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Determination of atrazine and four organophosphorus pesticides in ground water using solid phase microextraction (SPME) followed by gas chromatography with selected-ion monitoring

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Abstract

A rapid, sensitive, and convenient method is presented for the determination of atrazine and four organophosphorus pesticides (OPP) in small (10 ml) samples of ground water. Samples are initially fortified with ethion (internal standard), then extracted without organic solvent using a 65-μm thickness polydimethylsiloxane/divinylbenzene (PDMS–DVB) solid-phase microextraction (SPME) fiber. The analytes collected are thermally desorbed in a heated gas chromatographic inlet, separated using a fused-silica capillary column, and detected using a mass selective detector in its selected-ion monitoring (SIM) mode. Two independent statistical procedures were used to evaluate the detection limits, which typically range between 2 and 8 $\mu g\ l^{-1}$ for these analytes. Method performance was also evaluated using ''performance evaluation'' samples, in which clean authentic ground waters were fortified to known concentrations with at least two of the analytes of interest. Sample-to-sample analysis time is approximately 30 min, making the new method ideal for ''quick turn'' determinations.

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1. Introduction

Shortly after the beginning of World War II, the US Army constructed and operated several facilities for the manufacture of chemical warfare agents, including sarin (GB), Lewisite, sulfur mustard, and chlorine gas. When hostilities ceased, private companies were encouraged to lease space on these sites and both construct and operate plants that would produce commercial chemical products. At one of these facilities, vapona (*syn*. dichlorvos, DDVP, or phosphoric acid 2,2-dichloroethenyl dimethyl ester; CAS registry no. [62-73-7]) and supona (*syn*. chlorfenvinphos or phosphoric acid 2-chloro-1-(2,4-dichlorophenyl)ethenyl diethyl ester; CAS registry no. [470-90-6]) were manufactured in the periods 1960–1982 and 1963–1967, respectively [1]. When these plants were closed in the mid-1980s and site remediation began, containment system remediation goals (CSRGs) were established both for the specific

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pesticides produced on site and for related compounds that might be present in the corresponding ground waters. These CSRGs included 3 μg atrazine l^{-1} (ng ml^{-1}) (*syn*.6-chloro-*N*-ethyl-*N′*-(1-methylethyl)-1,3,5-triazine-2,4-diamine; CAS registry no. [1912-24-9]) ([2,3]) and 140 μg malathion l^{-1} (*syn*.[(dimethyoxyphosphinothioyl)thio]-butanedioic acid diethyl ester; CAS registry no. [121-75-5]) [4]. Later, parathion (*syn.* ethyl parathion or phosphorothioic acid *O*,*O*-diethyl *O*-(4-nitrophenyl) ester; CAS registry no. [56-38-2]) was added as a target analyte. The chemical structures of these compounds are given in Fig. 1.

The US Army recently requested the development and formal certification of a new analytical procedure that would be capable of detecting each of the aforementioned OPP in ground water at a ''target reporting level'', or TRL, of 1 μg l^{-1} and atrazine at 4 μg l^{-1} [5]. The US Army also requested that the candidate method be capable of solventless extraction of the target analytes, which would be subsequently detected using a mass-selective detector (MSD) in its selected ion monitoring (SIM) mode. Furthermore, the new method needed to employ instrumentation and procedures that could be readily-implemented by most commercial analytical service laboratories. An MSD operated in its SIM would be allowed, but the quantitation procedure had to use at

