METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF TRIAZINE AND OTHER NITROGEN-CONTAINING COMPOUNDS BY GAS CHROMATOGRAPHY WITH NITROGEN PHOSPHORUS DETECTORS

By Dennis J. Markovchick, James A. Lewis, Ronald W. Brenton, Jana L. Iverson, and Helen L. Wharry

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
gram (g)	0.0353	ounce, avoirdupois
liter (L)	1.06	quart
meter (m)	3.3	foot
microgram (µg)	35.27×10^{-8}	ounce, avoirdupois
microliter (µL)	33.8×10^{-6}	ounce, fluid
micrometer (µm)	3.3×10^{-6}	foot
milligram (mg)	35.27×10^{-5}	ounce, avoirdupois
microgram per liter (µg/L)	1	part per billion
milligram per liter (mg/L)	1	part per million
milliliter (mL)	0.0338	ounce, fluid
millimeter (mm)	0.0394	inch
nanogram (ng)	35.27×10^{-11}	ounce, avoirdupois
picogram (pg)	35.27×10^{-14}	ounce, avoirdupois

Temperature can be converted from degree Celsius (^{o}C) to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F = 9/5\ (^{o}C) + 32.$$

Water-quality units abbreviated in this report are as follows:

centimeter per second (cm/sec)
milliliter per minute (mL/min)
microgram per liter (µg/L)
picogram per area (pg/area)
picogram per microliter (pg/µL)
pound per square inch (lb/in^2)

The following abbreviations also are used in this report:

ACS	American Chemical Society
DI	deionized water
EDL	estimated detection limit
FRW	fortified reagent water
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
K-D	Kuderna-Danish
LRB	laboratory reagent-water blank
MSDS	material safety data sheet
MTBE	methyl tert-butyl ether
NAWQA	National Water-Quality Assessment Program
NPD	nitrogen phosphorus detector
NWQL	National Water Quality Laboratory
RSD	relative standard deviation
SIM	selected ion monitoring
TFE	tetrafluoroethylene
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WATSTORE	Water Data Storage and Retrieval System

Use of firm and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY-- DETERMINATION OF TRIAZINE AND OTHER NITROGEN-CONTAINING COMPOUNDS BY GAS CHROMATOGRAPHY WITH NITROGEN PHOSPHORUS DETECTORS

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ABSTRACT

A gas chromatographic technique using nitrogen phosphorus detection and two dissimilar fused-silica capillary columns is the method currently (1994) used by the National Water Quality Laboratory (NWQL) for the analysis of triazine and other selected nitrogen-containing compounds (NWQL schedule 1389). The original method was developed for a schedule containing 10 compounds.

This report provides updated recovery and precision information obtained for 22 compounds, 2 metabolites, and 1 fungicide (carboxin) currently (1994) on NWQL schedule 1389. This information was compiled by spiking all compounds into three different water matrices at two different levels of concentration. Seven replicates were analyzed at each concentration level in each matrix.

The recoveries ranged from 69 to 120 percent for all compounds except the six that follow: bromacil, butylate, desisopropylatrazine, hexazinone, terbacil, and vernolate. For these compounds, the recoveries had a much wider range and generally were less than 69 percent.

INTRODUCTION

This report describes a U.S. Geological Survey (USGS) method for determining triazine and other nitrogen-containing compounds. The method supplements other methods of USGS for determination of organic substances in water that are described by Wershaw and others (1987). Historically, the National Water Quality Laboratory (NWQL) has analyzed water samples for 10 nitrogen-containing compounds, using NWQL schedule 1389 (Triazine Herbicides). An NWQL organic schedule is a list of compounds usually determined by one methodology. This method of analysis is described in Wershaw and others (1987, p. 46-49). Subsequently, two additional compounds--metolachlor and metribuzin--were added to the schedule.

In 1986, Battelle developed method 507 for the U.S. Environmental Protection Agency (USEPA), which included a number of additional nitrogen-containing compounds (Graves, 1988, p. 143-170). Administrators for USGS, National Water-Quality Assessment (NAWQA) Program, requested that the NWQL provide the analysis for several additional compounds included in USEPA method 507.

The 12 compounds reported using NWQL schedule 1389 are as follows: alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, simetryn, and trifluralin. The 10 additional compounds requested by the NAWQA Program are bromacil, butachlor, butylate, carboxin, cycloate, diphenamid, hexazinone, propachlor, terbacil and vernolate. Also, there has been considerable interest in atrazine metabolites. Two of these metabolites--desethylatrazine and desisopropylatrazine--can be recovered from water samples by liquid-liquid extraction and analyzed using gas chromatographic techniques. Terbuthylazine--a compound not used in the United States--also is included in this schedule for use as a surrogate compound.

