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DETERMINATION OF SMALL DIALKYL ORGANOPHOSPHONATES AT MICROGRAM/L CONCENTRATIONS IN CONTAMINATED GROUNDWATERS USING MULTIPLE EXTRACTION MEMBRANE DISKS

KEY WORDS: Di-isopropyl methylphosphonate, dimethyl methylphosphonate, groundwater, extraction disks, gas chromatography

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DISCLAIMER

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ABSTRACT

Di-isopropyl methylphosphonate (DIMP) and dimethyl methylphosphonate (DMMP), which are manufacturing by-products of, and surrogate compounds for, the nerve agents Sarin (GB) and VX, respectively, are readily quantitated at microgram per liter concentrations in contaminated groundwaters. Aqueous samples (typically 1 L) are first fortified with triethylphosphate (TEP) as a surrogate, then passed through a "sandwiched" set of three preconditioned extraction disks consisting of the following (in filtration order): (a) glass fiber filter, to remove unwanted particulate matter; (b) C_{18}-based extraction disk, to collect DIMP; and (c) carbon-based extraction disk, to collect DMMP. The glass fiber filter is discarded; the two extraction disks are dried and extracted with a small volume of methanol.

After the extract is fortified with diethyl ethylphosphonate (DEEP) internal standard, it is analyzed using a gas chromatograph equipped with a nitrogen-phosphorus detector (NPD). Quantitation of DMMP, DIMP, and TEP is performed using the method of internal standards.

The procedure was used to obtain statistically-unbiased reporting limits for a "regulatory" criterion of 0.39 µg/L and a "pump and treat" criterion of 2 µg/L for both analytes. Two standardized protocols were used to validate a detection limit of 0.20 µg/L for DMMP and 0.48 µg/L for DIMP when the regulatory criterion was used as the "target concentration". When the "pump and treat" criterion was used as the "target concentration," the detection limits for both DMMP and DIMP were both 2 µg/L using the same protocols as for the "regulatory" criterion. The method recovery is approximately 40-50%, based on synthetic groundwaters containing between 0.2-50 µg/L of each analyte. DIMP and DMMP are cleanly resolved from each other, the internal standard, the surrogate, and the potential interference trimethylphosphate (TMP).

INTRODUCTION

Di-isopropyl methylphosphonate (DIMP, CAS 1445-75-6) is a chemical manufacturing by-product of the nerve agent Sarin or GB (isopropyl methylphosphono-fluoridate, CAS 107-44-8). Groundwater contamination occurred when industrial effluent containing elevated concentrations of DIMP seeped into the water table below unlined industrial waste-disposal ponds during 1952-1956, and was found within 1.6 km of municipal wells supplying water to a city in the western United States[1]. At least two engineering studies have evaluated methods for reducing the concentration of DIMP in groundwaters from levels as great as 44,000 µg/L near the abandoned waste-disposal

ponds[2] and 800 μg/L in the North Boundary groundwater[3] to 2 μg/L[4], the currently-mandated "pump and treat" criterion. In addition, the concentration of DIMP must not exceed the current "regulatory" criterion of 0.39 μg/L[5] for well water samples collected "off-post". Both criteria also applied to dimethyl methylphosphonate (DMMP, CAS 756-79-6), which is often used as a surrogate for the nerve agent VX (*O*-ethyl *S*-[(di-isopropylamino)ethyl]methylphosphonothioate, CAS 50782-69-9), and which must be clearly distinguished from DIMP.

