Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organophosphate Pesticides in Filtered Water by Gas Chromatography with Flame Photometric Detection

U.S. GEOLOGICAL SURVEY

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U.S. Department of the Interior
U.S. Geological Survey

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By Virendra K. Jha and Duane S. Wydoski

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Gale A. Norton, Secretary

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Charles G. Groat, Director

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For additional information write to:

Chief, National Water Quality Laboratory
U.S. Geological Survey
Box 25046, Mail Stop 407
Federal Center
Denver, CO 80225-0046

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Federal Center
Denver, CO 80225-0286

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.53×10^{-2}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	2.64×10^{-1}	gallon
meter (m)	3.281	foot
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
microliter (µL)	2.64×10^{-7}	gallon
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce, avoirdupois
nanometer (nm)	3.94×10^{-8}	inch

Degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) using the following equation:

$$°F = 9/5\ (°C) + 32.$$

ABBREVIATIONS AND ACRONYMS

CCV	continuing calibration verification standard
FPD	flame photometric detector
GC	gas chromatograph
GC/FPD	gas chromatograph/flame photometric detector
HPLC	high-performance liquid chromatography
LRB	laboratory reagent blank
LRS	laboratory reagent spike
LS	laboratory schedule
LT–MDL	long-term method detection level
MDL	method detection limit
mL/min	milliliter per minute
MRL	minimum reporting level
MSDS	Material Safety Data Sheet
NWQL	National Water Quality Laboratory
OP	organophosphate
pg/L	picogram per liter
pg/µL	picogram per microliter
QC	quality control
RSD	relative standard deviation
SOP	standard operating procedure
SPE	solid-phase extraction
TPC	third-party check standard
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
µg/µL	microgram per microliter
<	less than

GLOSSARY

Compound—The pesticide or pesticide degradate determined in an analysis.

Continuing calibration verification (CCV)—A calibration standard containing method compounds that is used to measure and control the bias of the existing calibration curve for these compounds. The CCV is an instrumental standard only and is not processed through preparative steps of the method.

Fortified reagent-water-set sample—A quality-control sample prepared by adding known amount of compounds to a reagent-water sample and analyzed with each set of environmental samples (usually 10). Also known as a “set spike.”

Laboratory reporting level (LRL)—The concentration where the false-positive error is minimized to no more than 1 percent and the false-negative error is minimized to no more than 1 percent. The LRL is calculated as 2 times the method detection limit. A compound determined to be not identified, confirmed, or measured in a sample is reported as <LRL.

Long-term method detection level (LT–MDL)—A detection level derived by determining the standard deviation of a minimum of 24 method detection limit spike-sample measurements over an extended period. LT–MDL data are collected on a continuous basis to assess year-to-year variations in the LT–MDL. The LT–MDL controls false positive error. The chance of false reporting a concentration at or greater than the LT–MDL for a sample that did not contain the compound is determined to be less than or equal to 1 percent.

Method detection limit (MDL)—The minimum concentration of a compound that can be measured and reported with 99-percent confidence that the compound concentration is greater than zero. At this concentration the false positive error is minimized to no more than 1-percent probability (U.S. Environmental Protection Agency, 1997).

Minimum reporting level (MRL)—Smallest measured concentration of a constituent that may be reported reliably by using a given analytical method.

Surrogate—A compound not expected to be found in any environmental sample that is added to every sample in a known amount prior to sample processing. The surrogate is used to monitor method performance for each sample.

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Editorial Review

Jon W. Raese U.S. Geological Survey

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By **Virendra K. Jha and Duane S. Wydoski**

Abstract

A method for the isolation of 20 parent organophosphate pesticides and 5 pesticide degradates from filtered natural-water samples is described. Seven of these compounds are reported permanently with an estimated concentration because of performance issues. Water samples are filtered to remove suspended particulate matter, and then 1 liter of filtrate is pumped through disposable solid-phase extraction columns that contain octadecyl-bonded porous silica to extract the compounds. The C-18 columns are dried with nitrogen gas, and method compounds are eluted from the columns with ethyl acetate. The extract is analyzed by dual capillary-column gas chromatography with flame photometric detection. Single-operator method detection limits in all three water-matrix samples ranged from 0.004 to 0.012 microgram per liter. Method performance was validated by spiking all compounds into three different matrices at three different concentrations. Eight replicates were analyzed at each concentration level in each matrix. Mean recoveries of method compounds spiked in surface-water samples ranged from 39 to 149 percent and those in ground-water samples ranged from 40 to 124 percent for all pesticides except dimethoate. Mean recoveries of method compounds spiked in reagent-water samples ranged from 41 to 119 percent for all pesticides except dimethoate. Dimethoate exhibited reduced recoveries (mean of 43 percent in low- and medium-concentration level spiked samples and 20 percent in high-concentration level spiked samples) in all matrices because of incomplete collection on the C-18 column. As a result, concentrations of dimethoate and six other compounds (based on performance issues) in samples are reported in this method with an estimated remark code.

INTRODUCTION

The U.S. Geological Survey (USGS) is responsible for assessing the Nation's water availability and utility as a resource for all uses. This appraisal of the Nation's water includes not only assessments of location, quantity, and availability, but also determinations of water quality, which require extensive and diverse studies along with supporting research. This part of the USGS mission produces much of the water-quality data used by planners, developers, water-quality managers, and agencies dealing with water-quality issues, which require reliable, standardized data.

Historically, the USGS National Water Quality Laboratory (NWQL) determined whole-water recoverable (method O-3104-83; NWQL laboratory schedules 1319, 1334, or 1399) and dissolved (method O-1104-83; NWQL laboratory schedule 1316, discontinued in 1997) organophosphorus pesticides by using the USGS methods described by

Wershaw and others (1987, p. 27–31). These methods consisted of extracting either unfiltered or filtered water samples with hexane and analyzing the extracts by using packed-column gas chromatography with flame-photometric detectors (GC/FPD). In 1990, the packed-column technology was replaced by megabore fused-silica column technology (0.25-mm diameter). These original methods included only seven compounds (diazinon, ethion, malathion, methyl parathion, methyl trithion, parathion, and trithion). In 1987, the NWQL offered the determination of five other organophosphate compounds: chlorpyrifos, DEF, disulfoton, fonofos, and phorate as a custom add-on to the methods, and methyl trithion was dropped from the methods because a standard was no longer available. These five compounds became permanent (although undocumented) additions to the methods.

The hexane extraction procedure used in these methods has produced lower and highly variable recoveries for malathion and disulfoton. Various procedures were used to improve the recoveries for these two compounds, however, none has proven satisfactory to date (2002). The NWQL decided to develop a new filtered-water method that incorporates a solid-phase extraction (SPE) procedure that would improve organophosphate pesticide recoveries. This new method also expands the selected list of determined compounds from 11 to 25, and 7 of these compounds are permanently reported with an estimated remark code because of performance issues. Isofenfos is used as a surrogate standard. The purpose of this method report is to cover the following topics: application and principles of the method, apparatus and reagents required, details of the preparation and analytical procedures, calculations, reporting of results (units and significant figures), and method performance. This new method was implemented as a custom method at the NWQL in January 2002. It is important to note that this new method is for filtered-water samples only, and, thus, is most applicable for those compounds that are primarily in the dissolved phase in the water sample, whereas the old method O-1104-83 (Wershaw and others, 1987) primarily has been used for the analysis of whole-water samples (LS 1319, 1334, and 1399).

The authors wish to thank William T. Foreman, NWQL's Methods Research and Development Program, for his valuable suggestions.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Organophosphate Pesticides, Filtered Water, Gas Chromatography, O–1402–01 (see table 1)

1. Scope and Application

This method is suitable for the determination of 20 parent organo-phosphate pesticides and 5 degradation products in filtered-water samples (table 1). Seven of these compounds are reported permanently with an estimated concentra-tion because of performance issues. The method is applicable for determining pesticides and pesticide degradates that are (1) primarily in the dissolved phase because this is a filtered-water method, (2) efficiently isolated from the sample matrix and sorbed onto a C-18 SPE column, (3) efficiently displaced from the SPE column by the ethyl acetate elution solvent, (4) chromatographically resolved and identified by using a gas chromatograph (GC) equipped with flame photometric

Table 1. Method compounds name, parameter codes, laboratory codes, and Chemical Abstracts Service registry numbers used by the U.S. Geological Survey National Water Quality Laboratory

[Compounds marked with an asterisk (*) are reported permanently with an "E" code (estimated concentration) in this method. Compound degradates are indented. CAS, Chemical Abstracts Service; LS, laboratory schedule]