Several meetings were held to agree on the experimental protocol that would be used to develop the information. The meetings were attended by members of the NWQL Organic Program, the Chief of the NWQL Quality Management Program, and the Chief of the NWQL Methods Research and Development Program.

The main guidelines for the protocol are as follows:

1. The recovery, precision, and bias information would be based on analytical data produced from three different spiked-water matrices: ground water, surface water, and reagent water.

2. Each water matrix would be spiked at two different concentration levels. One concentration would be 10 times the estimated reporting level, and the other concentration would be large enough to help define the upper concentration limit of the analysis.

3. There would be seven replicates for each concentration in each matrix.

4. The spiked-water samples would be held in a refrigerator at about 4°C for at least 48 hours prior to the start of analysis, to approximate the holding time for real samples.

5. The method used would be an adaptation of USEPA method 507. Fifty g of sodium chloride (NaCl) would be added to each sample and dissolved prior to extraction with methylene chloride (5 g has been used in the method since 1980). The extract would be concentrated by evaporation in a steam bath. The concentrated extract would be solvent exchanged into methyl t-butyl ether. Final analysis would employ dual capillary column gas chromatography (GC) and two nitrogen phosphorus detectors.

Precision and bias information need to be developed for the analytical method used before compounds can be assigned parameter codes and analytical data entered into the Water Data Storage and Retrieval System (WATSTORE). Precision and bias information for the 10 additional compounds were not available in 1987 when analyses of water samples for the NWQL schedule 1389 compounds were begun.

The purpose of the method described in this report is (1) to enhance recovery and precision by improving the technique; (2) to use the method to gather information on recovery, precision, and bias; and (3) to expand the method to include 24 compounds and a surrogate. This revised method was implemented in the NWQL in January 1994.

ANALYTICAL METHOD

Parameter and Code:
Triazines, total recoverable, gas chromatography, O-3106-93

1. List of parameters, reporting levels, and codes

Compounds, reporting levels, and codes included in the triazine schedule are listed in table 1.

Table 1.--Compounds included in National Water Quality Laboratory triazine schedule 1389

[µg/L, micrograms per liter; WATSTORE, Water Data Storage and Retrieval System]

Compounds	Reporting level (µg/L)	WATSTORE code, total recoverable	Laboratory code
Alachlor	0.2	77825	1331
Ametryn	.1	82184	848
Atrazine	.1	39630	717
Bromacil	.2	30234	1463
Butachlor	.1	30235	1468
Butylate	.1	30236	1470
Carboxin	.2	30245	1464
Cyanazine	.2	81757	846
Cycloate	.1	30254	1469
Desethylatrazine	.2	75981	1612
Desisopropylatrazine	.2	75980	1613
Diphenamid	.1	30255	1465
Hexazinone	.2	30264	1466
Metolachlor	.2	82612	1334
Metribuzin	.1	82611	1333
Prometon	.2	39056	718
Prometryn	.1	39057	631
Propachlor	.1	30295	1471
Propazine	.1	39024	844
Simazine	.1	39055	719
Simetryn	.1	30954	720
Terbacil	.2	30311	1462
Trifluralin	.1	39030	1332
Vernolate	.1	30324	1467

2. Application

This method is suitable for the determination of triazine herbicides and other selected nitrogen-containing compounds in water and mixtures of water-suspended sediment.

3. Summary of method

The pH of a measured volume (about 1 L) of sample is adjusted to range from 7.0 to 9.0. Then 50 g of NaCl is added and dissolved. The sample is extracted with methylene chloride. The methylene chloride extract is isolated, dried, and concentrated to a volume of 1 mL during a solvent exchange to methyl t-butyl ether (MTBE). Chromatographic conditions are described that permit the separation and determination of the compounds in the extract by capillary column GC with a nitrogen phosphorus detector (NPD).

4. Interferences

4.1 *Method interferences* might 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 need to be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

4.1.1 Prior to use, rinse all glassware with the solvent to be used in the sample preparation procedure. Clean all glassware as soon as possible after use by thoroughly rinsing with deionized (DI) water. This procedure is followed by washing with hot water and detergent and a thorough rinsing with tap water followed by deionized water. Drain dry, and heat in an oven or muffle furnace at 450°C for 8 hours. Do not heat volumetric glassware. Thermally stable materials might not be eliminated by this treatment. After drying and cooling, store glassware in a clean environment to prevent any accumulation of dust or other contaminants. The use of ultrapure solvents and reagents will help to minimize interference problems.