At present, there are very few methods available for detecting DMMP and DIMP in aqueous samples, and no certified procedures for the determination of both analytes in contaminated groundwater at the recommended regulatory level have been reported. Several authors have reported the use of various microsensor coatings[6,7,8,9], interdigitated gate electrode field-effect transistors[10], secondary ion mass spectrometry (SIMS)[11], and piezoelectric sensors[12,13] for the determination of either DIMP or DMMP at low concentrations in vapors, not in aqueous samples. Griest et al[14] employed supercritical methanol-carbon dioxide (5:95) to extract both DMMP and DIMP from soil, each at 2 μg/g, with recoveries of 79 ± 23% and 95 ± 17%, respectively. Buchanan et al[15] described the determination of two chemical warfare agent simultants, DIMP and chloroethylethylsulfide, in beef tissue and milk at concentrations as low as 50-100 parts-per-billion using procedures based on solid phase extraction/thermal desorption/ion trap mass spectrometry. Hedrick and Taylor[16] described the supercritical fluid extraction of polar compounds, including DIMP, from aqueous samples; a flame ionization detector was used to monitor the effluent. These authors noted that the determination of analyte concentrations much below approximately 500 pbb was thought to be impossible while maintaining chromatographic efficiency. A sample loop larger than 500 μL would increase the amount of sample loaded onto the

column, but would result in unacceptably large peak widths when using the normal 1 mm i.d. HPLC column. Priebe and Howell[17] described a post-column reaction detection system for the determination of organophosphorus compounds in aqueous samples by liquid chromatography based upon their photodegradation to orthophosphate followed by the formation of reduced heteropolymolybdate (blue product). The optimization photodegradation yield for DMMP was 97% at a test mass of 0.1 μg phosphorus injected, but no detection limits for DIMP were given.

The solid phase extraction procedures for nerve agents and their manufacturing products described in Tørnes et al[18,19] provided a substantial advance over traditional liquid-liquid extraction methods such as those given in Sass et al[20]. As an example, DIMP was recovered from 50 mL aqueous samples fortified to 20 μg/mL or 20 ng/mL at 87 ± 10% and 46 ± 4%, respectively, using solid phase extraction (SPE) columns which had been packed with 200 mg C_{18} sorbent and wetted with both methanol and water. These authors also established recovery data for both Sarin and VX, but did not test DMMP. In our experience, DIMP can be recovered in good yield from aqueous samples up to 1 L in volume when either a C_{18} or C_8 membrane extraction disk is substituted for SPE columns packed with similar materials, but none were effective in recovering DMMP. On the other hand, DMMP was readily recovered from these samples using either small SPE columns packed with a variety of Ambersorb® carbonaceous sorbents or newly-introduced carbon-based membrane extraction disks[21].

The procedure described herein employs three sequential disks for the rapid extraction of DIMP and DMMP from 1 L samples of groundwater: A glass fiber disk removes particulate matter and is otherwise inert; a C_{18} membrane extraction disk removes DIMP but not DMMP; and a carbon-based membrane extraction disk removes DMMP and

some extra DIMP. After the aqueous extraction is completed, the glass fiber disk is discarded. The remaining disks are dried and eluted with a small volume of methanol which is subsequently fortified with a known quantity of diethyl ethylphosphonate (DEEP) internal standard. The methanolic extract is analyzed by gas chromatography equipped with a nitrogen-phosphorus detector (NPD); DIMP and DMMP are quantitated by the method of internal standards. Triethylphosphate (TEP) is added to all aqueous samples prior to extraction and serves as a surrogate. The reporting limits for DIMP and DMMP were calculated using two statistically-unbiased protocols, and either approximated or surpassed the desired criteria.

EXPERIMENTAL SECTION

Reagents

HPLC-grade water and methanol were obtained from J. T. Baker, Phillipsburg, NJ. Trimethylphosphate (TMP, CAS 512-56-1) and triethylphosphate (TEP, CAS 78-40-0) were both purchased at 99+% purity from Aldrich Chemical Co. (Milwaukee, WI). DIMP (98% purity) and DMMP (97% purity) were procured from Lancaster Synthesis, Inc. (Windham, NH) and Pfaltz & Bauer, Inc. (Waterbury, CT), respectively. Diethyl ethylphosphonate (DEEP, 98% purity, CAS 78-38-6) was purchased from Pfaltz & Bauer, Inc. (Waterbury, CT). All solvents and phosphorus-containing compounds, as well as reagent-grade sodium chloride and anhydrous sodium sulfate, were used as received.

