terbacil	33.79	–[b]
Metribuzin	35.20	34.73
Methyl Paraoxon	35.58	34.10
Simetryn	35.72	34.55
Alachlor	35.96	34.10
Ametryn	36.00	34.52
Prometyrn	36.14	34.23
Terbutryn	36.80	34.80
Bromacil	37.22	40.00
Metolachlor	37.74	35.70
Triademefon	38.12	37.00
MGK 264[c]	38.73	36.73
Diphenamid	38.87	37.97
Stirofos	41.27	39.65
Disulfoton Sulfone	41.31	42.42
Butachlor	41.45	39.00
Fenamiphos	41.78	41.00

TABLE 1. RETENTION TIMES FOR METHOD ANALYTES

Analyte	Retention Time[a] Column 1	Retention Time[a] Column 2
Napropamide	41.83	–[b]
Tricyclazole	42.25	44.33
Merphos[d]	42.35	39.28
Carboxin	42.77	42.05
Norflurazon	45.92	47.58
Triphenyl Phosphate (internal standard)	47.00	45.40
Hexazinone	46.58	47.80
Fenarimol	51.32	50.02
Fluridone	56.68	59.07

[a]Columns and analytical conditions are described in Sections 6.8.1 and 6.8.2.
[b]Data not available.
[c]MGK 264 gives two peaks; peak identified in this table used for quantification.
[d]Merphos is converted to S,S,S-tributylphosphoro-trithioate (DEF) in the hot GC injection port; DEF is actually detected using these analyses conditions.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Conc µg/L	Reagent Water		Synthetic Water 1[d]		Synthetic Water 2[e]	
		R[b]	S_r[c]	R	S_R	R	S_R
Alachlor	3.8	95	11	82	6	90	8
Ametryn	20	91	10	102	11	96	4
Atraton	6	91	11	84	7	91	8
Atrazine	1.3	92	8	89	6	92	5
Bromacil	25	91	9	81	5	88	8
Butachlor	3.8	96	4	93	15	84	5
Butylate	1.5	97	21	36	8	83	8
Carboxin	6	102	4	98	13	87	5
Chlorpropham	5	93	11	82	7	93	8
Cycloate	2.5	89	9	97	14	93	3
Diazinon	2.5	115	7	83	8	84	3
Dichlorvos	25	97	6	86	6	106	16
Diphenamid	6	93	8	88	4	93	5
Disulfoton	3	89	10	107	12	95	5
Disulfoton Sulfone	7.5	98	10	92	5	96	3
Disulfoton Sulfoxide	3.8	87	11	88	22	54	19
EPTC	2.5	85	9	83	5	86	4
Ethoprop	1.9	103	5	91	7	79	3
Fenamiphos	10	90	8	87	5	89	2
Fenarimol	3.8	99	5	89	6	89	6
Fluridone	38	87	9	91	11	86	10
Hexazinone	7.6	90	7	86	6	95	9
Merphos	2.5	96	8	90	4	92	4
Methyl Paraoxon	25	98	10	97	8	94	4
Metolachlor	7.5	93	4	92	10	84	4
Metribuzin	1.5	101	5	99	10	86	4
Mevinphos	50	95	11	93	6	92	4
MGK 264	5	100	4	91	11	83	6
Molinate	1.5	98	18	83	8	89	9
Napropamide	2.5	101	6	89	5	104	18
Norflurazon	5	94	5	101	15	87	4
Pebulate	1.3	94	9	80	6	98	15
Prometon	3	78	9	89	5	63	2
Prometryn	1.9	93	8	91	8	93	4
Pronamide	7.6	91	10	84	7	92	8
Propazine	1.3	92	8	89	6	92	5
Simazine	0.75	100	7	86	5	103	14
Simetryn	2.5	99	5	88	4	103	14

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION FOR ANALYTES FROM REAGENT WATER AND SYNTHETIC GROUNDWATERS[a]

Analyte	Conc µg/L	Reagent Water		Synthetic Water 1[d]		Synthetic Water 2[e]	
		R^b	S_r^c	R	S_R	R	S_R
Stirofos	7.6	98	6	84	6	95	10
Tebuthiuron	13	84	9	85	10	98	13
Terbacil	45	97	6	86	5	102	12
Terbufos	5	97	4	80	6	77	7
Terbutryn	2.5	94	9	91	8	92	4
Triademefon	6.5	93	8	94	5	95	5
Tricyclazole	10	86	7	90	6	90	11
Vernolate	1.3	93	6	79	9	81	2