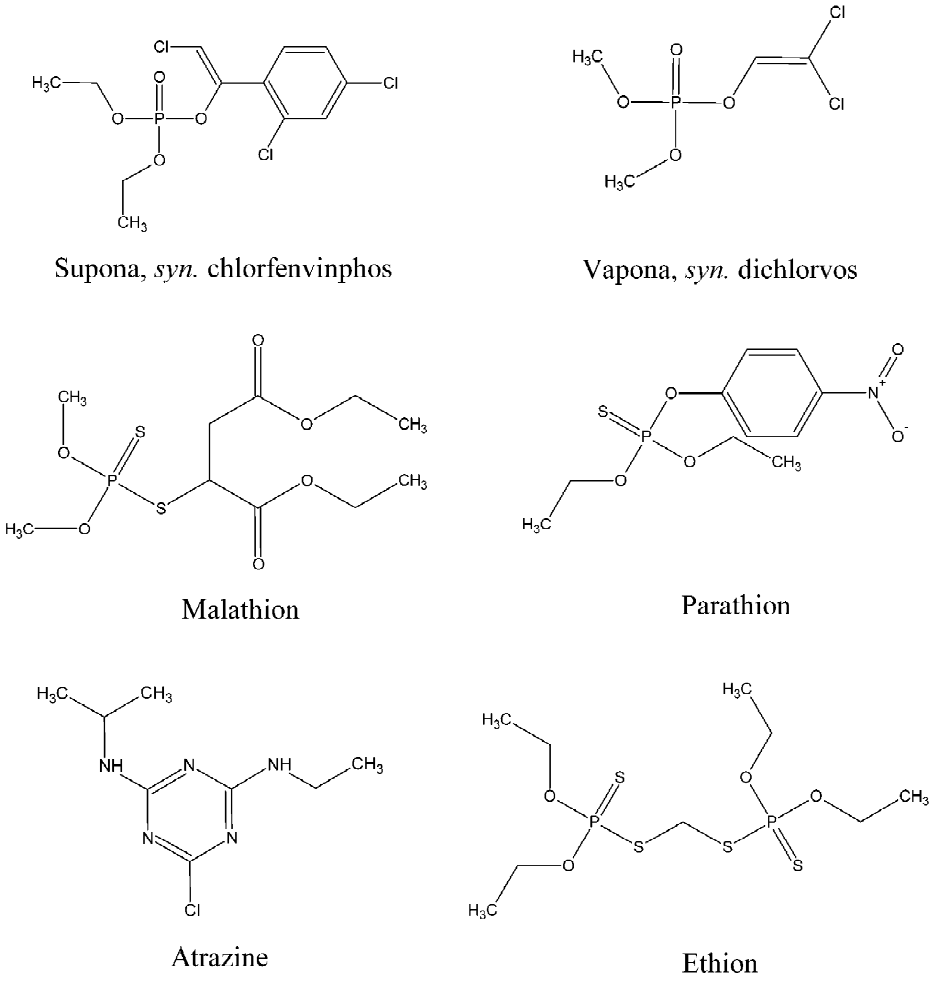

Fig. 1. Chemical structures of the analytes and internal standard.

least three well-chosen mass-to-charge ratios $(m/z)^+$ characteristic of each analyte. The stated and preferred quantitation procedure was the method of internal standards.

Solid-phase microextraction (SPME), a solventless extraction procedure that usually employs a fused-silica fiber with an organic coating, was ideally suited for this task. Various investigators have described SPME procedures for the target analytes described, but not all of them in the same sample and at the same time. Magdic et al. [6] discussed the SPME of 20 different OPP, including vapona and parathion, using 100-μm thickness polydimethylsiloxane (PDMS) and 85-μm thickness polyacrylate (PA) fibers, and reported that extractions employing the latter were usually more effective. Varying the aqueous sample pH did not affect analyte recovery; in contrast, addition of salt decreased the recovery of certain OPP. For those reasons, neither sample treatment was recommended. These results were similar to those reported by Yao et al. [7], who evaluated five coatings (three PDMS thicknesses, PA, and 65-μm thickness polydimethylsiloxane/divinylbenzene (PDMS–DVB)) for their effectiveness in extracting six OPP, including malathion and parathion. The recoveries obtained using PA and 100-μm PDMS were comparable; those from the PDMS–DVB fiber were the poorest among all fibers and analytes. Optimal sampling conditions included extractions carried out at 40 °C with 3% sodium chloride content and no pH adjustment. In marked contrast, Sng et al. [8] also extracted malathion and parathion using five fiber coatings (7- and 30-μm thickness PDMS, 85-μm thickness PA, 65-μm thickness Carbowax-divinylbenzene, and PDMS–DVB), and reported that the PDMS–DVB fiber was clearly the most effective. Valor et al. [9] recently reported partition ratios for 52 pesticides and polychlorinated biphenyls representing the distribution between aqueous media and five SPME fiber coatings under true equilibrium conditions. Partition ratios that were specifically reported for atrazine and parathion employing PDMS–DVB fibers were larger than those from any other coating.

Beltran et al. [10] noted the difficulties in fully equilibrating 11 OPP with either 85-μm PA or 100-μm PDMS coatings. In the specific cases of malathion and supona, equilibrium was achieved after 5 and 8 h of sampling, respectively. Two application notes from a commercial vendor discuss SPME of 20 organophosphorus [11] and 22 organonitrogen [12] pesticides using the 85-μm thickness PA fiber and sampling times exceeding 50 min. Taken together, Yao et al. [7], Sng et al. [8], and Beltran et al. [10] recommended 30-min sampling times. This was well short of the time required to achieve complete equilibration between fiber coating and the aqueous medium, but was convenient because it approximated the time required to complete a gas chromatographic analysis. Massat and Laurent [13] reported similar behavior for atrazine and recommended an identical sampling time. In addition, these authors compared the extraction behavior of 60 organochlorine, organonitrogen (including atrazine), and organophosphorus (including supona, vapona, and malathion) pesticides using both 100-μm PDMS and 65-μm PDMS–DVB fibers. In all cases, the PDMS–DVB fibers frequently permitted lower detection limits than the PDMS fibers. In the specific cases of atrazine, supona, vapona, and malathion, the improvement was approximately a factor of 150, 1, 4, and 2, respectively. Analyte detection was achieved using an MSD/SIM with two or three $(m/z)^+$ values per analyte.