Organophosphate pesticide or degradate	Parameter code	Laboratory code	CAS number
Chlorpyrifos	38933G	4421	2921-88-2
Diazinon	39572G	4422	333-41-5
Dimethoate*	82662G	4423	60-51-5
Disulfoton	82677F	4424	298-04-4
Disulfoton sulfone	61640B	4425	2497-06-5
Ethion	82346C	4426	563-12-2
Ethion monoxon*	61644B	4427	17356-42-2
Ethoprop	82672F	4428	13194-48-4
O-Ethyl-O-methyl-S-propylphosphorothioate [O-Ethyl-O-meth_ioate]	61660B	4429	76960-87-7
Fenthion	38801C	4430	55-38-9
Fonofos	04095F	4431	944-22-9
Fonofos oxygen analog* (fonofos oxon)	61649B	4432	944-21-8
Malathion	39532F	4433	121-75-5
Methidathion	61598B	4434	950-37-8
Methyl parathion	39602B	4435	298-00-0
Parathion	39542F	4436	56-38-2
Phorate	82664F	4437	298-02-2
Phorate oxygen analog* (phorate oxon)	61666B	4438	2600-69-3
Profenofos	61603B	4439	41198-08-7
Propetamphos	61604B	4440	31218-83-4
Sulfotepp*	61605B	4441	3689-24-5
Sulprofos*	38716B	4442	35400-43-2
Terbufos	82675F	4443	13071-79-9
Tribufos (DEF or S,S,S-Tributyl phosphorotrithioate)*	61610B	4444	78-48-8
Trithion (Carbophenothion)	82342B	4445	786-19-6
Isofenfos (surrogate)	99574A	4446	25311-71-1

[ ] Name in bracket is an abbreviation used in the National Water Information System (NWIS) because of character number limitation.

( ) Name in parentheses is alternative compound name.

NOTE: All method compounds except trithion also are found in one or more other filtered-water methods (LS 2001/2010, 2002/2011, Zaugg and others, 1995) and in the new wastewater method (LS 1433, Zaugg and others, 2002).

NOTE: Letter after parameter code is the method code.

detectors (FPD), and (5) sufficiently stable to chemical or thermal degradation to allow accurate quantification by using all sampling and analysis steps of the method. Method compounds are listed in table 1.

2. Summary of Method

2.1 Water samples (about 900 to 1,000 mL) are filtered through a 0.7-µm glass-fiber filter to remove suspended particulate matter.

2.2 Sample filtrate (about 1,000 mL) is pumped through disposable C-18 SPE columns.

2.3 The SPE columns are dried with nitrogen to remove interstitial water.

2.4 The sorbed method compounds are removed from the SPE columns by elution with 2.0 mL of ethyl acetate.

2.5 The eluant is evaporated by using nitrogen to a final volume of 1 mL.

2.6 Extracts are analyzed by dual capillary-column GC/FPD.

3. Safety Precautions

Always observe proper laboratory safety procedures when handling chemicals and operating equipment. Organophosphate compounds and especially the degradates in this method are recognized potent cholinesterase inhibitors. Liver function can be affected adversely or other health problems can occur from prolonged exposure. All appropriate safety equipment should be worn and extreme care exercised when handling these compounds and solvents. Always wear appropriate clothing, nitrile gloves, and eye protection, and use adequate ventilation when preparing samples or standard solutions. It is important to read the Material Safety Data Sheet (MSDS) on each compound and solvent prior to using this method. MSDS's can be found in the sample preparation laboratory and in safety office files at the receptionist's desk. Disposal of all organic solvents, water samples, and rinse wastes should be performed in accordance with NWQL hazardous waste-disposal rules and regulations.

4. Interferences

This method involves solid-phase extraction of water samples for organophosphates followed by elution with ethyl acetate. There are many organophosphate compounds in natural matrices that GC/FPD will detect. This method is designed to minimize false positives through dual GC column confirmation. Mass-spectral confirmation also should be used to confirm identification, if uncertain. Sulfur and organosulfur compounds and unknown organophosphate compounds occasionally might interfere with qualification and quantification of other individual organophosphate compounds.

5. Sampling Methods, Sample Handling, Sample Filtration, Preservation, and Holding Time

Detailed descriptions of sampling methods used by the USGS for obtaining depth- and width-integrated surface-water samples and of sampling methods for obtaining ground-water samples, and of sample processing (splitting, filtration, shipping) are described by Wilde and others (1999). Additional field-sample collection considerations, including equipment and cleaning procedures that should be applied to samples collected for this SPE-based method, along with aspects of field quality-control sample types, including field blanks,

replicate samples, and fortified matrix spikes, are provided in Sandstrom and others (2001) and Wilde and others (1999).

Samples are logged into the laboratory data base and stored at 4°C until ready for filtration and extraction. Samples submitted for this method must be filtered through a 0.7-µm glass-fiber filter prior to isolation of method compounds by SPE. The filtration procedure is described in Sandstrom (1995). Currently (2002), no chemical preservatives are used to preserve the compounds in the water sample, and no sample or extract holding-time studies have been performed for this method. Holding times in reagent water and on the dry SPE have been studied by Sandstrom and others (2001) for laboratory schedule (LS) 2002 method, which nearly has identical sample-preparation steps as this new method. Recently, Winslow and others (2001) have shown that the addition of chemical preservatives are required to preserve selected organophosphates (OP) and obtain acceptable recoveries in U.S. Environmental Protection Agency (USEPA) method 526 (Winslow and others, 2001), a similar SPE GC/MS method.

6. Apparatus and Instrumentation

6.1 *Analytical balance*: Capable of accurately weighing to the nearest 0.00001g.

6.2 *AutoTrace SPE Workstation*: Configured for simultaneous extraction of six samples using 3-mL syringe-barrel SPE columns; Zymark Inc., or equivalent.

6.3 Nitrogen gas solvent evaporation device, Organomation Associates, Inc., or equivalent.

6.4 *GC/FPD*: Hewlett-Packard, Model 5890 GC or comparable with HP 7673A automated sample injector. Dual HP flame photometric detectors or equivalent, and a data system with Turbochrom chromatography data-acquisition software and Target data-processing software or equivalent.

7. Consumable Materials

7.1 *SPE columns*: International Sorbent Technology, Isolute C-18 (EC), Part Number 221-0050-BS or equivalent. The columns are packed with 500 mg of silica containing a chemically bonded C-18 hydrocarbon phase, and the silica material also is partially end-capped.

7.2 15-mL Kuderna-Danish receiver tubes baked at 450°C for 2 hours.

7.3 *Glass bottles, amber*: 1,000-mL, 33-mm neck, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps; NWQL 1-L amber glass bottle or equivalent.

7.4 *Solvents*: Ethyl acetate, methanol, toluene, dichloromethane, and isopropanol; Burdick and Jackson (B&J) Brand ultrapure pesticide quality or equivalent.

7.5 *Reagent water*: Ultrapure, B&J Brand for high-performance liquid chromatography (HPLC) or equivalent.

7.6 *Detergent solution*: Prepare a dilute mixture (0.2 percent) of laboratory-grade phosphate-free liquid detergent in tap water; Liquinox, Alconox Inc. or equivalent.

7.7 *Pasteur pipets*: Baked and clean disposable, both large and small sizes with rubber bulbs.

7.8 *Vial*: 1.5- or 2-mL, amber glass, with aluminum crimp caps that have dual PTFE-faced silicon rubber septa or open-top screw-cap with PTFE-faced silicon rubber septum, Supelco Inc. or equivalent.

7.9 *GC consumables*: GC consumable materials, such as guard column, inlet liner, y splitter, and gases are described in section 10.

7.10 Solvent for spike and surrogate: Pesticide-grade methanol, free of known compounds.

7.11 *Solvent for calibration standards:* Pesticide-grade ethyl acetate, free of known compounds.

8. Calibration and Quality-Control Standards and Criteria

Quality-control information must be evaluated in aggregate to determine whether analytical data are of acceptable quality to be reported. Minimum quality-control requirements include (1) analysis of laboratory reagent water blanks; (2) determination of surrogate standard compound recoveries in each sample, blank, fortified reagent-water sample; (3) determination of compound recoveries in the fortified reagent-water sample; and (4) assessment of the GC/FPD chromatographic performance.

8.1 *Calibration standards*. Stock standards for the pesticides and degradates were obtained as pure materials from the USEPA National Pesticide Standard Repository (Ft. Meade, Md.) or commercial vendors (ChemService; EQ Laboratories). Prepare calibration standards at six different concentrations (5, 10, 20, 50, 80, and 100 pg/µL) for each compound and surrogate compound by adding known volume of stock standard solutions to a volumetric flask. Dilute to volume with ethyl acetate. The lowest standard needs to represent compound concentrations near, but greater than, their respective method detection limit (MDL). The remaining standards need to bracket the compound concentrations expected in the sample extracts.