Standards

"Master" stock solutions were prepared by weighing 100 μL of each organophosphonate or organophosphate into individual 10 mL portions of methanol, giving concentrations of approximately 10 mg/mL for each component. Aliquots of these

"master" stock solutions were further diluted to produce the following three "working" stock solutions: (a) individual 100 µg/mL DEEP in methanol; (b) individual 100 µg/mL TEP in methanol; and (c) 100 µg/mL each DIMP, DMMP, TMP, and TEP in methanol ("master calibration solution", MCS). Varying portions of the MCS and a constant 250 µL of the DEEP "working stock solution" were further diluted to a final volume of 10 mL methanol to produce mixed standards ranging in concentration between 0.1-10.0 µg/mL in all four components except DEEP, which was maintained at a constant 2.5 µg/mL. Two independently-prepared sets of these standards were employed during method certification. A separate "master spiking solution" (MSS) containing 100 µg/mL DIMP and DMMP in methanol was prepared specifically for fortifying synthetic groundwater samples.

Synthetic Groundwater Samples

A salt stock solution was prepared by diluting 1.48 g sodium chloride and 1.65 g anhydrous sodium sulfate to a final volume of 1 L with HPLC-grade water. Individual 100 mL portions of this solution were further diluted to a final volume of 1 L with HPLC-grade water to form synthetic groundwater samples whose chloride and sulfate concentrations were both 100 mg/L. Two independently-prepared sets of eight synthetic groundwaters were fortified with DMMP and DIMP to final concentrations of 0.2-20 µg/L each (i.e., 0.5 to 50 times the regulatory Target Reporting Limit (TRL) of 0.39 µg/L), using appropriate volumes of the MSS, and 5 µg TEP/L using 50 µL of the TEP "working stock solution." A synthetic groundwater blank accompanied each set.

When the method was further evaluated using the "pump and treat" criterion as the target concentration, two independently-prepared sets of eight synthetic groundwaters were fortified with DMMP and DIMP to final concentrations of 1 to 50 µg/L each (i.e., 0.5 to 25 times the Target Reporting Limit (TRL) of 2 µg/L), using appropriate volumes of the MSS.

Each sample was further fortified to 15 µg TEP/L using 150 µL of the TEP "working stock solution".

Extraction and Filter Disks

Whatman glass microfiber filters, GF/A, 5.5 cm diameter, were purchased from VWR. Empore® filter disks, 47 mm diameter, containing C_{18} (octadecyl) groups chemically bonded to silica, were obtained from J. T. Baker. Carbon-based Empore® filter disks, 47 mm diameter, part no. 98-0405-0047-6, were procured from 3M Industrial and Consumer Sector, New Products, 3 M Center, Building 220-9E-10, St. Paul, MN 55144-1000. All disks were conditioned prior to use as described under "Extraction Procedure."

Glassware

All sample filtrations were performed using an all-glass funnel/support assembly compatible with 47 mm diameter disks, containing a 1-L filtration flask (Erlenmeyer flask equipped with a ⅋ 40/35 male joint) available from VWR. The normal 300 mL sample reservoir was replaced with a 1000 reservoir available from Kontes, Vineland, NJ, part no. 953781-0000. A PVC-coated "LEAD DONUT"™ (I^2R, Cheltenham, PA) was used to stabilize the filtration apparatus.

All disk drying was performed using a second all-glass filter support assembly compatible with 47 mm diameter disks, described above. The normal 1-L filtration flask was replaced with a custom-designed glass "cap" prepared from a stock borosilicate full-length "inner" ground glass joint, ⅋ 40/50, cut down and ground to a final ⅋ 40/35. Final dimensions are: 37 mm diameter at the base, 60 mm height, 25 mm between the bottom of the "cap" and the beginning of the glass joint. The drying assembly, by its very nature, must be stabilized with a universal "three-finger" clamp attached to a ring stand.

Precleaned 20 mL borosilicate screw-cap vials were purchased from I-CHEM

RESEARCH, Hayward, CA or New Castle, DE, and capped with solid plastic tops equipped with Teflon® liners. Target DP amber 2-mL autosampler vials with a white area for writing identification markings were obtained from National Scientific Co., Lawrenceville, GA. The same company provided Target DP assembled caps with Teflon®/Silicone/Teflon® septa.