In the present work, small portions of ground water fortified with a known quantity of ethion (*syn.* phosphorodithioic acid *S*,*S*′-methylene *O*,*O*,*O*′,*O*′-tetraethyl ester; CAS registry no. [563-12-2]) as the internal standard were sampled without adjustment for pH or salt content for 20 min at room temperature using PDMS–DVB SPME fibers. The analytes were subsequently desorbed thermally in the injection port of a gas chromatograph, separated using a fused-silica capillary column, and detected using an MSD in its selected-ion mode. Compound identities were established using both compound retention time and at least three $(m/z)^+$ values chosen for each analyte (one ‘‘primary’’ and at least two ‘‘confirmatory’’). All quantitations were performed using the method of internal standards. Two independent statistical procedures were used to calculate the detection limits for these analytes. The performance of the new method was also evaluated using ‘‘performance evaluation’’ samples. These would be prepared independently by a third-party

laboratory, then submitted to candidate laboratories for analysis. The results obtained by a given laboratory could then be compared to the ''known'' or ''true'' values and evaluated statistically for accuracy and/or precision.

2. Materials and methods

2.1. Chemicals

Vapona, atrazine, malathion, parathion, supona, and ethion were purchased either from Supelco (Bellefonte, PA, USA) or Ultra Scientific (North Kingstown, RI, USA) in 98% or better purity, and were used as received. Supona exists in two isomeric forms, viz, *trans* (also known as ''Z'' or beta) and *cis* (also known as ''E'' or alpha). The ratio between the two forms is at least 8.5:1 (w/w) in technical-grade supona [14]; in this work, the measured ratio was approximately 11:1 (w/w). For purposes of this study, all quantitations for supona were based on the Z-isomer, which is the more physiologically-active of the two [15]. Anhydrous sodium sulfate, sodium chloride, HPLC-grade methanol, and HPLC-grade acetone were purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Stock and spiking solutions

Portions (10 mg) of each solid were diluted with 10 ml HPLC-grade acetone to form six individual stock solutions containing 1 mg ml^{-1} of the desired analyte or internal standard. A 500-μl aliquot of the ethion stock solution was then diluted to a final volume of 10 ml with HPLC-grade methanol; its concentration is 50 μg ethion ml^{-1} in methanol–acetone. A 1-ml portion of this solution was diluted to a final volume of 10 ml with HPLC-grade methanol to form the Internal Standard Solution; its concentration is 5 μg ethion ml^{-1}. Portions (1-ml) from each of the remaining five stock solutions were combined and diluted to a final volume of 10 ml with HPLC-grade methanol; the concentration of each analyte is 100 μg ml^{-1} in methanol–acetone. A 1-ml portion of this solution was diluted to a final volume of 10 ml with HPLC-grade methanol to form the Master Calibrating or Master Spiking Solution. (When formal method certification is performed, the two spiking solutions must be prepared independently by different operators using the same instructions.)

2.3. Ground water samples

American Society for Testing and Materials (ASTM) ''model'' ground water was prepared as follows: 1.64 g sodium chloride and 1.48 g anhydrous sodium sulfate were diluted to exactly 1 liter with HPLC-grade water. A 100-ml portion of this stock solution was further diluted to exactly 1 liter with HPLC-grade water to form ''model'' ground water. Samples of clean authentic ground water were kindly provided by the Quality Planning and Assessment Group, Environmental Protection and Waste Services Division, Oak Ridge National Laboratory (Oak Ridge, TN, USA).

2.4. ''Performance evaluation'' samples

''Performance evaluation'' samples were prepared and provided by the Quality Planning and Assessment Group, Environmental Protection and Waste Services Division, Oak Ridge National Laboratory. These were samples of clean authentic ground water fortified to known concentrations of at least two of the named analytes. They are used to check the performance (identification, accuracy, and precision) of a given analytical laboratory for the determination of OPP and atrazine, and are designed to mimic authentic contaminated ground water that would be found at a customer's work site. Additional discussion regarding performance evaluation samples is provided below.

2.5. Solid-phase microextraction equipment

SPME fibers designed for manual sampling (65-μm PDMS–DVB, standard fused-silica core, part no. 57310-U; same coating and thickness on a StabilFlex fiber core, part no. 57346-U), the corresponding holder for manual sampling (part no. 57330-U), and sampling stand (part no. 57333-U), and a heat/stir plate (part no. Z262129-1) were all purchased from Supelco. All fibers (at least five per coating type) were conditioned for at least 1 h at 260 °C, according to the manufacturer's instructions. Micro stirrer bars

(''fleas''), 10 mm×3 mm, were purchased from VWR (USA).