8.2 *Calibration curve*. Starting with the lowest concentration, analyze each calibration standard and tabulate response (peak area) in relation to the concentration in the standard. Use the results to prepare a linear calibration curve for each compound. For each sample set analyze all six calibration standard solutions prior to analyzing the samples. The determined concentration should be within 20 percent of the expected concentration for all analytes (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998). The correlation coefficient (r^2) for the calibration curve regression should be equal to or greater than 0.995. If the instrument does not meet these calibration criteria, correct the problem by servicing the GC or by preparing and reanalyzing new calibration standards.

8.3 *Surrogate standard solution*. The surrogate standard solution is prepared with isofenfos, which is available through Absolute Standard Inc. or equivalent. Surrogate solution is prepared by adding 250 µL of isofenfos stock solution (100 µg/mL in hexane) into 25 mL of methanol. The final concentration of isofenfos in methanol is 1,000 pg/µL. Add 100 µL of the surrogate standard to 1 L of each field sample and to the laboratory reagent-water spike and blank samples. Add the surrogate standard solution to the sample at the time of extraction and use it to monitor performance of the sample preparation procedure

(M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998). When surrogate recovery for a sample is above the upper or below the lower control limits, check the following: (1) calculations, so as to locate possible mathematical errors; (2) spiking or calibration solutions for possible surrogate (and other compounds) degradation; (3) contamination, which usually produces positive bias; and (4) instrument performance (see Section 8.8). If those steps do not reveal the cause of the problem, reanalyze the extract. If a set blank extract reanalysis fails the surrogate control-limit criteria (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998), then the problem needs to be identified and corrected before continuing the analysis. If sample extract reanalysis meets the surrogate recovery and other QC criteria, then report results using the reanalyzed extract data. If sample extract continues to fail the recovery criteria, either report all data for that sample as suspect with an estimated ("E"code) qualifier, raise the reporting level, or do not report the sample data.

8.4 *Spiking solution*. The reagent water spike solution is prepared in methanol by adding 125 µL of an organophosphate stock (100 µg/mL in hexane) into 25 mL methanol. This solution contains all of the organophosphate compounds of interest, except the current surrogate compound (isofenfos). The spike solution concentration is 500 pg/µL, and 100 µL of this solution is added to 1 L of reagent water to prepare the laboratory reagent spike (LRS). Use the LRS to monitor recovery efficiencies for all method compounds (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998). For this report, spike solution was added to spike samples at three different concentrations (0.02, 0.05, and 0.5 µg/L) for the method performance determinations. The laboratory needs to analyze at least one LRS sample with every 10 samples or one per sample set (all samples extracted within a 24-hour period), whichever is greater. The concentration of each compound in the LRS sample needs to be within the range of the calibration standards. Standard statistical techniques (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998) are used to establish control limits for compound recovery for the LRS. If the recovery of any compound falls outside the control-limit criteria, that compound is judged out of control, and the source of the problem needs to be identified and resolved before continuing the analyses. The data for compounds that fail should have an "estimated" remark code, or raise the reporting level, or do not report the sample data.

The laboratory periodically needs to determine and document its detection capabilities for the method compounds. The detection levels for this method will be continuously evaluated using the long-term method detection level (LT–MDL) procedure (Childress and others, 1999) or other procedure as adopted by the NWQL.

8.5 *Third-party check (TPC) standard*. The third-party check standard is available commercially through a vendor such as Supelco. This solution contains most of the organophosphate compounds of interest, except the current surrogate compound (isofenfos). A working third-party check standard is prepared in ethyl acetate by adding 10 µL of the TPC stock standard (100 µg/mL in hexane) to 10 mL ethyl acetate. The final working concentration of the TPC

is 100 pg/μL. This standard is analyzed in each sequence after the calibration standards to verify the calibration curve. The determined concentration for all analytes in the TPC standard should be within ± 30 percent of the expected concentration (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

8.6 *Continuing calibration verification (CCV)*. The continuing calibration verification standard concentration is typically at the midpoint of the calibration range, usually the 20- or 50-pg/μL organophosphate standard. A 20- or 50-pg/μL calibration standard containing all of the method compounds is inserted in an autosampler vial and placed after every 10 field or QC samples throughout the GC analytical sequence. This CCV sample is used to monitor the calibration of the GC for bias and variance. The calculated CCV concentration must be within 20 percent of the expected concentration for each compound. If the determined concentrations of compounds in the CCV are outside these control limits, the environmental samples are reanalyzed (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

8.7 *Laboratory reagent blank (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, an LRB needs to be analyzed. If the LRB contains interfering peaks that would prevent the determination of one or more compounds, then determine the source of contamination and eliminate the interference before continuing future sample processing and analysis (M.R. Burkhardt and T.J. Maloney, U.S. Geological Survey, written commun., 1998).

8.8 *Instrument system*. Instrument performance needs to be monitored daily. Gas chromatographic performance normally is reflected in the variation of determined concentration of the selected compound in calibration standards, TPC, and CCVs relative to the concentrations obtained by using a new capillary column and freshly prepared standards. Failure to meet the calibration, TPC, or CCV criteria indicates that the column or the GC needs to be maintained to bring the system into compliance. A portion of the guard column might be cut off and removed to restore performance, or the injection port liner might be replaced.

8.9 *Other GC/FPD performance requirements*. Sample concentrations that exceed the high concentration calibration standard must be diluted to within the calibration range and reanalyzed.

The laboratory might adopt additional quality-control practices for use with this method (see Pirkey and Glodt, 1998). The specific practices that are most productive depend on the needs of the laboratory and the nature of the samples.

9. Procedure

9.1 Preclean and dry the C-18 column (Jeffrey Stewart and others, U.S. Geological Survey, written commun., 2001).

9.2 Weigh and record (W_1) the sample bottle containing the sample to the nearest gram.

9.3 Prepare two additional bottles for each set of 10 samples, each containing 1,000 mL of reagent water for the laboratory reagent (set) blank (LRB) and the laboratory reagent (set) spike (LRS). Add 10 mL of

methanol conditioner to each environmental and QC sample. Add 100 µL (500 pg/µL) of primary fortification (spike) into reagent water spike bottle. And 100 µL (1,000 pg/µL) of surrogate solution to each sample, including LRB and LRS. Cap all the bottles and shake well to mix.

9.4 Preclean the AutoTrace instrument (Jeffrey Stewart and others, U.S. Geological Survey, written commun., 2001).

9.5 Place the bottles containing the samples in the AutoTrace SPE rack. Place AutoTrace intake tubing into the sample bottles.

9.6 Weigh each SPE column to 0.0001g and write the SPE column weight and sample "Lab ID" number on the side of the SPE column with waterproof ink. Install the SPE columns on theAutoTrace Workstation. Set up and program the AutoTrace Workstation in accordance with the steps listed in table 2.

9.7 Load samples in sample rack corresponding to the SPE column installed. Insert corresponding intake tubing in sample. Start AutoTrace extraction (Jeffrey Stewart and others, U.S. Geological Survey, written commun., 2001).

9.8 After the AutoTrace finishes its program, remove the SPE columns and dry them "off-line" with nitrogen gas at 138 kPa (20 lb/in^2) for 15 to 20 minutes until completely dry. Verify that the SPE column weights are the same or less than the weights written on the side of the columns. Store dry sample column in desiccator at room temperature until ready for elution.

9.9 Weigh and record (W_2) the sample bottle plus residual water in bottle not processed through the SPE column. Subtract W_2 from W_1 to obtain the exact volume of sample extracted.

9.10 Obtain one 15-mL Kuderna-Danish receiver tube per SPE column and label with sample ID.

9.11 Elute compounds from the SPE column into the labeled receiver tube, with the help of elution rack, by using 2 mL ethyl acetate. Allow the solvent to elute through the column gravimetrically. Elution will take 15 to 20 minutes.

9.12 Place the receiver tube on a nitrogen gas solvent evaporation device. Evaporate with a gentle stream of nitrogen until the volume of the sample is 1 mL. Vortex and transfer the extracts to 1.8-mL autosampler vial.

9.13 Cap autosampler vial and store in a refrigerator at 4°C until ready to analyze.

10. Gas Chromatography/Flame Photometric Detection Analysis

10.1 Analyze the sample extracts by gas chromatography with flame photometric detection (GC/FPD) by using a dual capillary-column system equipped with an autosampler; one split/splitless injection port (operated in the splitless mode); a 1-m, 0.32-mm inside diameter (ID) section of fused silica capillary tubing, uncoated, deactivated guard column; a Y-type column connector to connect the guard column to the primary and secondary capillary columns; and two flame photometric detectors. Use a computer system to control the autosampler, GC operational conditions, and to acquire and process responses from the dual detectors.