Instrumentation

A Hewlett-Packard Model 5890 Series II gas chromatograph equipped with an NPD and a Hewlett-Packard Model 7673 automatic sampler was used for all determinations of DMMP and DIMP. The analytical column was Rtx®-200 (Crossbond® trifluoropropyl-methyl), 3.00 μm film thickness, 0.53 mm i.d. x 30 mm coupled to a deactivated and uncoated fused silica guard column , 0.53 mm i.d. x 5 m, with a Universal Press-Tight® connector, all products of Restek Corp., Bellefonte, PA. The injector, which contained a "double-gooseneck" deactivated glass liner, was maintained at 150°C, while the detector temperature was 220°C. The injector purge valve was "off" at 0.00 min and "on" at 2.00 min. The carrier gas (99.9999% helium) flow rate was 5.5 mL/min; the combined flow rate of the make-up (also 99.9999% helium) and the carrier gases was at least 30 mL/min (nominal value 34 mL/min). The detector flow rates for hydrogen (ultrahigh purity) and air were 4 mL/min (specified 3-4 mL/min) and 109 mL/min (specified 100-110 mL/min), respectively. The "bead power" was adjusted to give a nominal bead current of 20-30 picoamps. The column oven temperature was programmed linearly from 90°C to 150°C (hold for 5 min) at 2°C/min. The total gas chromatographic run time was therefore 35 min. Hewlett-Packard Model 3365 ChemStation software loaded onto a 486/50 personal computer was used to both operate the gas chromatograph and its associated automatic sampler, and integrate, identify, and mark the relevant peaks. All analyses employed automatic 2 μL sample injections with adequate methanol washes before and after delivery.

Procedure

Analysis of the Calibration Standards

Two independently-prepared sets of calibration standards were analyzed on separate days using the equipment described in "Instrumentation" above. The area ratios A_{DMMP}/A_{DEEP}, A_{TMP}/A_{DEEP}, A_{DIMP}/A_{DEEP}, and A_{TEP}/A_{DEEP} were determined from the relevant integrated peak areas and plotted against the corresponding calculated concentration ratios. These data were subsequently evaluated statistically for lack-of-fit to linear models with and without a zero intercept as well as the statistical significance of the calculated zero intercept using two pre-certification software packages supplied by the United States Army.[22,23]

Analysis of the Synthetic Groundwater Samples: Determination of the Method Reporting Limit (MRL)

The carbon-based and C_{18} extraction disks were wetted with methanol and laid successively over the fritted glass support, followed by the glass microfiber filter disk and the 1000 mL sample reservoir. The disks were conditioned sequentially with two 10-mL portions of methanol (each stands undisturbed for 1 min) followed by two 10-mL portions of HPLC-grade water (each stands undisturbed for 1 min), each partially removed (ca. 80%) with vacuum. *Note: The disks should not be allowed to go dry after conditioning has begun.* The aqueous sample (typical volume 1 L) is then added to the sample reservoir and pulled through the extraction disks under vacuum. After the sample has been completely extracted (typical time is 20-30 min), the funnel support apparatus is disassembled, the glass microfiber filter disk discarded or set aside, and the extraction disks are dried under vacuum for 10 min. After the vacuum is released, a clean, labeled, 20 mL vial is placed in the custom-made "cap" and the usual 300 mL sample reservoir is attached to the filter support of the drying unit.

Disk Extraction and Extract Preparation: Regulatory Criterion

A 3 mL aliquot of methanol is added to the sample reservoir, allowed to stand undisturbed for 1 min, and pulled through the disks under vacuum directly into the 20 mL vial. Approximately 2 mL of methanolic extract will be recovered. A 50 μL aliquot of the DEEP "working stock solution" (delivering a total mass of 5 μg DEEP) is added to the extract, which is then analyzed using the same conditions as the calibration standards. The two sets of fortified synthetic groundwater samples were analyzed independently on two different days.