4.1.2 System contamination might interfere when a sample containing small concentrations of compounds is analyzed immediately following a sample containing large concentrations of compounds. After a sample is injected, the syringe is rinsed 10 times with solvent to reduce the chance of cross-contamination.

4.2 *Matrix interferences* might be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary from source to source, depending on the water sampled. This potential problem is addressed using a dual column confirmation procedure. If there are further questions about compound identification, the sample is submitted for confirmation using gas chromatography/mass spectrometry (GC/MS).

4.2.1 It is important that samples and calibration standards be contained in the same solvent. If this is not the case, chromatographic comparability of standards to sample might be affected.

5. Instrumentation

5.1 *Gas chromatograph/nitrogen phosphorus detector (NPD)*. Hewlett-Packard 5890 or equivalent. An automated sample injector may be used.

5.1.1 *Gas chromatographic configuration*

Column 1 (primary column)--30-m long X 0.25-mm inside diameter (ID) RTX-5 bonded fused-silica columns, 0.25-µm film thickness (Restec Corp.) or equivalent.

Column 2 (confirmation column)--30-m long X 0.25-mm ID RTX 35 bonded fused-silica column, 0.25-µm film thickness (Restec Corp.) or equivalent.

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

Make-up gas--Helium flow, 30 mL/min. Nitrogen may be used as a substitute gas.

Detector gases--Hydrogen flow, 3 to 5 mL/min. Air flow, 90 to 110 mL/min.

Injection mode--Splitless, injection port sweep 30 mL/min. Column head pressure 20 lb/in^2. Septum purge rate 1 to 2 mL/min. Purge valve on (open) at 2 minutes and off (closed) 2 minutes prior to end of sample run.

Both columns are connected to one injection port. An injection volume of 4 µL is divided onto both columns.

Oven temperature program--Initial temperature 50°C, hold 1 minute.

Ramp 1 -- 10°C/min to 157°C, hold 28.3 minutes.

Ramp 2 -- 5°C/min to 175°C, hold 1.4 minutes.

Ramp 3 -- 3°C/min to 225°C, hold 6.34 minutes.

5.1.2 *Detector system*

Use two nitrogen phosphorus detectors (NPD) to generate the validation data presented in the method. Detector temperature is 300°C. Alternative detectors, including a mass spectrometer in a selected ion monitoring (SIM) mode, may be used.

6. Apparatus

6.1 *Separatory funnel*--2,000-mL, with tetrafluoroethylene (TFE) fluorocarbon stopcock, ground glass or TFE fluorocarbon stopper.

6.2 *Flask*, Erlenmeyer--500-mL.

6.3 *Concentrator tube*, Kuderna-Danish (K-D)--10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration needs to be checked at the volumes used in the test. Ground glass stoppers are used to prevent evaporation of eluants.

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

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

6.6 *Vials*--1-mL, gas chromatographic, Wheaton type or equivalent.

6.7 *Boiling stones*--Carborundum, No. 12, granules (Arthur H. Thomas Co., No. 1590-033 or equivalent). Heat at 400°C for 30 minutes prior to use. Cool and store in desiccator.

6.8 *Water bath*--Heated, capable of temperature control (± 5°C). Use the bath in a well-ventilated hood.

6.9 *Balance*--Analytical, capable of accurately weighing to the nearest 0.00001 g.

7. Reagents

7.1 *Acetone, methylene chloride, methyl t-butyl ether* (MTBE)--Distilled-in-glass, pesticide analysis grade. Organic-free reagent water.

7.2 *Potassium hydroxide (KOH) solution*, American Chemical Society (ACS) grade.

7.3 *Sodium chloride* (NaCl), crystal, ACS grade--Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.4 *Sodium sulfate*, granular, anhydrous, ACS grade--Heat treat in a shallow tray at 450°C for a minimum of 4 hours to remove interfering organic substances.

7.5 *Stock standard solutions*--Stock standard solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedure:

7.5.1 Prepare accurate stock standard solutions by weighing about 0.00300 g of pure material. Dissolve the material in MTBE or acetone, and dilute to volume in a 25-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solutions.

7.5.2 Transfer the stock standard solutions into TFE fluorocarbon-sealed screw cap amber vials. Store at from 5 to 15°C and protect from light.