Table 2. Automated solid-phase extraction procedure using AutoTrace workstation for the analytical method

ZYMARK AUTOTRACE EXTRACTION

[mL, milliliters]

AUTOTRACE EXTRACTION PROCEDURE

Estimated time for samples : 57.8 minutes
Step 1 : Process 6 samples using the following procedures.
Step 2 : Condition column with 3 mL of METHANOL into SOLVENT WASTE
Step 3 : Condition column with 6 mL of WATER into SOLVENT WASTE
Step 4 : Load 900 to 1,000 mL of filtered sample onto column
Step 5 : Dry column with N_2 gas for 4 minutes
Step 6 : Pause and alert operator, resume when CONTINUE is pressed
Step 7 : Clean each sample path with 50 mL cleaning solution (isopropanol: methylene chloride: toluene (7:2:1) into SOLVENT WASTE
Step 8 : Clean each sample path with 50 mL methanol into SOLVENT WASTE
Step 9 : Clean each sample path with 100 mL distilled water into solvent WASTE
Step 10 : Dry column with N_2 gas for 0.1 minute
Step 11 : END

SETUP CONDITIONS

[mL/min, milliliters per minute; mL, milliliter]

AUTOTRACE EXTRACTION WORKSTATION

FLOW RATES (mL/min)	
Condition flow:	25
Load flow:	25
Rinse flow:	25
Elute flow:	5
Condition air push:	25
Rinse air push:	25
Elute air push:	5

NAME SOLVENTS	
Solvent 1 :	Water
Solvent 2 :	Methanol
Solvent 3 :	NONE
Solvent 4 :	NONE
Solvent 5 :	NONE

SOLID-PHASE EXTRACTION CONDITIONS	
Push delay:	2 seconds
Air factor:	0.5
Autowash volume:	0.00 mL

WORKSTATION CONDITIONS		
Maximum elution volume:		12.0 mL
Exhaust fan on:	Y	Y=Yes N=No
Beeper on:	N	Y=Yes N=No

10.2 Gas chromatographic configuration

Column 1 (primary column): 30-m long by 0.25-mm ID, 5 percent diphenyl and 95 percent dimethyl polysiloxane bonded fused silica capillary column, 0.25-µm film thickness (Restek Corp. RTX-5 or equivalent).

Column 2 (confirmation column): 30-m long by 0.25-mm ID, 14 percent cyanpropylphenyl and 86 percent dimethyl polysiloxane bonded fused silica capillary column, 0.25-µm film thickness (Restek Corp. RTX-1701 or equivalent).

Carrier gas: Helium, 99.999 percent purity, 1 to 3 mL/min column flow. This flow range corresponds to a linear flow velocity of 20 to 40 cm/sec on the Van Deemter plot, when using 30-m by 0.25-mm ID columns.

Detector make-up gas: Nitrogen, 99.999 percent purity, 4 to 10 mL/min flow.

Detector gas: Hydrogen, 99.999 percent, 3 to 5 mL/min flow.

Air: 99.6 percent purity, 90 to 110 mL/min flow.

Injection mode: Splitless, injection port sweep 30 mL/min. Column head pressure 138 kPa (20 lb/in^2). Septum purge flow is 1 to 2 mL/min. Split purge valve is turned on (open) at 2 minutes and off (closed) 2 minutes prior to end of sample analysis. Both columns are connected to guard column using “Y” splitter, and the guard column is connected to injection port. If flows through the GC columns are equivalent, then an injection volume of 4 µL of extract is divided evenly onto both columns.

Injector temperature: 220°C.

Detector temperature: 220°C.

Detectors: Two flame photometric detectors (FPD), set for “P” mode, with optical filters that transmit 525-nm wavelength for specific phosphorus response.

Oven temperature program: Initial temperature 60°C, hold 1 minute.

Ramp 1: 15°C/min to 160°C, hold 0 minute.

Ramp 2: 1°C/min to 186°C, hold 0 minute.

Ramp 3: 7°C/min to 280°C, hold for 7 minutes.

Total analysis time is about 54 minutes.

10.3 Determine compound retention times (RT)—Following GC setup, establish compound retention times using the calibration standard solutions. A typical separation and peak shape obtained using the GC operating conditions in section 10.2 for the individual OP pesticides on the Rtx-5 column are shown in figure 1. Separation and peak shape on the Rtx-1701 column are shown in figure 2. Peak identifications and retention times are listed in table 3 for the method compounds on the Rtx-5 and Rtx-1701 columns shown in figures 1 and 2.

10.4 *Coelution problems*—Two coelutions (one with fonofos and propetamphos and a second with fenthion, chlorpyrifos, and parathion) were observed on Rtx-5 column, and three coelutions (one with chlorpyrifos with methyl parathion, second with methidathion and profenophos, and a third with disulfoton sulfone, ethion,

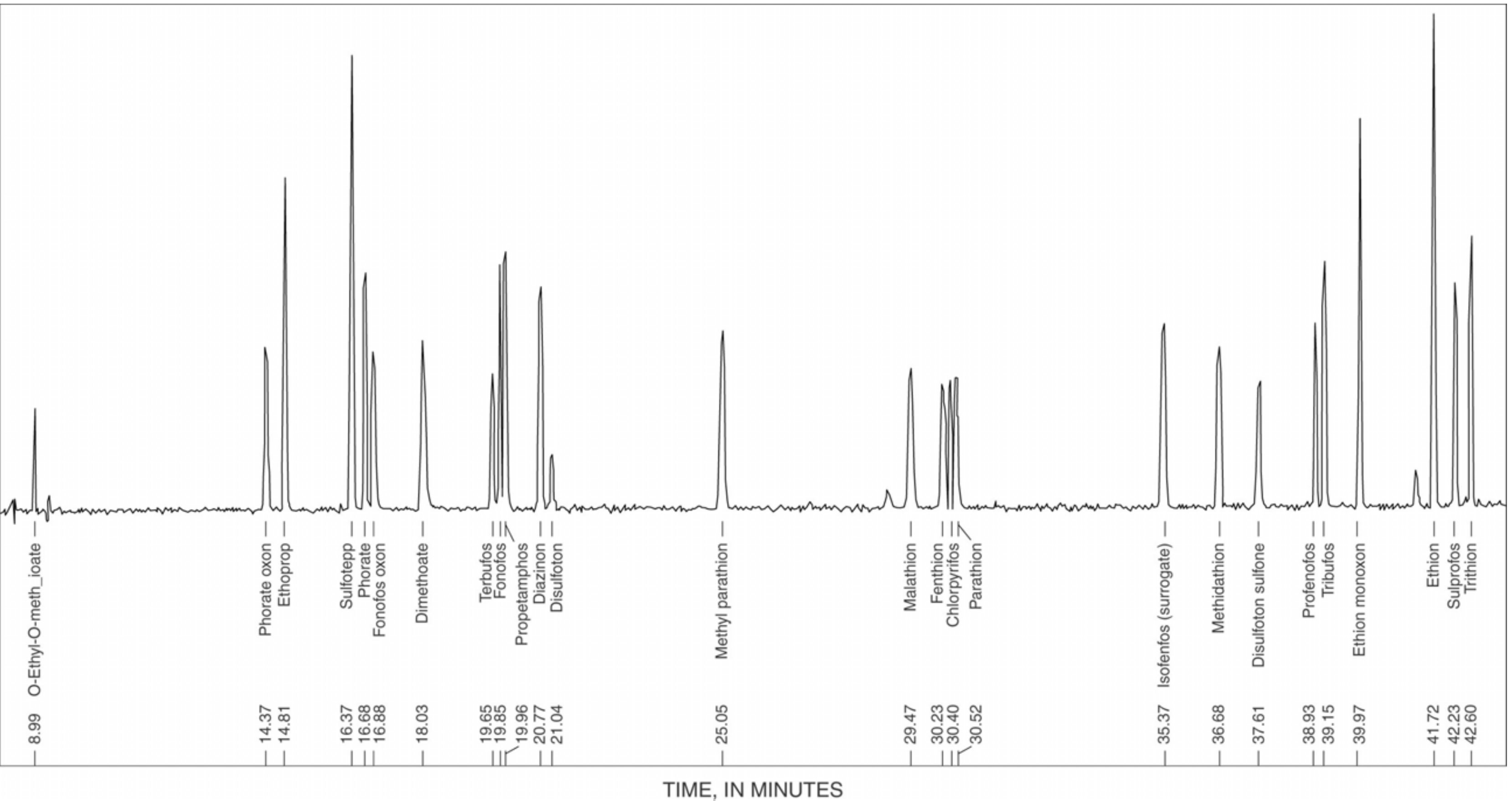

Figure 1. Gas chromatogram with flame photometric detection of a 50-picograms-per-microliter calibration standard solution of the individual organophosphate pesticides on a Restek Rtx-5 column for the analytical method. Compound identifications are listed in table 3. Chromatographic conditions are given in the text.