Disk Extraction and Extract Preparation: Pump-and-Treat Criterion

A 5 mL aliquot of methanol is added to the sample reservoir, allowed to stand undisturbed for 1 min, and pulled through the disks under vacuum directly into the 20 mL vial. This procedure is repeated, yielding a methanolic extract of approximately 8 mL. A 150 μL aliquot of the DEEP "working stock solution" (delivering a total mass of 15 μg DEEP) is added to the extract, which is then analyzed using the same conditions as the calibration standards. The two sets of fortified synthetic groundwater samples were analyzed independently on two different days.

Internal Standard Calculations

The area ratios A_{DMMP}/A_{DEEP}, A_{TMP}/A_{DEEP}, A_{DIMP}/A_{DEEP}, and A_{TEP}/A_{DEEP} were determined from the relevant integrated peak areas and converted to their corresponding concentration ratios using the method of internal standards and the calibration data described previously. The calculation of the MRL is described under **RESULTS AND DISCUSSION**.

Analysis of the Synthetic Groundwater Samples: Determination of the Method Detection Limit (MDL)

Eight (seven required) 1-L samples of synthetic groundwater fortified to 2 μg/L each in DMMP and DIMP (i.e., 5 times the regulatory TRL for each compound) and 5 μg/L TEP were extracted and analyzed in the same manner as the synthetic groundwater samples used in the determination of the MRL, described above. A separate set of similar samples fortified to 10 μg/L each in DMMP and DIMP (i.e., 5 times the "pump-and-treat" TRL for each compound) and 15 μg/L TEP were treated similarly.

The area ratios A_{DMMP}/A_{DEEP}, A_{TMP}/A_{DEEP}, A_{DIMP}/A_{DEEP}, and A_{TEP}/A_{DEEP} were determined from the relevant integrated peak areas and converted to their corresponding concentration ratios using the method of internal standards and the calibration data described previously. The calculation of the MDL is described under **RESULTS AND DISCUSSION.**

Analysis of Authentic Groundwater Samples

Aliquots (50-200 mL) of four authentic contaminated groundwaters were diluted to a final volume of 1 L, fortified with 25 μg TEP, then subjected to the procedures described above in *Analysis of the Synthetic Groundwater Samples: Determination of the Method Reporting Limit (MRL)* and *Disk Extraction and Extract Preparation: Pump-and-Treat Criterion*. The resulting methanolic extract was spiked with 25 μg DEEP and analyzed in the same manner as the method certification samples.

RESULTS AND DISCUSSION

Instrument Optimization

Because the gas chromatography of certain organophosphorus compounds can produce peaks with severe tailing, the instrument was optimized to maximize peak resolution while simultaneously minimizing the undesirable tailing. The double-gooseneck liner

employed in the injector significantly reduces the degradation of thermally-labile compounds. Three analytical columns with comparable physical dimensions (0.53 mm i.d. x 30 m) were also evaluated to determine which column produced the best peak shape. Narrow, symmetrical peaks were observed for all five organophosphorus compounds when a thick-film crossbond® trifluoropropylmethyl phase (moderately polar) was employed; the peak shapes obtained using either thick-film Stabilwax® (highly polar) or DB™-5 (nonpolar) were less satisfactory. During the course of method certification, peak tailing, sometimes quite severe, was observed, but it was caused by degradation of the active element (bead) of the NPD, rather than degradation of the column. The exact reason for the bead degradation is not known, and it may be minimized by additional optimization of both gas flows and bead current. This peak tailing was not observed if a flame ionization detector was substituted for the NPD, even after extensive use; however, the latter was preferred for this application because of its superior sensitivity and selectivity.

The crossbond® trifluoropropylmethyl column also permitted baseline resolution of all five organophosphorus compounds, as shown in Figure 1. It was important to demonstrate that DMMP and DIMP could be resolved cleanly from other potentially-interfering phosphorus-containing species, such as TMP. A candidate interference which did not contain phosphorus would have to exhibit the same extraction characteristics and retention time of an organophosphonate analyte and possess sufficient concentration to overpower the measured molar selectivity of the NPD (pmole P/pmole C ~56,000).