2.6. Gas chromatograph with flame photometric detector

A Varian 3400 gas chromatograph (Varian, Sunnyvale, CA, USA) equipped with a flame photometric detector (phosphorus-selective mode) and splitless septum programmable injector (SPI) was used in the exploratory phase of this work. The injector was equipped with a Siltek™ 0.5-mm SPI injection sleeve (part no. 20775-214.1, Restek, Bellefonte, PA, USA) and a ''pre-drilled'' Thermogreen septum (part no. 23168, Supelco) specifically designed for SPME. (After an SPME injection was carried out, the fiber remained in the injection port to seal the pre-drilled septum.) An SPME inlet guide (part no. 57356-U, Supelco) was used to support the manual holder and its fiber during the desorption process. The injector temperature was programmed from 100 to 250 °C (hold for 5 min) at 180 °C/min. The instrument was equipped with a fused-silica analytical column (Rtx®-5, 30 m×0.32 mm I.D., 1 μm film thickness, part no. 10254, Restek). The column oven temperature was programmed from 100 °C (hold for 2 min) to 275 °C (hold for 7 min) at 20 °C/min (total column oven temperature program time, 17.75 min; estimated sample-to-sample analysis time 25 min). The flow rates for helium (carrier gas), nitrogen (make-up gas), air, and hydrogen (purity of all gases >99.999%) were set to factory-recommended values.

2.7. Gas chromatograph with mass-selective detector

A Hewlett-Packard Model 5890 gas chromatograph configured for split/splitless injections and interfaced to a Hewlett-Packard Model 5970 Series Mass Selective Detector was used for the analysis of all method certification and performance evaluation samples. The injector was equipped with a 0.75 mm I.D. low dead-volume splitless liner specifically designed for SPME performed on Hewlett-Packard instruments (part no. 26375-01, Supelco) and a pre-drilled Thermogreen septum (described above) and maintained isothermally at 260 °C. The purge valve was ''closed'' at the beginning of each analysis and ''opened'' after 2 min. The oven was equipped with a 30 m×0.25 mm I.D. DB™-5, 1.00 μm film thickness fused-silica column (part no. 122-5033, J&W Scientific, Folsom, CA, USA) and programmed as described in Section 2.6. The carrier gas flow (helium, 99.999% purity) was maintained at 1.0 ml min^{-1} (37.1 cm s^{-1}); the initial head pressure was 73 kPa (10.6 p.s.i.) at 100 °C oven temperature.

The MSD was programmed in its single-ion monitoring (SIM) mode to respond to the five analytes and the internal standard, ethion, at their corresponding gas chromatographic retention times. The programming software permits up to six ions to be monitored in a given window defined by two ''group start times.'' The appropriate $(m/z)^+$ values, minimum three, were selected for each analyte both by analyzing single-component standard solutions and by considering literature values [16,17]. The compounds, their corresponding ''group start times,'' and $(m/z)^+$ values are as follows: vapona, 7.00 min, $(m/z)^+$ 109, 185, 79; atrazine, 10.50 min, $(m/z)^+$ 200, 215, 173; malathion, 12.00 min, $(m/z)^+$ 127, 173, 93; parathion, 12.85 min, $(m/z)^+$ 109, 291, 97, 137; supona, 13.30 min, $(m/z)^+$ 267, 323, 269; ethion, 15.00 min, $(m/z)^+$ 97, 231, 384. The ''dwell time,'' or the time during which the MSD monitored only the selected ions for each analyte, was maintained at 100 ms. A ''standard autotune'' program was performed daily to ensure that the mass calibration of the MSD was accurate to within ±0.3 a.m.u. and to demonstrate a negligible presence of water vapor and air.

All data handling, including chromatogram display and automatic peak integration, was carried out using Hewlett-Packard G1034C Version C.0.3.00 ChemStation software. Manual peak integrations were implemented if the automatic integration data were deemed unsatisfactory due to incorrect baseline settings.

2.8. Quality assurance check for fiber performance

A 10-μl aliquot of Master Calibration Solution (10 ng μl^{-1} in each of five analytes) and 10-μl aliquot of Internal Standard Solution (5 ng μl^{-1} in ethion) were added to 10 ml model ground water in a precleaned 20-ml screwcap vial. A micro stirring bar was added

to the diluted solution (final concentrations 10 ng ml^{-1} in all five analytes, 5 ng ml^{-1} in ethion), which was stirred briskly and immediately sampled for 20±0.1 min with a PDMS–DVB SPME fiber. Caution: Vortex formation must not occur. The analytes so collected were immediately desorbed in the injection port of the gas chromatograph, separated, and detected as described in Section 2.7. The same solution was used to check the performance of all SPME fibers used on any given day. The two SPME fibers with the closest extraction behavior for all five analytes (normally within ±15%) were selected for sample extractions on a particular day. The SPME fiber with the ''next closest'' extraction behavior for all five analytes was designated the ''spare''; it was set aside and not used unless one of the other two fibers broke or became irreversibly contaminated.

2.9. Analysis of calibration, certification, performance evaluation, or authentic ground water samples

Aliquots of the Master Calibration Solution (1 to 25 μl) and the Internal Standard Solution (10 μl) were added to 10 ml model ground water in a 20-ml precleaned screwcap vial. A micro stirring bar was added to the diluted solution, which was then stirred briskly (vortex formation must not occur) and immediately sampled for 20±0.1 min with a PDMS–DVB SPME fiber. The analytes so collected were immediately desorbed in the injector port of the gas chromatograph, separated, and detected as described in Section 2.7. At least eight calibration samples and a model ground water blank were required to prepare a calibration curve. A similar approach was employed for the analysis of certification samples, except that the Master Spiking Solution replaced the Master Calibration Solution. A 10-μl aliquot of Internal Standard Solution was added to 10 ml performance evaluation or authentic ground water samples, sampled with the PDMS–DVB SPME fiber, and analyzed in the same manner as either the calibration or certification samples.