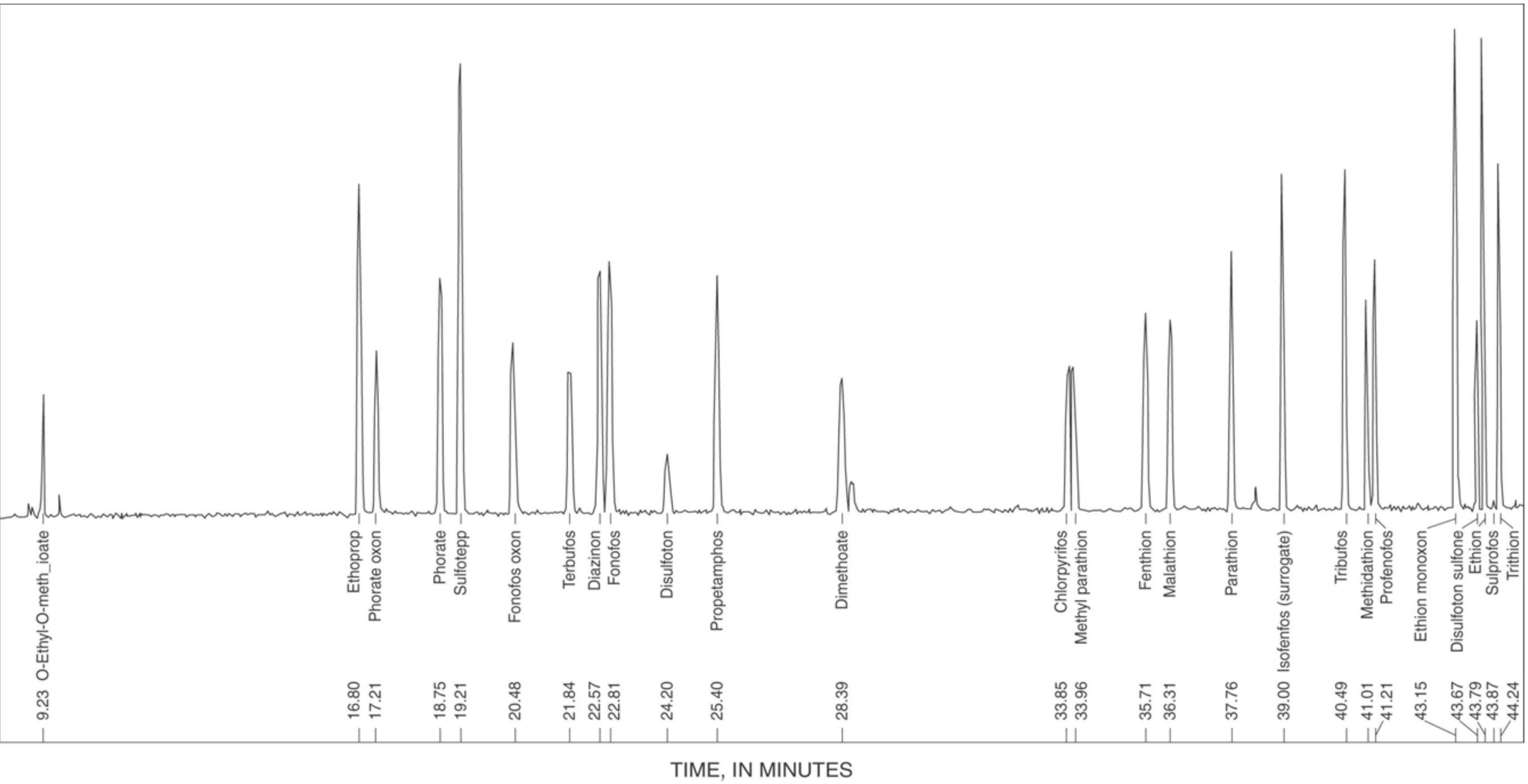

Figure 2. Gas chromatogram with flame photometric detection of a 50-picograms-per-microliter calibration standard solution of the individual organophosphate pesticides on a Restek Rtx-1701 column for the analytical method. Compound identifications are listed in table 3. Chromatographic conditions are given in the text.

and sulprofos) were observed on Rtx-1701 column using the GC conditions described in section 10.2. Compounds with coelutions on one column are well separated from other method compounds on the other column (see table 3).

Coelution conditions require special identification and calibration considerations. Compounds that show coelution with another method compound on one column must be quantified on the other column, where no coelution problem occurs.

Table 3. Retention times of method compounds on the Rtx-5 and Rtx-1701 columns for the analytical method

[Listed in Rtx-5 retention time order]

Compound	Retention time (minutes)	
	Rtx-5	Rtx-1701
O-Ethyl-O-meth_ioate	8.99	9.23
Phorate oxon	14.37	17.21
Ethoprop	14.81	16.80
Sulfotepp	16.37	19.21
Phorate	16.68	18.75
Fonofos oxon	16.88	20.48
Dimethoate	18.03	28.39
Terbufos	19.65	21.84
Fonofos	[1] 19.85	22.81
Propetamphos	[1] 19.96	25.40
Diazinon	20.77	22.57
Disulfoton	21.04	24.20
Methyl parathion	25.05	[5] 33.96
Malathion	29.47	36.31
Fenthion	[2] 30.23	35.71
Chlorpyrifos	[2] 30.40	[5] 33.85
Parathion	[2] 30.52	37.76
Isofenfos (surrogate)	35.37	39.00
Methidathion	36.68	[4] 41.01
Disulfoton sulfone	37.61	[3] 43.67
Profenofos	38.93	[4] 41.21
Tribufos	39.15	40.49
Ethion monoxon	39.97	43.15
Ethion	41.72	[3] 43.79
Sulprofos	42.23	[3] 43.87
Trithion	42.60	44.24

[1]Coelutions on Rtx-5, well separated on Rtx-1701.
[2]Coelutions on Rtx-5, well separated on Rtx-1701.
[3]Coelutions on Rtx-1701, well separated on Rtx-5.
[4]Coelutions on Rtx-1701, well separated on Rtx-5.
[5]Coelutions on Rtx-1701, well separated on Rtx-5.

10.5 *GC autosequence*—The recommended sequence for an automated analysis is listed in table 4.

11. Calculation of Results

11.1 Inject calibration standards and tabulate peak area of compound (A_1) and concentration of compound (C_1) in each calibration standard, in picograms per microliter. Plot A_1 in relation to C_1V_1 as follows:

$$A_1 = mC_1V_1 \pm b \quad , \qquad (1)$$

where m = slope of regression curve, in area per picograms;
V_1 = volume of calibration standard injected, in microliters;
b = y–intercept of regression curve, in area.

11.2 Inject samples and obtain peak area response for identified analytes in sample. Calculate concentration of analyte in sample by rearrangement of equation (1) and inclusion of other conditions as follows:

$$C_2 = \frac{(A_2 - b)}{mV_3} \times \frac{V_2}{V_4} \times DF \quad , \qquad (2)$$

where C_2 = concentration of compound in sample, in picograms per microliter;
A_2 = peak area of compound in sample;
V_2 = final volume of sample extract prior to injection into GC, in milliliters;
V_3 = volume of extract injected, in microliters (**NOTE:** $V_3 = V_1$ because 4 µL injected using an autosampler);
V_4 = volume of sample extracted by SPE, in milliliters, equals weight (W) of sample extracted by SPE (assuming 1 mL = 1 g);
V_4 = $W = W_1 – W_2$, where W_1= sample weight + bottle before SPE;
W_2 = weight of residual sample + bottle after SPE; and
DF = dilution factor.

11.3 Calculation of surrogate and spike recoveries. Surrogate and spike recoveries are calculated in percent as follows:

$$C_2 = \frac{C_S \times V_S}{V_4} \times 100 \quad , \qquad (3)$$

where C_S = concentration of the surrogate (section 8.3) or spike (section 8.4) solution, in picograms per microliter; and
V_S = volume added of surrogate (100 µL) or spike (100 µL) solution.

Table 4. Suggested gas chromatography/ flame photometric detection autosequence for the analytical method

[pg/µL, picograms per microliter]

Standard or sample type
Ethyl acetate gas chromatograph injection blank
Calibration standard 5 pg/µL
Calibration standard 10 pg/µL
Calibration standard 20 pg/µL
Calibration standard 50 pg/µL
Calibration standard 80 pg/µL
Calibration standard 100 pg/µL
Third-party check solution
Laboratory reagent blank (LRB)
Laboratory reagent spike sample (LRS)
Ten field samples
Continuing calibration verification (CCV) standard solution
Ten field samples (CCV)
Ten field samples (CCV)

12. Reporting of Results

The quantitative value that is reported is column dependent, and generally the lower of the two concentrations produced by the dual column GC analysis is reported. Compound concentrations in field samples are reported in micrograms per liter (μg/L). If the concentration is less than the lowest calibration standard, report the concentration to three significant figures after the decimal place, and use the "E" code to indicate that it has been estimated. If the concentration is greater than the highest calibration standard, dilute the sample to bring the concentration within calibration range and report the concentration to three significant figures after the decimal place. Surrogate data for all sample types are reported in percent recovered. The LRS results are reported in percent recovered. Interim reporting levels for this method are listed in table 5. Estimates of method detection limits (MDLs) using the procedures outlined by the U.S. Environmental Protection Agency (1997) are listed in table 6 (see following section titled Method Performance).