The initial method development work employed a gas chromatograph equipped with a flame ionization detector, which was simple and rugged but lacked both the sensitivity to achieve the desired TRL and the selectivity to discriminate against potential interferences. For that reason, a similar instrument equipped with an NPD was used for final method

development, testing, and certification. Because the NPD response will drift with time, use, age, and condition of the active element, the method of internal standards was used to achieve day-to-day reproducibility and reliability. Either TMP or DEEP could be used as the internal standard. DEEP is preferred because it, like DIMP and DMMP, is an organophosphonate, and because DEEP elutes close to, but is usually resolved from, DIMP.

Optimization and Selection of the Extraction Procedure

Previous work in our laboratory focused on conventional SPE columns packed with up to 1 g of C_{18} extraction material and various carbonaceous sorbents (Ambersorb®). While these sorbents proved effective for extracting DIMP and DMMP, respectively, the maximum flow rates permissible, typically 6 mL/min, implied an excessively lengthy extraction time for 1-L sample volumes needed to achieve the desired limits. By substituting membrane extraction disks for the SPE columns, the extraction time was reduced about eight-fold, to approximately 20-30 min/sample, with equivalent analyte recoveries. Both dichloromethane and methanol could elute DIMP and DMMP effectively from the sorbent disks; however, the use of methanol as the eluent substantially reduced the hazardous nature of the chemical waste produced.

Method Certification

The certification protocols described in this work consist of two parts. The first uses two sets of independently-prepared and analyzed calibration standards to evaluate the "lack of fit" and the statistical significance of a nonzero intercept. When the entire set of calibration data, obtained over the hundred-fold range 0.1-10 µg/mL, was evaluated for DMMP, DIMP, and the two organophosphates, significant nonlinearity was clearly evident at concentrations exceeding 3 µg/mL for each analyte. For that reason, the calibration data employed for the next portion of method of certification was truncated to the set spanning

0.1-3.0 μg/mL, where a satisfactory "lack of fit" test was obtained for the linear model with a zero intercept and where the calculated intercept was not significantly different from zero.

The second part of the certification protocol evaluated the analytical methodology itself and calculated the Method Reporting Limit (MRL), a statistically-unbiased detection limit value which permits the investigator to select levels of uncertainty for both false positives and false negatives (nominally 5% for each). When the MRL was calculated for the regulatory criterion (TRL = 0.39 μg/L, two independently-prepared sets of spiked synthetic groundwater samples with concentrations of DMMP and DMMP ranging between 0.5 x TRL and 50 x TRL (i.e., 0.2-20 μg/L of each analyte) were subjected to the candidate analytical method. The resulting integrated peak area ratios, relative to that of the internal standard DEEP, were converted to corresponding concentration ratios and analyte concentrations using the method of internal standards. These experimental values represent "found" concentration ratios or concentrations; they are compared to the corresponding "true" or "expected" values calculated knowing the starting concentrations of both analytes and the internal standard. The MRL value is located using the following four-step procedure: (1) calculate and plot a regression line, representing the "found" vs "true" concentrations or concentration ratios, with appropriate two-sided 90% confidence limits for a predicted observation; (2) locate the intercept of the upper 90% predictive confidence limits with the y-axis ("found" concentrations or concentration ratios); (3) draw a horizontal line from this intercept until it intersects the lower 90% predictive confidence limits; and (4) draw a vertical line from the intercept described in (3) to the x-axis ("true" or "expected" concentrations or concentration ratios). This intersection with the x-axis is the MRL. Additional details describing the calculation of the MRL are presented elsewhere.[24,25]

When the full set of "found" vs "true" certification data was employed, the

calculated MRL substantially exceeded the TRL. In such cases, both certification protocols permit truncation of the data set and recalculation of a new MRL *provided* that the slope of the regression line does not change more than 10% compared to that of the full set. For this reason, the data set used for calculating the MRL spanned the range between 0.2-4 μg/L, rather than the full 0.2-20 μg/L, in DMMP and DIMP. The MRL values for DMMP and DIMP so calculated were 0.19 and 0.48 μg/L, respectively. Furthermore, the slope of the least squares regression line may be taken as an estimate of overall method recovery. In this case, the slope for either DMMP or DIMP represented a recovery of approximately 42%. The recovery of DIMP using disk extraction was therefore comparable to that of Tørnes et al[17], which was 46 ± 4%, measured at 20 μg DIMP/L using SPE columns containing 200 mg of C_{18} packing material. No comparative data exist for DMMP at a similar concentration.