7.5.3 Replace stock standard solutions after 2 months if comparison with laboratory fortified blanks or with QC samples indicate a problem.

7.5.4 Material safety data sheets (MSDS) need to be on file for the materials used, and all personnel need to be informed of the safe storage use and disposal of these materials.

8. Standards

8.1 *External instrument calibration standard.* Prepare calibration standards at a minimum of two concentration levels for each compound of interest and surrogate compound by adding known volumes of one or more stock standard solutions to a volumetric flask. Dilute to volume with MTBE. The lowest standard needs to represent compound concentrations near, but greater than, their respective estimated detection limit (EDL). The remaining standards need to bracket the compound concentrations expected in the sample eluants, or need to be within the working range of the detector. Starting with the standard of highest concentration, analyze each calibration standard and tabulate response (peak height or area) in relation to the concentration in the standard. Use the results to prepare a calibration curve for each compound. When manual calculations are necessary and the ratio of response to concentration (response factor) is a constant over the working range [20 percent relative standard deviation (RSD) or less], linearity can be assumed. In that case, the average ratio or calibration factor can be used in place of a calibration curve.

8.1.1 *Working calibration curve.* Response factors need to be recalculated and verified on each working day by analyzing the high- and low-level standard solutions prior to analyzing samples. The variance between the response factors for each compound in the high- and low-level standards needs to be ±20 percent. If the instrument is out of calibration, rerun the calibration standards.

8.2 *Surrogate standard solution.* Prepare a solution of terbuthylazine in methanol, in a 25-mL volumetric flask. The concentration of this solution should be approximately midway between the high and low calibration standards, for terbuthylazine, when 100 µL is added to a 1-L sample. Add the surrogate standard solution to the sample at the time of extraction and use it to monitor sample preparation procedures.

8.3 *Target compound spike solutions.* Prepare two target compound spike solutions, each containing half the compounds of interest in 25-mL volumetric flasks. The concentration level of each compound needs to be sufficient to produce concentration values, in micrograms per liter (µg/L), within the range of the high and low calibration standards when 100 µL is added to 1 L of reagent water. Use the spike solutions to monitor recovery efficiencies for all target compounds.

9. Sample preparation

9.1 *Extraction (manual method)*

9.1.1 Weigh the bottle containing the sample to the nearest 0.1 g. Record the weight.

9.1.2 Adjust the sample to between pH 7 and 9 by adding potassium hydroxide solution.

9.1.3 Add 100 µL surrogate solution to each sample.

9.1.4 Add 100 µL spike solution to 1 L of organic-free water.

9.1.5 Pour sample into separatory funnel and add 50 g NaCl; seal and shake to dissolve.

9.1.6 Add 75 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 1 minute with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst will need to use mechanical techniques to complete the phase separation. The appropriate technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, and centrifugation. Collect the methylene chloride extract in a 500-mL glass-stoppered Erlenmeyer flask.

9.1.7 Add a second 50-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.

9.1.8 Weigh the empty sample bottle to the nearest 0.1 g, and record the weight. Determine the weight (and volume in milliliters; 1.000 mL = 1.000 g) of the sample by subtracting the weight of the empty bottle from the weight of the bottle and sample.

9.1.9 Add about 5 g anhydrous sodium sulfate to the extract in the glass-stoppered Erlenmeyer flask; shake the flask to dry the extract and allow to sit overnight.

9.2 *Extract concentration*

9.2.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL receiver tube to a 500-mL evaporative flask. Other equivalent concentration devices or techniques may be used in place of the K-D concentrator.

9.2.2 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. Add 0.5 mL MTBE to the K-D concentrator.

9.2.3 Add one or 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, with the temperature set between 60 and 67°C, so that the receiver 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 about 15 to 20 minutes. At the proper rate of concentration, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid extract reaches 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

9.2.4 Dry the joint between the receiver tube and the K-D flask. Remove the receiver tube and place it on a nitrogen evaporating device. Evaporate with a stream of dry nitrogen until the volume of the sample is less than 1 mL. Add 1 mL of MTBE, mix, and evaporate again to less than 1 mL. Repeat this procedure three times.

9.2.5 Adjust the volume of the sample to exactly 1.0 mL; mix well and transfer to a 2-mL crimp cap vial. Crimp a cap on the vial and store at 4°C until ready for analysis.

10. Instrument performance

10.1 *Instrument calibration.* Prior to the analysis of each set of samples, compare the response factor between the high and low calibration standards for each compound. A variance of ±20 percent RSD is acceptable.