13. Method Performance

13.1 Samples of (1) reagent water, (2) surface water collected from the South Platte River, near Dartmouth Street and Platte River Drive, Denver, Colo., and (3) ground water collected from a domestic well in Evergreen, Colo., were used to test method performance. Eight samples of each water type were fortified with each compound at three different concentrations of 0.02, 0.05, and 0.5 μg/L. One sample for each water type was unfortified to determine any potential background contamination or interference for each matrix.

Table 5. Interim minimum reporting levels for the analytical method

(μg/L, microgram per liter; SPE, solid-phase extraction)

Compound	Minimum reporting levels (μg/L)
Chlorpyrifos	0.013
Diazinon	010
Dimethoate[1]	E.012
Disulfoton	.015
Disulfoton sulfone	.025
Ethion	.007
Ethion monoxon[1]	E.018
Ethoprop	.010
O-Ethyl-O-meth_ioate	.008
Fenthion	.012
Fonofos	.008
Fonofos oxon[1]	E.020
Malathion	.010
Methidathion	.020
Methyl parathion	.010
Parathion	.012
Phorate	.012
Phorate oxon[1]	E.012
Profenofos	.014
Propetamphos	.009
Sulfotepp[1]	E.009
Sulprofos[1]	E.009
Terbufos	.013
Tribufos[1]	E.010
Trithion	.008

[1]These compounds will be reported permanently as "E" coded (estimated concentration) in this method, based on the holding-time study for methods 2002/2011 in relation to holding-time data in water and on dry SPE columns for method 2002 (Sandstrom and others, 2001).

13.2 All samples were extracted on one AutoTrace system. All samples for a given matrix were extracted on the same day. Extracts were analyzed by GC/FPD, but different concentrations and matrices were analyzed at different times. Bias and variability data are listed in tables 7 through 15.

Table 6. Bias and variability of method compounds spiked at 0.02 microgram per liter in reagent-water, surface-water, and ground-water matrices combined and estimated method detection limit for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter]

Compound	Number of observa-tions	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)	Estimated method detection limit (µg/L)
Chlorpyrifos	24	0.016	0.003	15.68	81.88	0.006
Diazinon	24	.018	.002	11.90	91.04	.005
Dimethoate (E)*	24	.010	.002	26.16	47.50	.006
Disulfoton	24	.020	.003	15.64	97.92	.008
Disulfoton sulfone	24	.024	.005	20.87	118.54	.012
Ethion	24	.017	.001	8.45	86.88	.004
Ethion monoxon (E)*	24	.021	.004	16.57	106.04	.009
Ethoprop	24	.019	.002	9.96	96.25	.005
O-Ethyl-O-meth_ioate	16	.020	.002	7.72	97.50	.004
Fenthion	24	.017	.002	14.11	82.92	.006
Fonofos	24	.019	.002	8.73	94.79	.004
Fonofos oxon (E)*	24	.018	.004	22.62	88.13	.010
Malathion	24	.020	.002	9.98	97.92	.005
Methidathion	24	.022	.004	18.44	109.58	.010
Methyl parathion	24	.019	.002	10.56	94.58	.005
Parathion	24	.017	.002	13.15	83.54	.006
Phorate	24	.017	.002	14.48	83.96	.006
Phorate oxon (E)*	24	.019	.002	12.85	94.58	.006
Profenofos	24	.020	.003	14.23	100.83	.007
Propetamphos	24	.018	.002	9.31	92.29	.004
Sulfotepp (E)*	24	.017	.002	10.27	87.29	.005
Sulprofos (E)*	24	.017	.002	11.09	83.54	.005
Terbufos	24	.018	.003	14.69	87.50	.006
Tribufos (E)*	24	.014	.002	14.13	70.00	.005
Trithion	24	.018	.002	9.51	87.71	.004

13.3 The unfortified surface-water samples contained low concentrations of diazinon (0.014 and 0.012 µg/L). The average concentration (0.013 µg/L) was subtracted from the diazinon concentrations determined in the surface-water-spiked subsamples to give corrected results in tables 10, 11, and 12. No other method compound was found in the surface-water sample, and no method compounds were detected in the reagent-water or ground-water samples.

13.4 Estimated MDLs were determined by fortifying eight reagent-water samples, eight surface-water samples, and eight ground-water samples, with the method compounds at 0.02 µg/L, a concentration that was twice the minimum reporting level of 0.01 µg/L used in the older method described by Wershaw and others (1987). (See table 6.) The MDL was calculated by using the following equation:

Table 7. Bias and variability from eight determinations of the method compounds spiked at 0.02 microgram per liter in reagent water for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; μg/L, microgram per liter]

Compound	Mean observed conc. (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.018	0.003	15.14	88.13
Diazinon	.018	.003	15.60	88.13
Dimethoate (E)*	.008	.001	8.80	41.88
Disulfoton	.016	.001	6.30	79.38
Disulfoton sulfone	.021	.003	13.30	103.13
Ethion	.017	.002	10.60	83.75
Ethion monoxon (E)*	.018	.002	12.20	90.63
Ethoprop	.018	.002	13.30	91.88
O-Ethyl-O-meth_ioate	.020	.002	7.72	97.50
Fenthion	.016	.002	10.00	77.50
Fonofos	.019	.002	11.60	95.00
Fonofos oxon (E)*	.017	.002	14.10	86.88
Malathion	.019	.002	11.10	92.50
Methidathion	.019	.002	12.60	93.13
Methyl parathion	.019	.002	12.60	93.13
Parathion	.016	.002	13.80	80.63
Phorate	.016	.002	12.50	80.63
Phorate oxon (E)*	.018	.002	12.80	90.00
Profenofos	.018	.002	11.70	91.88
Propetamphos	.019	.002	12.60	92.50
Sulfotepp (E)*	.018	.002	11.70	90.00
Sulprofos (E)*	.015	.001	9.30	74.38
Terbufos	.017	.002	10.60	84.38
Tribufos (E)*	.013	.002	14.60	63.13
Trithion	.017	.002	10.00	84.38
Isofenfos (Surrogate)	.018	.003	14.48	89.38

$$MDL = S \times t_{(n-1,1-\alpha=0.99)} , \quad (4)$$

where S = standard deviation of the determined concentration, in micrograms per liter, for the replicate analyses;

n = number of replicate analyses; and

$t_{(n-1,1-\alpha=0.99)}$ = Student's t value for the 99 percent ($\alpha = 0.01$) confidence level with $n-1$ degrees of freedom (U.S. Environmental Protection Agency, 1997).

NOTE: More than one significant figure was included for the standard deviations used to calculate the MDL.

Table 8. Bias and variability from eight determinations of the method compounds spiked at 0.05 microgram per liter in reagent water for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter; ni, not in spike solution; na, not applicable]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.040	0.002	6.05	80.50
Diazinon	.041	.003	6.47	81.00
Dimethoate (E)*	.020	.002	10.69	40.00
Disulfoton	.042	.002	5.54	83.50
Disulfoton sulfone	.045	.003	7.44	90.75
Ethion	.039	.002	5.87	78.25
Ethion monoxon (E)*	.043	.003	5.96	86.00
Ethoprop	.043	.003	6.25	86.25
O-Ethyl-O-meth_ioate	ni	na	na	na
Fenthion	.041	.002	3.54	82.25
Fonofos	.043	.002	5.22	86.75
Fonofos oxon (E)*	.039	.003	7.07	77.75
Malathion	.044	.003	5.77	87.75
Methidathion	.045	.003	5.64	90.75
Methyl parathion	.044	.003	5.64	87.75
Parathion	.042	.003	6.17	84.75
Phorate	.041	.003	6.30	81.25
Phorate oxon (E)*	.041	.003	8.27	82.50
Profenofos	.042	.003	6.79	84.75
Propetamphos	.044	.002	4.85	87.50
Sulfotepp (E)*	.043	.003	6.04	85.75
Sulprofos (E)*	.038	.002	5.67	75.25
Terbufos	.041	.003	6.39	81.50
Tribufos (E)*	.030	.002	6.23	59.25
Trithion	.040	.002	6.13	78.50
Isofenfos (Surrogate)	.043	.003	6.04	85.75

13.5 Method detection limits for all compounds generally were lower than the current (2002) minimum reporting level (MRL) of 0.01 µg/L for the old whole-water method (Wershaw and others, 1987). Only three compounds—disulfoton sulfone, fonofos oxon, and methidathion—have method detection limits equal to, or slightly above, 0.01µg/L.