A similar approach was taken for the calculation of the MRL using the "pump and treat" criterion (2 μg/L) as the TRL. Here, the synthetic groundwater samples were fortified to 1-50 μg/L DMMP or DIMP (i.e., 0.5-25 x TRL) and 15 μg/L TEP, then processed as before. The final methanolic extracts were fortified with 15 μg DEEP internal standard prior to gas chromatographic analysis. The initial MRL values for DMMP and DIMP, which were calculated using the full set of certification data, exceeded the desired TRL by approximately a factor of two. When the data set was truncated to 1-30 μg/L, for the reasons discussed above, the recalculated MRL values were 1.7 μg/L for DMMP and 2.0 μg/L for DIMP. The recoveries of both DMMP and DIMP were approximately 58%, somewhat greater than the values observed using the "regulatory" TRL of 0.39 μg/L. We observed that the additional methanol used in the "pump and treat" procedure would extract an additional 10% of either DMMP or DIMP, and would account for most of the differences in recovery observed between the two procedures.

The detection limit was also calculated using the procedure specified by the U. S. Environmental Protection Agency[26]. Briefly, eight (minimum seven required) 1-L synthetic groundwater samples were fortified to 5 x TRL and analyzed as described above. The standard deviation was then multiplied by the appropriate one-tailed Student's-*t* statistic for 99% confidence. The resulting value is the MDL. When the MDL for the regulatory criterion was evaluated, the eight samples were fortified to 2 μg/L each in DMMP and DIMP. The resulting MDL was approximately 0.2 μg/L for both DMMP and DIMP, as shown in Table 1. The MDL was virtually identical to the MRL calculated for DMMP, and about half that calculated for DIMP. These calculations also satisfy an additional criterion specified in References 22 and 23, viz. the magnitude of the TRL (0.39 μg/L) should be equal to or larger than that of the MDL (0.2 μg/L) for each analyte. The MDL was calculated for the "pump and treat" criterion in a similar fashion, where all eight samples were fortified to 10 μg/L each DMMP and DIMP. The resulting MDL values were 0.9 and 1.0 μg/L for DMMP and DIMP, respectively, as shown in Table 2. Again the criterion that the MDL should be equal to or less than the TRL (here 2 μg/L for each compound) was easily satisfied.

All of the aqueous samples used for evaluation either the MRL or MDL were fortified with either 5 or 15 μg/L triethylphosphate as a surrogate standard. The recovery of TEP observed during the determination of the MDL was approximately 40-50%, as shown in Tables 1 and 2, and observed during the determination of MRL values. Because the recovery of TEP parallels the two analytes, it was a reasonable surrogate compound for the procedures discussed.

Application to Authentic Groundwater Samples

The method described under "pump and treat" criterion was challenged using four

TABLE 1

Calculation of the Method Detection Limit for the Regulatory Criterion, 0.39 µg/L. All Samples Fortified to 5 x TRL (2 µg/L) Each in DIMP and DMMP.

Sample Code	C_{DMMP}, µg/L	C_{DIMP}, µg/L	C_{TEP}, µg/L[a]	Recovery of TEP, %
1	0.91	0.93	2.07	41.4
2	0.94	0.95	2.10	41.9
3	0.88	0.90	1.88	37.7
4	0.72	0.75	1.63	32.7
5	0.79	0.84	1.83	36.5
6	0.87	0.79	1.74	34.8
7	0.93	0.91	2.05	41.0
8	0.92	0.91	1.94	38.8
SD[b], all values	0.077	0.072		
Student's-t[c]	2.998	2.998		
MDL, µg/L, all values	**0.23**	**0.22**		

[a]All samples fortified to 5 µg/L TEP as surrogate.