[a]Data corrected for blank and represent the analysis of seven to eight samples using mechanical tumbling and internal standard calibration.
[b]R = average percent recovery.
[c]S = standard deviation of the percent recovery.
[d]Corrected for amount found in blank; Absopure Nature Artesian Spring Water obtained from the Absopure Water Company in Plymouth, Michigan.
[e]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. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

Analyte	Fortified Conc. µg/L	N[a]	Recovery µg/L	RSD %	MDL[b] µg/L	EDL[c] µg/L
Alachlor	0.38	8	119	10	0.14	0.38
Ametryn	2.0	8	100	3	0.20	2.0
Atraton	0.60	8	120	8	0.17	0.6
Atrazine	0.13	8	101	4	0.015	0.13
Bromacil	2.5	8	113	8	0.69	2.5
Butachlor	0.38	8	99	11	0.12	0.38
Butylate	0.15	8	93	13	0.053	0.15
Carboxin	0.60	8	101	10	0.18	0.60
Chlorpropham	0.50	8	124	11	0.20	0.50
Cycloate	0.25	8	101	3	0.022	0.25
Diazinon	0.25	8	94	18	0.13	0.25
Dichlorvos	2.5	8	78	5	0.28	2.5
Diphenamid	0.60	8	84	5	0.082	0.60
Disulfoton	0.30	8	100	3	0.029	0.30
Disulfoton Sulfone	3.8	7	94	6	0.63	3.8
Disulfoton Sulfoxide	0.38	7	110	6	0.082	0.38
EPTC	0.25	8	87	12	0.080	0.25
Ethoprop	0.19	8	108	3	0.021	0.19
Fenamiphos	1.0	8	91	4	0.12	1.0
Fenarimol	0.38	8	92	19	0.20	0.38
Fluridone	3.8	7	78	30	2.8	3.8
Hexazinone	0.76	8	127	5	0.15	0.76
Merphos	0.25	8	101	5	0.040	0.25
Methyl Paraoxon	2.5	8	100	4	0.30	2.5
Metolachlor	0.75	8	94	9	0.19	0.75
Metribuzin	0.15	8	114	6	0.029	0.15
Mevinphos	5.0	8	92	6	0.87	5.0
MGK 264	0.50	8	101	12	0.19	0.50
Molinate	0.15	8	117	12	0.061	0.15
Napropamide	0.25	8	97	9	0.069	0.25
Norflurazon	0.50	8	86	8	0.098	0.50
Pebulate	0.13	8	84	7	0.022	0.13
Prometon	0.30	7	48	9	0.041	0.30
Prometryn	0.19	8	88	5	0.024	0.19
Pronamide	0.76	8	123	10	0.28	0.76
Propazine	0.13	8	93	4	0.014	0.13
Simazine	0.075	8	99	6	0.014	0.075
Simetryn	0.25	8	97	5	0.035	0.25

TABLE 3. SINGLE LABORATORY ACCURACY, PRECISION, METHOD DETECTION LIMITS (MDLs) AND ESTIMATED DETECTION LIMITS (EDLs) FOR ANALYTES FROM REAGENT WATER

Analyte	Fortified Conc. µg/L	N[a]	Recovery µg/L	RSD %	MDL[b] µg/L	EDL[c] µg/L
Stirofos	0.76	8	121	7	0.18	0.76
Tebuthiuron	1.3	8	101	15	0.58	1.3
Terbacil	4.5	8	100	4	0.56	4.5
Terbufos	0.5	8	91	4	0.054	0.50
Terbutryn	0.25	8	91	4	0.031	0.25
Triademefon	0.65	8	95	5	0.093	0.65
Tricyclazole	1.0	8	216	3	0.21	1.0
Vernolate	0.13	8	100	14	0.055	0.13

[a]N = Number of Replicates

[b]With these data, the method detection limits (MDL) in the tables 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.

[c]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.

TABLE 4. LABORATORY PERFORMANCE CHECK SOLUTION

Test	Analyte	Conc. µg/mL	Requirements
Sensitivity	Vernolate	0.05	Detection of analyte; S/N >3
Chromatographic performance	Bromacil	5.0	0.80 < PGF <1.20[a]
Column performance	Prometon	0.30	
	Atrazine	0.15	Resolution >0.7[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) = the peak width at half height in seconds
W(1/10) = the peak width in seconds at 10th height

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

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

where: t = the difference in elution times between the two peaks
W = the average peak width, at the baseline, of the two peaks

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