13.6 Bias (percent mean recovery) and variability (percent relative standard deviation) are shown for all matrices in tables 7 through 15. Excellent performance is indicated for most compounds with mean recoveries in excess of 80 percent and relative standard deviation (RSD) below 10 percent in all three matrices, with slightly high RSDs in the 0.05-µg/L surface-water-spike samples. Mean recoveries of method compounds are comparable to or slightly greater than those observed in similar USGS filtered-water methods that use

Table 9. Bias and variability from eight determinations of the method compounds spiked at 0.5 microgram per liter in reagent water for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter; ni, not in spike solution; na, not applicable]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.500	0.043	8.53	100.00
Diazinon	.514	.040	7.82	102.89
Dimethoate (E)*	.143	.055	38.07	28.66
Disulfoton	.391	.172	43.97	78.14
Disulfoton sulfone	.595	.058	9.75	118.97
Ethion	.413	.015	3.65	82.51
Ethion monoxon (E)*	.325	.007	2.26	65.03
Ethoprop	ni	na	na	na
O-Ethyl-O-meth_ioate	.207	.005	2.48	41.34
Fenthion	.466	.026	5.64	93.11
Fonofos	.494	.052	10.42	98.86
Fonofos oxon (E)*	.533	.047	8.76	106.63
Malathion	.541	.036	6.73	108.14
Methidathion	.568	.047	8.28	113.63
Methyl parathion	.543	.038	7.08	108.54
Parathion	.469	.022	4.62	93.89
Phorate	.491	.049	9.93	98.26
Phorate oxon (E)*	.502	.058	11.50	100.40
Profenofos	.536	.044	8.18	107.23
Propetamphos	.522	.038	7.32	104.40
Sulfotepp (E)*	.395	.011	2.80	79.09
Sulprofos (E)*	.464	.042	8.98	92.80
Terbufos	.509	.049	9.58	101.89
Tribufos (E)*	.371	.023	6.12	74.26
Trithion	.513	.044	8.59	102.69
Isofenfos (Surrogate)	68.63	5.035	7.33	68.63

C-18 SPE and analysis by GC with mass spectrometric detection (Zaugg and others, 1995; Sandstrom and others, 2001). Dimethoate showed unacceptable performance in all three matrices in comparison to the performance of all other compounds, as expected based on its reported poor performance (Zaugg and others, 1995; Sandstrom and others, 2001). The recoveries for all compounds in all three matrices were greater than 60 percent, although dimethoate recovery only was about 30 percent because it has a high water solubility (20 g/L at 25°C; Mackay and others, 1997) and is incompletely collected by a C-18 SPE column (Foreman and Foster, 1991). Therefore, dimethoate concentrations are reported permanently as estimated ("E" coded) in this method because of the breakthrough problem.

13.7 Based on the holding-time studies in reagent water and on the dry

Table 10. Bias and variability from eight determinations of the method compounds spiked at 0.02 microgram per liter in surface water (South Platte River near Dartmouth St. and Platte River Dr., Denver, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.018	0.001	5.83	88.75
Diazinon[1]	.017	.002	11.61	84.38
Dimethoate (E)*	.013	.002	12.09	62.50
Disulfoton	.022	.002	6.96	108.13
Disulfoton sulfone	.030	.002	7.57	148.75
Ethion	.018	.001	7.48	90.63
Ethion monoxon (E)*	.025	.002	6.87	125.63
Ethoprop	.020	.001	5.83	101.88
O-Ethyl-O-meth_ioate	.021	.001	5.83	102.50
Fenthion	.019	.002	9.03	95.63
Fonofos	.020	.001	4.67	98.13
Fonofos oxon (E)*	.022	.002	6.87	110.00
Malathion	.021	.001	6.09	106.88
Methidathion	.027	.001	5.19	133.75
Methyl parathion	.020	.002	7.72	100.63
Parathion	.018	.002	13.02	91.25
Phorate	.020	.001	3.88	97.50
Phorate oxon (E)*	.021	.001	5.56	106.88
Profenofos	.023	.002	6.44	116.88
Propetamphos	.019	.001	4.36	95.63
Sulfotepp (E)*	.019	.001	4.09	92.50
Sulprofos (E)*	.018	.001	5.47	90.63
Terbufos	.020	.001	6.39	101.88
Tribufos (E)*	.016	.001	6.79	78.13
Trithion	.019	.001	4.87	95.00
Isofenfos (Surrogate)	.020	.001	3.88	97.50

[1]Mean observed concentration after subtracting background diazinon concentration of 0.013 µg/L.

SPE performed by Sandstrom and others (2001) for the LS 2002 method, which nearly has identical sample-preparation steps as this method, the following six compounds—ethion monoxon, fonofos oxon, phorate oxon, sulprofos, sulfotepp, and tribufos—also will be permanently reported as estimated ("E" coded) in this method.

13.8 In addition, the recoveries for methidathion, disulfoton sulfone, and ethion monoxon in surface water substantially were greater than 100 percent (110 to 150 percent). It is possible that they are present naturally at levels near or less than the MDL, but contribute to the percent recovered. This result also could be caused by matrix-enhanced sensitivity. The injection of a dirty sample extract coats surfaces with matrix components and protects the problem compounds from decomposition or adsorption. As a result, a

Table 11. Bias and variability from eight determinations of the method compounds spiked at 0.05 microgram per liter in surface water (South Platte River near Dartmouth St. and Platte River Dr., Denver, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently “E” coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.044	0.002	4.38	88.00
Diazinon[1]	.045	.002	4.78	89.25
Dimethoate (E)*	.024	.002	7.81	48.25
Disulfoton	.057	.002	3.65	113.25
Disulfoton sulfone	.073	.004	5.81	145.00
Ethion	.048	.003	5.60	96.25
Ethion monoxon (E)*	.064	.003	5.17	127.25
Ethoprop	.050	.002	2.99	100.75
O-Ethyl-O-meth_ioate	.049	.002	3.34	98.25
Fenthion	.042	.002	3.62	83.25
Fonofos	.048	.002	4.07	96.25
Fonofos oxon (E)*	.050	.002	4.85	100.50
Malathion	.054	.002	3.90	107.75
Methidathion	.065	.002	3.25	130.50
Methyl parathion	.051	.001	2.53	101.50
Parathion	.040	.003	6.74	79.25
Phorate	.050	.002	4.13	99.50
Phorate oxon (E)*	.053	.002	4.55	106.25
Profenofos	.060	.003	4.71	119.50
Propetamphos	.048	.002	3.80	96.50
Sulfotepp (E)*	.046	.002	3.81	92.75
Sulprofos (E)*	.047	.002	4.54	93.50
Terbufos	.051	.002	4.39	102.50
Tribufos (E)*	.043	.003	7.18	86.75
Trithion	.049	.002	4.82	97.75
Isofenfos (Surrogate)	.049	.002	4.67	98.25

[1]Mean observed concentration after subtracting background diazinon concentration of 0.013 µg/L.

relatively greater response is observed for compounds in sample extracts than in clean calibration solutions (Erney and others, 1993, 1997).

13.9 The recoveries of ethoprop degradate (O-Ethyl-O-meth_ioate) were low (average 40 percent) in all three matrices spiked at 0.5 µg/L. It might be degrading over time in the spike mix and, thus, represents a potential compound to be “E” coded.

13.10 The compounds that were evaluated during early testing of this method and the reason they were not suitable for inclusion are listed in table 16.

Table 12. Bias and variability from eight determinations of the method compounds spiked at 0.5 microgram per liter in surface water (South Platte River near Dartmouth St. and Platte River Dr., Denver, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter; ni, not in spike solution; na, not applicable]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.471	0.044	9.38	94.25
Diazinon[1]	.488	.043	8.74	97.65
Dimethoate (E)*	.059	.006	10.26	11.88
Disulfoton	.494	.042	8.46	98.70
Disulfoton sulfone	.613	.053	8.60	122.63
Ethion	.408	.018	4.37	81.58
Ethion monoxon (E)*	.323	.007	2.11	64.55
Ethoprop	ni	na	na	na
O-Ethyl-O-meth_ioate	.196	.004	1.97	39.20
Fenthion	.471	.020	4.20	94.10
Fonofos	.500	.043	8.60	100.05
Fonofos oxon (E)*	.506	.045	8.83	101.18
Malathion	.519	.037	7.04	103.80
Methidathion	.555	.049	8.88	110.93
Methyl parathion	.528	.041	7.84	105.65
Parathion	.457	.016	3.57	91.45
Phorate	.505	.047	9.26	100.90
Phorate oxon (E)*	.514	.048	9.39	102.88
Profenofos	.525	.049	9.28	104.90
Propetamphos	.492	.040	8.05	98.40
Sulfotepp (E)*	.387	.012	3.07	77.38
Sulprofos (E)*	.471	.042	8.97	94.28
Terbufos	.504	.046	9.03	100.83
Tribufos (E)*	.411	.026	6.39	82.10
Trithion	.484	.045	9.35	96.70
Isofenfos (Surrogate)	66.49	7.412	11.15	66.49

[1]Mean observed concentration after subtracting background diazinon concentration of 0.013 µg/L.