2.10. Calculations

The measured integrated peak area data from the MSD obtained for a given analyte spanning the range 0–25 ng ml^{-1} were fit to a calibration curve of the form $A/A_o = m \times (C/C_o) + b$, where A and C are the measured integrated peak area and concentration of an analyte; A_o and C_o are the corresponding quantities for the internal standard; m is the slope of the calibration line; and b is its (nonzero) intercept.

3. Results and discussion

3.1. Method optimization

The initial experiments performed in this work to define the optimized extraction conditions generally confirmed observations reported in the literature for other groups of OPP. For example, the optimum extraction times for vapona, malathion, parathion, and ethion were determined by sampling an aliquot of model ground water that had been fortified to 10 ng ml^{-1} in each analyte over a period of 120 min. As shown in Fig. 2, equilibrium was never achieved for any of these OPP between the PDMS–DVB fiber coating and the aqueous medium during a 2-h period, and another criterion had to be employed to set the SPME sampling time.

Because it was strongly desired to maximize sample throughput (i.e. increase the sample analysis rate), the key parameter became the sample-to-sam-

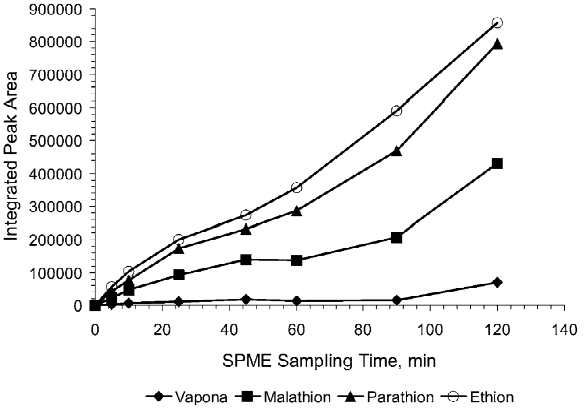

Fig. 2. Evaluation of the optimized SPME sampling time for four OPP.

ple gas chromatographic analysis time, which approximated 20 min. For that reason, the SPME sampling time was fixed at 20±0.1 min. The integrated peak areas, and hence the partition ratios, for ethion, parathion, malathion, and vapona appeared to be inversely related to their solubilities in water, which are 1, 24, 145, and 10 000 μg ml^{-1}, respectively [18,19]. Further work demonstrated that supona (solubility of 145 μg ml^{-1} in water) exhibited a response that was greater than that of parathion, while atrazine (solubility of 70 μg ml^{-1} in water) exhibited the smallest response of all the analytes evaluated. Clearly, water solubility was an important, but not the only, factor in determining the overall partition ratio for a given analyte between the PDMS–DVB fiber coating and water. The recovery of malathion at pH 2 showed no improvement over that observed at pH 7. Increasing the salt content at pH 7 from the usual 0.01% (w/v) in model ground water to 10 or 30% (w/v) also did not improve the recovery of malathion. For that reason, model ground water samples were analyzed without further adjustment of either pH or salt content. The recovery of analyte or internal standard was strongly dependent upon the thermal desorption temperature, as expected; hence, this value was maintained at 260 °C, just slightly below the manufacturer's recommended maximum temperature (270 °C) for PDMS–DVB fibers.

The manufacturer noted that SPME coatings bonded to ''StabilFlex'' flexible fused-silica cores tended to be more stable and the fiber would be less breakable. While these were attractive advantages, the manufacturer also noted that there might be a slight difference in extraction selectivity compared to the same coating on a standard fused-silica core. The extraction recoveries for solutions of clean authentic ground water that had been fortified to 10 ng ml^{-1} each in vapona, malathion, parathion, and ethion were evaluated using PDMS–DVB fibers employing both the standard and flexible fused-silica cores. In all cases, the extractions employing the flexible fused-silica fibers produced poorer extraction recoveries than those observed using the standard fused-silica cores. The differences ranged from 15% (for parathion) to 60% (for ethion). All further extractions were performed using PDMS–DVB fibers employing the standard fused-silica cores.

3.2. Determination of the method reporting limits

The performance of the proposed method was evaluated using two statistical protocols, viz, those of the US Army Rocky Mountain Arsenal [20] and the US Environmental Protection Agency (EPA) [21] to determine the ''method reporting limit'' (MRL) and the ''method detection limit'' (MDL), respectively. The former is equivalent to determining a ''found'' concentration so that the false positive and the false negative errors are both 5%, as discussed in Hubaux and Vos [22] and Grant et al. [23]. In contrast, the latter is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [21].