10.2 *Signal stability.* Monitor the signal stability of the NPD during sample analysis by placing a low standard in the middle and also at the end of each set of samples. Compare the area counts for each compound in these standards to the corresponding low standard used for instrument calibration. A variance in signal level reflected by the area count of ±20 percent RSD is acceptable.

10.3 *Retention time stability.* Also, use the low standards in the middle and at the end of each run of samples to monitor shifts in retention time.

11. Target compound calibration

Prior to the analysis of each sample set, analyze the calibration standards to recalibrate the instrument. Because of the large number of compounds, prepare the standard in three separate mixtures and at two concentration levels. The variance in response (amount per area count) for each compound at two concentration levels needs to be within ±20 percent RSD to be considered acceptable.

12. Sample analysis and data evaluation

12.1 *Analyze sample extracts*

Inject approximately 2 µL of sample onto each column. The injection volume of the standard solutions needs to be the same as the injection volume of the sample extracts. Record the resulting peak size in area units. If the response exceeds the working linear range of the instrument, dilute the extract and reanalyze.

12.2 *Identification of compounds*

Identify compounds by comparing their retention time to a reference chromatogram on both columns. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then consider identification positive. The width of the retention-time window used to identify compounds needs to be based on measurements of actual retention-time variations of standards over the course of a day. Calculate a suggested window size for a compound by using three times the standard deviation of a retention time. However, use the experience of the analyst to interpret the chromatograms.

13. Calculations

13.1 Calculate the response factor of each identified component in the calibration standard:

$$RF = \frac{A_1}{C_S \times V_1}$$

where RF = response factor of the identified component in the calibration standard, in area per picograms;

A_1 = integrated peak area of identified component in the calibration standard;

C_S = concentration of the standard, in picograms per microliter; and

V_1 = volume of standard injected, in microliters.

13.2 Calculate the concentration of each identified component in the original water sample from the equation

$$\text{Concentration } (\mu g/L) = \frac{A_2 \times V_2}{V_3 \times W \times RF}$$

where A_2 = integrated peak area of identified sample component;

V_2 = final volume of sample extract, in milliliters;

V_3 = volume of sample extract injected, in microliters;

W = weight of sample in grams, expressed in milliliters (1.000 mL = 1.000 g); and

RF = response factor of identified component in the calibration standard, in area per picograms.

14. Reporting of results

Report the concentrations of triazine compounds as follows: less than 0.1 µg/L, as <0.1 µg/L or 0.2 µg/L, as <0.2 µg/L; 0.1 to 1.0 µg/L, one significant figure; 1.0 µg/L and greater, two significant figures. For the recovery study, results are reported to two significant figures (table 2).

15. Precision

Precision and bias information for all 25 compounds are listed in table 2 in the following section. All compounds were spiked into three different water matrices at two different levels of concentration. The three matrices were ground water, surface water, and reagent water. There were seven replicates of each concentration level in each matrix.

DISCUSSION OF RESULTS

The results produced by the analysis of the spiked ground-water, surface-water, and reagent-water samples approximate single operator precision because they were extracted by three people, and then concentrated, solvent exchanged, and analyzed by one person. All of these data sets are listed in table 2.

Terbuthylazine is the surrogate used in this method. The recovery of the surrogate from all three matrices was greater than or equal to 79 percent.

As listed in table 2, all the compounds except for bromacil, butylate, desisopropylatrazine, hexazinone, terbacil, and vernolate had adequate recoveries from all three matrices; recovery ranged from 69 to 120 percent. Recoveries for bromacil ranged from 39 to 50 percent in samples of reagent water; the river water and well water matrices recovered 82 to 100 percent. Butylate recovery was low from all three matrices, ranging from 53 to 64 percent. Desisopropylatrazine recovery was less than 50 percent from all three matrices; recoveries ranged from 39 to 42 percent. Recovery of hexazinone ranged from 65 to 94 percent in samples of ground and surface water; the recovery of this compound in reagent water ranged from 53 to 75 percent. Recovery of terbacil ranged from 89 to 120 percent in samples of ground and surface water as compared to about 75 percent in the reagent-water matrix. Recovery of vernolate was low for all three matrices, ranging from 59 to 73 percent. Triazine compound recovery data are listed in table 2.