Table 13. Bias and variability from eight determinations of the method compounds spiked at 0.02 microgram per liter in ground water (domestic well water, Evergreen, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently “E” coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.014	0.001	9.32	68.75
Diazinon	.019	.002	8.12	95.63
Dimethoate (E)*	.008	.001	17.08	38.13
Disulfoton	.021	.002	9.33	106.25
Disulfoton sulfone	.021	.002	10.85	103.75
Ethion	.017	.001	5.14	86.25
Ethion monoxon (E)*	.020	.002	9.44	101.88
Ethoprop	.019	.002	7.96	95.00
O-Ethyl-O-meth_ioate	.019	.001	5.78	92.50
Fenthion	.015	.001	7.44	75.63
Fonofos	.018	.002	8.15	91.25
Fonofos oxon (E)*	.014	.002	11.88	67.50
Malathion	.019	.001	5.25	94.38
Methidathion	.020	.002	9.79	101.88
Methyl parathion	.018	.002	8.40	90.00
Parathion	.016	.001	6.57	78.75
Phorate	.015	.001	7.02	73.75
Phorate oxon (E)*	.017	.002	8.67	86.88
Profenofos	.019	.002	8.90	93.75
Propetamphos	.018	.002	8.38	88.75
Sulfotepp (E)*	.016	.001	7.09	79.38
Sulprofos (E)*	.017	.002	8.51	85.63
Terbufos	.015	.001	6.79	76.25
Tribufos (E)*	.014	.002	12.14	68.75
Trithion	.017	.001	7.65	83.75
Isofenfos (Surrogate)	.019	.001	5.25	94.38

Table 14. Bias and variability from eight determinations of the method compounds spiked at 0.05 microgram per liter in ground water (domestic well water, Evergreen, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.039	0.004	11.15	77.25
Diazinon	.047	.005	10.02	93.00
Dimethoate (E)*	.016	.006	36.89	32.50
Disulfoton	.055	.005	8.18	109.25
Disulfoton sulfone	.057	.008	13.71	113.25
Ethion	.043	.005	10.98	86.00
Ethion monoxon (E)*	.050	.006	11.74	100.50
Ethoprop	.047	.004	8.90	93.00
O-Ethyl-O-meth_ioate	.046	.004	9.07	92.75
Fenthion	.042	.006	14.32	84.25
Fonofos	.046	.004	8.88	91.50
Fonofos oxon (E)*	.042	.005	12.34	84.00
Malathion	.048	.005	10.03	95.25
Methidathion	.051	.007	14.37	102.00
Methyl parathion	.047	.005	10.06	93.25
Parathion	.041	.007	15.92	82.75
Phorate	.044	.006	13.03	87.50
Phorate oxon (E)*	.045	.004	9.64	90.75
Profenofos	.048	.005	10.45	96.25
Propetamphos	.046	.004	8.36	91.75
Sulfotepp (E)*	.042	.004	9.09	84.00
Sulprofos (E)*	.043	.004	9.70	86.75
Terbufos	.044	.006	13.03	87.75
Tribufos (E)*	.034	.005	14.14	67.50
Trithion	.043	.004	9.93	86.75
Isofenfos (Surrogate)	.046	.005	10.50	91.50

Table 15. Bias and variability from eight determinations of the method compounds spiked at 0.5 microgram per liter in ground water (domestic well water, Evergreen, Colo.) for the analytical method

[Compounds marked with an asterisk (*) are permanently "E" coded (estimated concentration) in this method. Compound degradates are indented. conc., concentration; µg/L, microgram per liter; ni, not in spike solution; na, not applicable]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Bias (percent of true conc.)
Chlorpyrifos	0.486	0.030	6.20	97.13
Diazinon	.512	.039	7.66	102.48
Dimethoate (E)*	.092	.040	43.01	18.45
Disulfoton	.358	.026	7.22	71.58
Disulfoton sulfone	.619	.049	7.87	123.70
Ethion	.417	.013	3.12	83.38
Ethion monoxon (E)*	.328	.008	2.38	65.53
Ethoprop	ni	na	na	na
O-Ethyl-O-meth_ioate	.202	.005	2.34	40.40
Fenthion	.471	.017	3.60	94.20
Fonofos	.507	.038	7.58	101.45
Fonofos oxon (E)*	.533	.042	7.83	106.50
Malathion	.534	.033	6.10	106.83
Methidathion	.565	.039	6.84	112.95
Methyl parathion	.540	.038	7.02	108.03
Parathion	.470	.015	3.21	93.90
Phorate	.492	.039	7.87	98.38
Phorate oxon (E)*	.536	.043	7.92	107.23
Profenofos	.544	.039	7.10	108.70
Propetamphos	.493	.035	7.06	98.60
Sulfotepp (E)*	.391	.010	2.65	78.28
Sulprofos (E)*	.468	.033	7.10	93.65
Terbufos	.499	.038	7.54	99.78
Tribufos (E)*	.418	.018	4.33	83.55
Trithion	.502	.035	7.04	100.35
Isofenfos (Surrogate)	70.813	4.933	6.97	70.81

Table 16. Compounds tested and the reason for their deletion from this method

Compound tested	Reason for deletion
Acephate	Very poor flame photometric detection response
Cadusaphos	Very poor flame photometric detection response
Dichlorovos	Very poor flame photometric detection response
Dicrotophos	Very poor flame photometric detection response
Fenamiphos	Very poor flame photometric detection response
Guthion	Very poor flame photometric detection response
Metamidophos	Very poor flame photometric detection response
Naled	Very poor flame photometric detection response
Phosmet	Very poor flame photometric detection response
Temephos	Very poor flame photometric detection response
Azinphos methyl oxon	Very poor flame photometric detection response
Chlorpyrifos oxon	Very poor flame photometric detection response
Diazinon oxon	Very poor flame photometric detection response
Dimethoate oxon	Very poor flame photometric detection response
Fenamiphos sulfone	Poor with solid-phase extraction recovery
Fenamiphos sulfoxide	Very poor flame photometric detection response
Fenthion sulfone	Poor with solid-phase extraction recovery
Malaoxon	Very poor flame photometric detection response
Paraoxon methyl	Poor with solid-phase extraction recovery
Paraoxon ethyl	Poor with solid-phase extraction recovery
Phosmet oxon	Very poor flame photometric detection response
Temephos sulfoxide	Very poor flame photometric detection response
Terbufos oxygen analog sulfone	Very poor flame photometric detection response

Insufficient research on these compounds (table 16) precluded the exact reason for performance failure. Some compounds did not respond because of nondetectability by GC/FPD and low solubility in hexane, the solvent used to prepare the initial GC/FPD evaluation standard. In addition, photodecomposition or rapid degradation in water, volatility (excessive volatilization losses during sample preparation), and thermal liability could be other reasons for unacceptable performance of these compounds.

SUMMARY AND CONCLUSIONS

This report presents a method for the routine analysis of 20 parent organophosphate pesticides and 5 pesticide degradates in filtered-water samples that includes 7 compounds to be reported permanently as estimated ("E" coded) concentration. Recoveries of method compounds, except dimethoate, in spiked reagent-water samples ranged from 41 to 119 percent. Dimethoate was the only compound that showed low recovery (about 35 percent) because of incomplete collection of this compound on the C-18 solid-phase extraction (SPE) column, and, thus, is reported in the method with an estimated remark code. Based on the holding-time studies in reagent water and on the dry SPE by Sandstrom and others (2001) for the laboratory schedule (LS) 2002 method, which nearly has identical sample preparation steps as this method, the following six compounds—ethion monoxon, fonofos oxon, phorate oxon, sulprofos, sulfotepp, and tribufos—also will be permanently reported as estimated ("E" coded). Single-operator

method detection limits (determined and combined in all three matrices) range from 0.004 to 0.012 µg/L. Malathion and disulfoton, which have been poor performing compounds in the whole-water method (Wershaw and others, 1987), demonstrated good recoveries (greater than 70 percent) and precision in all matrices tested at three different concentrations in this filtered-water method.

This new method is for filtered-water samples only, and, thus, is most applicable for those compounds that primarily are in the dissolved phase in the water sample. Historically, the majority of USGS samples analyzed at the NWQL by gas chromatography with flame photometric detection for organophosphates have been whole-water samples measured by method O-3104-83 (Wershaw and others, 1987). No comparison data between the whole-water method and this new filtered-water SPE method are available. However, differences in reported organophosphate concentrations from these two methods are expected, especially for those compounds that exhibit substantial sorption to suspended particulate matter, colloids, or dissolved organic carbon, which would produce low bias in reported concentrations of organophosphates determined by the filtered-water method compared to the whole-water method.

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