The MRL was evaluated using a procedure established by the US Army [20] and discussed in detail elsewhere [24]. Briefly, 10-ml portions of model ground water are fortified with the target analytes to concentrations ranging between 0.5 and 20 ng ml^{-1}. Aliquots ranging in volume between 0.5 and 20 μl of the Master Calibration Solution (for calibration) or Master Spiking Solution (for preparing test samples) were employed for this purpose. These freshly-spiked samples represent 0.5 to 20 times the ''target reporting limit'' (TRL) of 1 ng ml^{-1} required for all analytes except atrazine. All samples, regardless of whether they were considered ''calibration'' or ''test'' samples were further fortified to 5 ng ethion ml^{-1} using 10 μl of the Internal Standard Solution. These samples are extracted and analyzed as described above, and the resulting concentrations calculated using calibration data obtained on each of two independent method certification days. The MRL values were calculated using these concentration data and the current software recommended by the Program Manager Rocky Mountain Arsenal for each analyte [25]. The method certification protocol usually requires the demonstration and evaluation of a ''confirmatory'' analytical procedure; however, because the mass-selective detector is considered self-confirming, such an exercise is not required here.

Table 1 summarizes the MRL values that were calculated for the five analytes considered. The MRL values for malathion, parathion, and supona were at or below 3 ng ml^{-1}, thereby approximating the TRL. The MRL for malathion is particularly noteworthy

Table 1
Summary of MRL and MDL values for atrazine and four OPP in ground water, calculated using the method of internal standards

Analyte	MDL (ng ml^{-1})		MRL (ng ml^{-1})
	All data	''Best seven'' values	
Supona	3	2	1
Parathion	3	2	3
Malathion	4	2	2
Atrazine	9	6	8
Vapona	9	5	6

because it is 70 times lower than the regulatory limit cited in ''The Basic Standards for Ground Water'' [4]. The slope of the calculated linear regression line representing the relationship between the ''found'' (calculated) values, and the ''true'' (expected) values may be taken as a measure of ''method accuracy'' relative to the calibration recoveries. These values ranged between 86% (for vapona) to >95% (for supona). The calibration curves for all five analytes were linear over the range 0–25 ng ml^{-1}, as shown in Fig. 3. The coefficient of determination, r^2, exceeded 0.99 for supona, parathion, and malathion, and was slightly smaller for vapona (0.98) and atrazine (0.96).

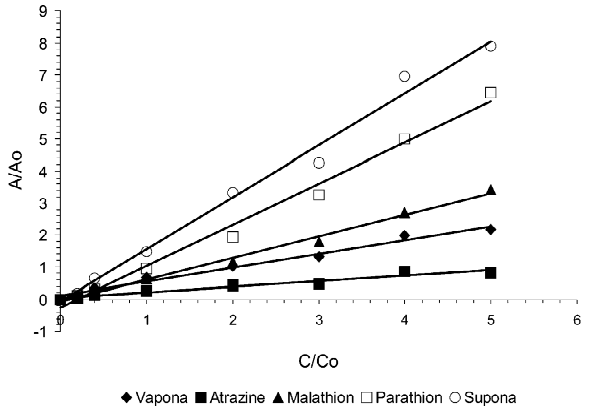

Fig. 3. Calibration curves for all analytes using the method of internal standards, as described in the text. The concentration for each analyte, C, ranged between 0 and 25 ng ml^{-1}, while that of the internal standard, C_o, was always 5 ng ml^{-1} ethion. A/A_o represents the ratio of the peak area of the analyte, A, to that of the internal standard, A_o.

3.3. Determination of the method detection limits

MDL values were calculated for all analytes using both analytical columns, as described in Ref. [20]. A set of nine 10-ml model ground water samples (seven required) were independently fortified to 10 ng ml^{-1} in each analyte and 5 ng ml^{-1} in the internal standard, then processed as described above. The sample standard deviation of the calculated concentrations for each analyte was multiplied by 2.896, which is the one-tailed Student's t-value corresponding to eight degrees of freedom (df) and 99% confidence to obtain the MDL. The procedure is demonstrated in Table 2. During the calculation of the MDL, the data from two samples appeared to be ''high'' compared to those from the other samples, even though each had been prepared and analyzed in the same manner, and there was no clear reason why these two samples should produce different results than the others. For comparison, the data from the two ''suspect'' samples were removed from the data set and the MDL values recalculated based on the

Table 2
Calculation of the method detection limit (MDL) for Vapona, Malathion, and Supona

Sample	Measured analyte concentration (ng ml^{-1})		
	Vapona	Malathion	Supona
MDL-1	9.25	9.56	10.54
MDL-2	9.32	8.98	11.52
MDL-3[a]	13.99	11.67	12.55
MDL-4	11.78	9.18	12.01
MDL-5[a]	16.32	12.48	13.63
MDL-6	7.14	8.26	9.96
MDL-7	8.94	9.72	10.56
MDL-8	8.20	8.32	10.55
MDL-9	9.90	10.26	11.11
SD, all values	2.958	1.439	1.173
Student's t-value	2.896	2.896	2.896
MDL, ng ml^{-1}	9	4	3
SD, ''best seven'' values	1.442	0.734	0.697
Student's t-value	3.143	3.143	3.143
MDL, ng ml^{-1}	5	2	2

[a] Data removed from the calculation of the MDL based on the ''best seven'' values.

remaining seven samples. In this case, the respective sample standard deviations were each multiplied by 3.143, which is the one-tailed Student's *t*-value corresponding to 6 df and 99% confidence. The MDL values based on the ''best seven'' data were somewhat lower than those obtained using all of the available data, as expected. However, there was very reasonable agreement between all of the MRL and MDL values calculated as described.