Table 2.--Triazine recovery data from three water matrices

[Note: There were seven replicates of each concentration level in each matrix. µg/L, micrograms per liter]

Compound	Matrix	Spike concentration (µg/L)	Concentration found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Alachlor	Arvada well water	0.97	0.96	0.05	5.6	99
	Arvada well water	4.8	4.7	.34	7.1	97
	South Platte River water	.97	.92	.04	4.4	95
	South Platte River water	4.8	4.0	.38	7.9	83
	Reagent water	1.0	.96	.14	13	93
	Reagent water	5.2	4.4	.24	4.6	86
Ametryn	Arvada well water	.96	.83	.11	11	86
	Arvada well water	4.8	4.5	.47	9.7	94
	South Platte River water	.96	.83	.05	5.5	86
	South Platte River water	4.8	3.8	.22	4.5	80
	Reagent water	.89	.82	.02	2.3	92
	Reagent water	4.5	3.9	.35	8.0	88
Atrazine	Arvada well water	1.0	.88	.05	4.8	90
	Arvada well water	4.9	4.2	.27	5.5	86
	South Platte River water	.98	.91	.04	3.6	93
	South Platte River water	4.9	3.8	.19	3.9	78
	Reagent water	1.0	.93	.02	2.3	90
	Reagent water	5.1	4.5	.23	4.5	87
Bromacil	Arvada well water	1.2	1.2	.06	5.4	100
	Arvada well water	6.0	5.8	1.0	17	96
	South Platte River water	1.2	1.2	.05	4.3	98
	South Platte River water	6.0	4.9	.52	8.6	82
	Reagent water	1.0	.50	.70	7.0	50
	Reagent water	5.0	2.0	.24	4.7	39
Butachlor	Arvada well water	.96	.93	.06	6.7	97
	Arvada well water	4.8	4.9	.28	5.8	100
	South Platte River water	.96	.86	.04	4.2	90
	South Platte River water	4.8	3.8	.37	7.6	79
	Reagent water	1.0	.96	.13	13	93
	Reagent water	5.1	4.4	.27	5.3	85

Table 2.--Triazine recovery data from three water matrices--Continued

Compound	Matrix	Spike concentration (µg/L)	Concentration found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Butylate	Arvada well water	1.0	0.63	0.09	8.5	61
	Arvada well water	5.2	3.3	.50	9.6	64
	South Platte River water	1.0	.63	.11	10	60
	South Platte River water	5.2	2.8	.28	5.3	53
	Reagent water	1.2	.76	.06	5.0	64
	Reagent water	6.0	3.2	.46	7.7	54
Carboxin	Arvada well water	.94	.83	.05	4.9	88
	Arvada well water	4.7	3.9	.28	5.9	83
	South Platte River water	.94	.79	.03	3.1	84
	South Platte River water	4.7	3.6	.14	3.0	76
	Reagent water	1.1	.89	.03	2.9	82
	Reagent water	5.5	4.5	.23	4.2	82
Cyanazine	Arvada well water	1.0	.97	.07	7.2	96
	Arvada well water	5.0	5.6	.38	7.6	110
	South Platte River water	1.0	1.0	.04	4.2	99
	South Platte River water	5.0	4.4	.36	7.1	87
	Reagent water	1.0	.98	.13	13	94
	Reagent water	5.2	4.5	.25	4.9	87
Cycloate	Arvada well water	1.0	.83	.09	8.7	82
	Arvada well water	5.0	4.0	.58	11	79
	South Platte River water	1.0	.79	.08	7.7	78
	South Platte River water	5.0	3.6	.39	7.7	71
	Reagent water	1.2	.91	.20	16	73
	Reagent water	6.3	4.4	.22	3.6	70
Desethyl-atrazine	Arvada well water	1.0	.81	.02	2.0	81
	Arvada well water	5.0	3.9	.16	3.3	79
	South Platte River water	1.0	.77	.05	4.5	77
	South Platte River water	5.0	4.1	.29	5.9	82
	Reagent water	1.4	1.0	.03	2.3	73
	Reagent water	6.9	4.9	.57	8.2	71