3.4. Evaluation of performance evaluation samples and other routine measures of quality assurance

All of the calibration and certification sample sets described above were accompanied by additional samples designed to ensure data quality. At least two model ground water blanks were analyzed daily to ensure minimal ''sample memory.'' In addition, a ''mid-range check'' sample, which was a model ground water sample freshly fortified to 10 ng ml^{-1} in all analytes and 5 ng ml^{-1} in ethion, was analyzed as the last sample of the day to ensure minimal drift of the calibration data.

An independent approach for assessing the overall performance of the new method and adding a further level of quality assurance is the routine and periodic determination of OPP and atrazine in ''performance evaluation'' (PE) samples [26]. These are samples of ground water that have been fortified with the analytes in question to known concentrations by an independent (third-party) laboratory under a strictly observed and generally accepted protocol. Such samples may contain any or all of the analytes in question; however, in general, the suite of analytes selected and their respective concentrations are representative of those that may be found at a particular worksite. The concentrations of the target compounds are chosen to be at or above the detection limits claimed by a candidate analytical laboratory. PE samples are sent to candidate analytical laboratories under approved storage conditions (here, 4 ± 2 °C) within the normal approved ''holding time'' (here, 7 days) from the time that such a sample is prepared to the time that it must be extracted [20]. Depending upon the quality assurance protocol selected, the PE samples may be submitted as ''single-blind'' (i.e. the candidate laboratory knows that this is a PE sample, but does not know the identity or concentration of the analytes present), or as ''double-blind'' (i.e. the candidate laboratory does not know that the sample in question is a PE sample and does not know either the identity or concentration of the analytes present). In this work, PE samples were prepared and analyzed under the ''single-blind'' protocol in order to provide the investigators immediate information concerning the suitability and reliability, or the lack thereof, of the candidate analytical procedure.

Up to four PE samples were analyzed routinely during the certification of this new analytical method. The results of these determinations, as well as those of the ''mid-range check'' samples, are displayed in Table 3. The calculated concentrations for malathion, parathion, and supona usually agreed well with the ''true'' values in all four PE samples. In several cases, particularly for low concentrations of vapona, atrazine, and malathion, the value calculated was below either the MRL or MDL reported in Table 2. These values are marked in Table 3 with a ''J'' qualifier, and should be considered for information only, rather than ''for record.'' The GC–MSD-SIM chromatograms obtained for a calibration and PE sample, both fortified to 10 ng ml^{-1}, are presented in Fig. 4.

The most severe discrepancies between the ''calculated'' and ''true'' values occurred with vapona, as shown in PE1 and PE4, even though the ''mid-range check'' sample showed acceptable agreement between the calculated and ''true'' values for this compound. The ''mid-range check'' sample was routinely spiked immediately prior to SPME sampling, while the PE samples were stored for up to a week at the recommended temperature of 4 ± 2 °C prior to analysis. This information suggests, but does not prove, that vapona may have hydrolyzed substantially, even under the recommended sample storage conditions. Vapona is rapidly degraded in the air and damp media such as soil, and the pH of the medium determines the rate of breakdown. Alkaline soils and waters produce the most rapid breakdown, whereas acidic media show very slow degradation. For example, the half-life of vapona at pH 9.1 and 1 are 4.5 and 50 h, respectively [27]. Some of the losses of atrazine, particularly in sample PE1, may also be explained by hydrolysis. However, in contrast to the hydrolysis of vapona, that of atrazine is rapid in

Table 3
Summary of analytical results for performance evaluation samples

Sample name	Analyte	Analyte concentration (ng ml^{-1})			
		''True''	Day 1	Day 2	Day 3
PE1	Atrazine	10.0	4.4 (J)[a]	2.8 (J)	5.2
	Malathion	10.5	8.0	8.0	5.9
	Parathion	10.0	9.2	9.3	7.6
	Supona	10.2	8.5	10.2	9.5
	Vapona	9.9	0.3 (J)	nd[b]	0.3 (J)
PE2	Atrazine	3.0	2.3 (J)	3.1 (J)	4.6 (J)
	Malathion	2.1	1.8 (J)	1.3 (J)	1.8 (J)
PE3	Atrazine	15.0		11.0	12.0
	Malathion	10.5		8.8	10.2
PE4	Atrazine	10.0		8.1	9.1
	Malathion	10.5		13.2	10.6
	Parathion	10.0		12.3	10.8
	Supona	10.2		13.0	10.6
	Vapona	9.9		4.5 (J)	3.0 (J)
Mid-range check	Atrazine	10.0		13.3	11.4
	Malathion	10.0		9.7	10.2
	Parathion	10.0		8.7	10.0
	Supona	10.0		9.6	9.7
	Vapona	10.0		11.5	11.1

[a] Indicates that the analyte was observed, but below the method MRL or MDL.
[b] Not detected.

acidic or basic environments but slower at neutral pH [28]. Taken together, it is strongly recommended that authentic ground water samples be adjusted to near-neutral pH prior to shipment and short-term storage if either vapona or atrazine are suspected contaminants.

4. Conclusions

Solid-phase microextraction is an effective and solventless procedure for extracting atrazine and four OPP present in ground water at concentrations as low as 2–8 ng ml^{-1}. The applicability and reliability of the candidate method was evaluated using sets of ''performance evaluation'' samples. In general, the calculated concentration data obtained for malathion, parathion, and supona were in substantial agreement with the known ''true'' values in these samples. Similar data for atrazine and vapona, two analytes that may hydrolyze in ground water, usually did not agree with the ''true'' values, suggesting that authentic ground water samples should be adjusted, if necessary, to pH~7 prior to shipment from a worksite and subsequent analysis. The new procedure exhibits several advantages over more conventional methods based on liquid–liquid extraction, including the use of smaller volumes of aqueous samples (10 ml vs. 1 liter), minimal sample handling, and an absence of expensive high-purity organic extracting solvent that would be regarded and handled as chemically hazardous waste after the analysis. A single operator may process approximately 16 ground water samples per 8-h working day.

A potentially serious limitation in the procedure as described is the use of only manual SPME to extract both sample ground water and to perform the gas chromatographic analysis. This feature permits a very simple holder to be used successfully, but also introduces the possibility of severe irreproducibility as operator fatigue becomes apparent or several independent operators with slightly different injec-

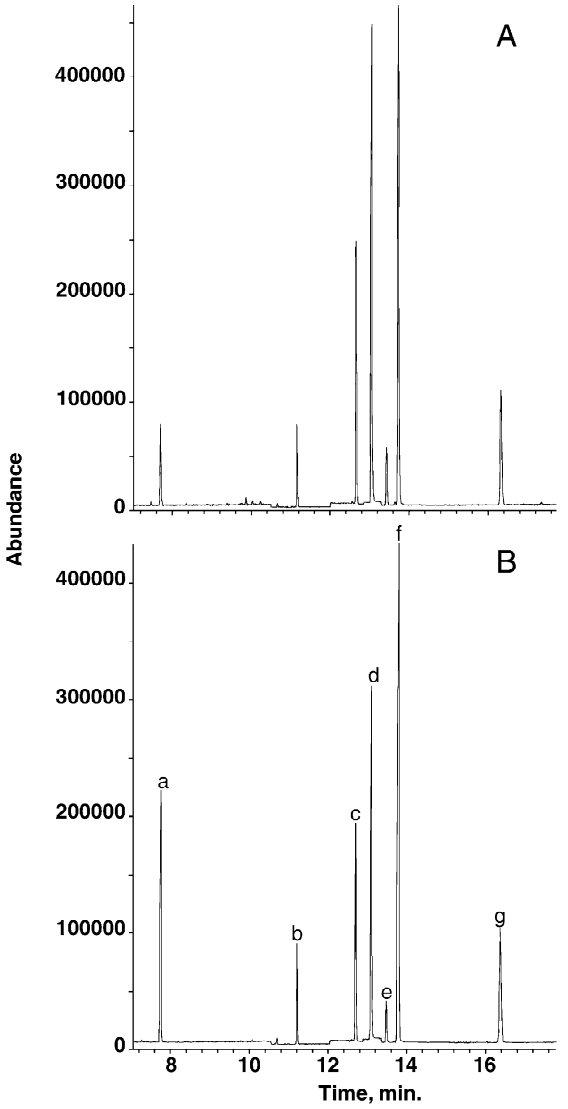

Fig. 4. Comparison of a performance evaluation sample with stated concentrations of 10 ng ml^{-1} per analyte in clean authentic ground water (A) with a freshly prepared 10 ng ml^{-1} calibration standard prepared in model ground water (B). Legend: (a) vapona; (b) atrazine; (c) malathion; (d) parathion; (e) ''E'' isomer of supona, not used for quantitation; (f) ''Z'' isomer of supona, used for quantitation; (g) ethion, internal standard, concentration 5 ng ml^{-1}.

tion techniques are employed. The overall sample throughput can be improved at least threefold by employing an automated SPME sampler such as the CTC Combi-Pal™ (Laboratory Environmental Analytical and Pharmaceutical (LEAP) Technologies, Carrboro, NC, USA) [29–31]. Reducing the SPME sampling time, and thus the mass of analytes extracted, is a possible, but less favorable, option.

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