Table 2.--Triazine recovery data from three water matrices--Continued

Compound	Matrix	Spike concentration (µg/L)	Concentration found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Desisopropyl-atrazine	Arvada well water	1.1	0.45	0.02	1.7	42
	Arvada well water	5.4	2.1	.08	1.5	39
	South Platte River water	1.1	.43	.04	3.4	40
	South Platte River water	5.4	2.2	.18	3.4	41
	Reagent water	.91	.36	.01	1.3	40
	Reagent water	4.5	1.8	.34	7.5	39
Diphenamid	Arvada well water	.99	.94	.94	5.3	94
	Arvada well water	5.0	4.4	.29	5.9	89
	South Platte River water	.99	.90	.04	3.7	90
	South Platte River water	5.0	3.8	.18	3.6	76
	Reagent water	.98	.89	.02	2.5	91
	Reagent water	4.9	4.3	.21	4.2	87
Hexazinone	Arvada well water	1.2	.78	.16	13	65
	Arvada well water	6.0	5.4	.46	7.7	90
	South Platte River water	1.2	1.1	.04	3.5	94
	South Platte River water	6.0	4.9	.45	7.6	82
	Reagent water	1.0	.53	.07	6.9	53
	Reagent water	5.0	3.8	.29	5.9	75
Metolachlor	Arvada well water	1.1	1.0	.06	5.3	91
	Arvada well water	5.5	5.2	.29	5.2	95
	South Platte River water	1.1	.97	.04	3.9	88
	South Platte River water	5.5	4.3	.38	6.9	78
	Reagent water	1.2	.99	.11	9.3	86
	Reagent water	5.7	4.9	.28	5.0	85
Metribuzin	Arvada well water	1.1	1.1	.06	5.6	95
	Arvada well water	5.6	5.4	.51	9.1	96
	South Platte River water	1.1	1.1	.03	3.1	100
	South Platte River water	5.6	4.5	.21	3.7	79
	Reagent water	1.1	.95	.13	12	90
	Reagent water	5.3	4.5	.24	4.6	84

Table 2.--Triazine recovery data from three water matrices--Continued

Compound	Matrix	Spike concentration (µg/L)	Concentration found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Prometon	Arvada well water	0.93	0.69	0.10	11	74
	Arvada well water	4.6	4.4	.29	6.3	96
	South Platte River water	.93	.87	.04	4.0	93
	South Platte River water	4.6	3.7	.36	7.7	80
	Reagent water	1.0	.89	.10	9.1	84
	Reagent water	5.3	4.4	.27	5.0	84
Prometryn	Arvada well water	1.1	1.0	.09	8.4	88
	Arvada well water	5.5	4.6	.59	11	83
	South Platte River water	1.1	1.0	.04	3.8	92
	South Platte River water	5.5	4.4	.22	3.9	79
	Reagent water	1.1	1.0	.04	3.1	91
	Reagent water	5.7	4.9	.24	4.2	87
Propachlor	Arvada well water	1.0	.86	.05	5.2	86
	Arvada well water	5.0	4.3	.34	6.8	85
	South Platte River water	1.0	.85	.03	3.4	84
	South Platte River water	5.0	3.8	.19	3.7	76
	Reagent water	.84	.69	.02	2.6	82
	Reagent water	4.2	3.5	.21	4.9	84
Propazine	Arvada well water	.96	1.0	.06	6.2	98
	Arvada well water	4.8	4.8	.25	5.2	100
	South Platte River water	.96	.85	.04	3.9	89
	South Platte River water	4.8	3.6	.53	11	76
	Reagent water	1.0	.99	.15	14	95
	Reagent water	5.2	4.5	.25	4.8	86
Simazine	Arvada well water	.89	1.1	.05	5.9	120
	Arvada well water	4.5	5.1	.32	7.1	110
	South Platte River water	.89	.87	.03	3.8	97
	South Platte River water	4.5	3.7	.18	3.9	83
	Reagent water	1.0	.96	.02	1.6	92
	Reagent water	5.2	4.6	.24	4.6	89

Table 2.--Triazine recovery data from three water matrices--Continued

Compound	Matrix	Spike concentration (µg/L)	Concentration found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Simetryn	Arvada well water	1.1	0.86	0.14	12	79
	Arvada well water	5.5	4.5	.38	6.9	83
	South Platte River water	1.1	1.0	.04	3.5	96
	South Platte River water	5.5	4.4	.21	3.9	81
	Reagent water	1.2	1.0	.02	1.6	89
	Reagent water	6.0	5.1	.27	4.5	86
Terbacil	Arvada well water	1.1	1.1	.12	11	98
	Arvada well water	5.6	5.2	.39	6.9	92
	South Platte River water	1.1	1.3	.04	3.6	120
	South Platte River water	5.6	5.0	.27	4.7	89
	Reagent water	1.2	.93	.10	8.1	75
	Reagent water	6.2	4.6	.35	5.6	75
Terbuthy-lazine[1]	Arvada well water	.97	.88	.04	4.6	90
	Arvada well water	4.9	4.2	.27	5.6	87
	South Platte River water	.97	.90	.04	3.6	93
	South Platte River water	4.9	3.9	.18	3.7	80
	Reagent water	1.1	.98	.02	2.2	90
	Reagent water	5.5	4.8	.18	3.3	87
Trifluralin	Arvada well water	.96	.82	.07	7.2	86
	Arvada well water	4.8	4.1	.42	8.8	85
	South Platte River water	.96	.76	.03	3.6	79
	South Platte River water	4.8	3.4	.30	6.3	71
	Reagent water	1.0	.79	.15	14	76
	Reagent water	5.2	3.6	.23	4.4	69
Vernolate	Arvada well water	1.0	.70	.10	10	73
	Arvada well water	5	3.4	.57	11	67
	South Platte River water	.99	.70	.17	18	70
	South Platte River water	5	3.1	.49	9.8	63
	Reagent water	1.2	.79	.17	14	66
	Reagent water	6.0	3.5	.29	4.9	59

[1]Terbuthylazine is the surrogate compound.

CONCLUSIONS

Recoveries are adequate for alachlor, ametryn, atrazine, butachlor, carboxin, cyanazine, cycloate, desethylatrazine, diphenamid, metolachlor, metribuzin, prometon, prometryn, propachlor, propazine, simazine, simetryn, terbacil, and trifluralin.

The recoveries of bromacil and hexazinone were marginal in the reagent-water matrix, but adequate for both the surface-water and ground-water matrices.

Vernolate and butylate recoveries were marginal from all three matrices. Recoveries generally were in the 60-percent range for both compounds. Vernolate recoveries ranged from 59 to 73 percent. The recovery of desisopropylatrazine ranged from 39 to 42 percent in all three water matrices.

Requests for bromacil, butylate, desisopropylatrazine, hexazinone, and vernolate need to be made with the understanding that recoveries for these compounds are less than ideal. Greater recoveries for some of these compounds are available from the NWQL using other procedures. For example, schedule 2001/2010 includes butylate with a recovery of about 80 percent, and schedule 1379 includes bromacil (80-percent recovery), hexazinone (87-percent recovery), vernolate (57-percent recovery, also low), and desisopropylatrazine (also low at 48-percent recovery).

QUALITY ASSURANCE

Minimum quality-control requirements include analysis of laboratory reagent blanks, determination of surrogate recoveries in each sample, reagent-water blank, laboratory-spiked reagent water, and assessment of the instrument system. As an additional check, reagent-water and natural-water matricies are occasionally spiked in the field and sent to the laboratory as a routine sample.

Laboratory reagent-water blanks (LRB). Before processing any samples, the analyst needs to demonstrate that all glassware and reagents are free of contaminants that might interfere with the analysis. Each time a set of samples is extracted or reagents are changed, an LRB needs to be analyzed. If an unknown peak is within a range of three standard deviations of the retention-time window of a compound of interest, then the source of contamination must be determined and eliminated before processing samples.

Assessing surrogate recovery. When surrogate recovery from a sample or method blank is low, on the basis of accepted statistical methods of establishing control limits, check the following: (1) calculations to locate possible errors, (2) spiking solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

If an LRB extract reanalysis fails the control limit criterion, the problem needs to be identified and corrected before continuing.

If sample extract reanalysis meets the statistical control limits for surrogate recovery, report data for the analyzed extract. If sample extract continues to fail the recovery criterion, report that the quality of the data for that sample is questionable.

Assessing laboratory performance--fortified reagent water. A fortified reagent-water (FRW) sample is reagent water that has received measured quantities of selected compounds. The laboratory needs to analyze at least one FRW sample with every 10 samples or one per sample set. The concentration of each compound in the FRW is within the range of the calibration standards. Standard statistical techniques are used to establish control limits for compound recovery. If the recovery of any compound falls outside the control limit criterion, that compound is judged out of control, and the source of the problem needs to be identified and resolved before continuing analyses. The laboratory periodically needs to determine and document its detection limit capabilities for the compounds of interest.

Assessing instrument system. Monitor instrument performance daily by placing a standard with known concentrations of the compounds in the middle and at the end of each run of samples. The instrument is considered stable if the signal generated for each compound in the standard is within a 10-percent variance. If the signal level exceeds the 10-percent variance limit, those samples need to be rerun.

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

REFERENCES CITED

Graves, R.L., 1988, Method 507--Determination of nitrogen- and phosphorus-containing pesticides in water by gas chromatography with a nitrogen-phosphorus detector, Revision 2.0, *in* Methods for the determination of organic compounds in drinking water, USEPA/600/4-88/039, p. 143-170.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, p. 46-49.

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