[b]Experimental standard deviation

[c]One-tailed at 0.99 for eight samples, df = 7

TABLE 2

Calculation of the Method Detection Limit for the "Pump and Treat" Criterion, 2 µg/L. All Samples Fortified to 5 x TRL (10 µg/L) Each in DMMP and DIMP.

Sample Code	C_{DMMP}, µg/L	C_{DIMP}, µg/L	C_{TEP}[a], µg/L	Recovery of TEP, %
1	5.07	5.84	7.08	47.2
2	4.37	4.96	5.82	38.8
3	4.76	5.23	6.79	45.2
4	5.07	5.72	8.07	53.8
5	5.13	5.63	8.36	55.8
6	4.59	5.07	7.83	52.2
7	4.77	5.31	7.79	51.9
8	4.50	5.03	7.34	48.9
SD[b], all values	0.29	0.34		
Student's-t[c]	2.998	2.998		
MDL, µg/L	**0.86**	**1.02**		

[a]All samples fortified to 15 µg/L TEP as a surrogate

[b]Experimental standard deviation

[c]One-tailed at 0.99 for eight samples, df = 7

authentic highly-contaminated groundwaters. These groundwaters were diluted with synthetic groundwater prior to analysis using some noncertified concentration data for DIMP as a guide and to force the resulting analyte peaks to fall within the bounds of the calibration curve. Each diluted sample was fortified with 25 μg TEP surrogate, which was quantitated in the same manner as the organophosphonates. The set of test samples included duplicates from each groundwater, a blank containing only TEP, and a control sample containing 50 μg/L each DMMP and DIMP and 25 μg/L TEP.

The results for these groundwaters are summarized in Table 3. The recovery of TEP in both the samples, blank, and control closely tracked those of both DMMP and DEEP in the control (ca. 46% for both species). DMMP was not observed in any sample at or above its MRL. In general, the measured concentrations of DIMP agreed with those values observed previously, ranging between 300-1300 μg/L, with the exception of site A. Further examination of the Site A samples showed a substantial quantity of black particulate matter which may have sorbed DIMP irreversibly over time, thereby reducing its concentration in the groundwater to nonreportable levels.

CONCLUSIONS

The analytical methodology described above provides a procedure for determining either DMMP or DIMP at their "regulatory" or "pump and treat" criteria at or below approximately 0.39 μg/L or 2 μg/L, respectively, each in contaminated groundwaters. Approximately eight to ten samples can be analyzed every two days under ideal conditions. During the first day, the analyst would prepare the sample extracts as described herein. DMMP and DIMP should be determined and quantitated in these methanolic extracts automatically using a gas chromatograph equipped with an automatic sampler and

TABLE 3

DIMP Concentrations in Authentic Contaminated Groundwaters[a]

Site	This Work[b]		Previous Work
	DIMP Concentration, μg/L[c]	Surrogate Recovery, %	DIMP Concentration, μg/L
A[d]	<2	40	100-300
	7	42	
B	300	39	500-600
C	1300	40	900-1700
	1200	42	
D	1100	43	1000-1600
	1200	45	
Blank	<2	46	
Control[e]	24	46	

[a]DMMP not observed in any samples at concentrations exceeding the MRL.

[b]Represents results from duplicate trials for all sites except B

[c]All values corrected for recovery

[d]Black particulate matter observed in sample jar, may have adsorbed DIMP

[e]50 μg/L each in DIMP and DMMP, 25 μg/L in TEP surrogate in synthetic groundwater

automated data system. It is not likely that many compounds will interfere with the determination of either analyte because a candidate interference must display extraction characteristics and chromatographic retention time identical to that of either DMMP or DIMP, and then exhibit an NPD response. The latter is unlikely unless the interfering species itself contains phosphorus because the molar selectivity (pmole P/pmole C) for the NPD typically exceeds 50,000.

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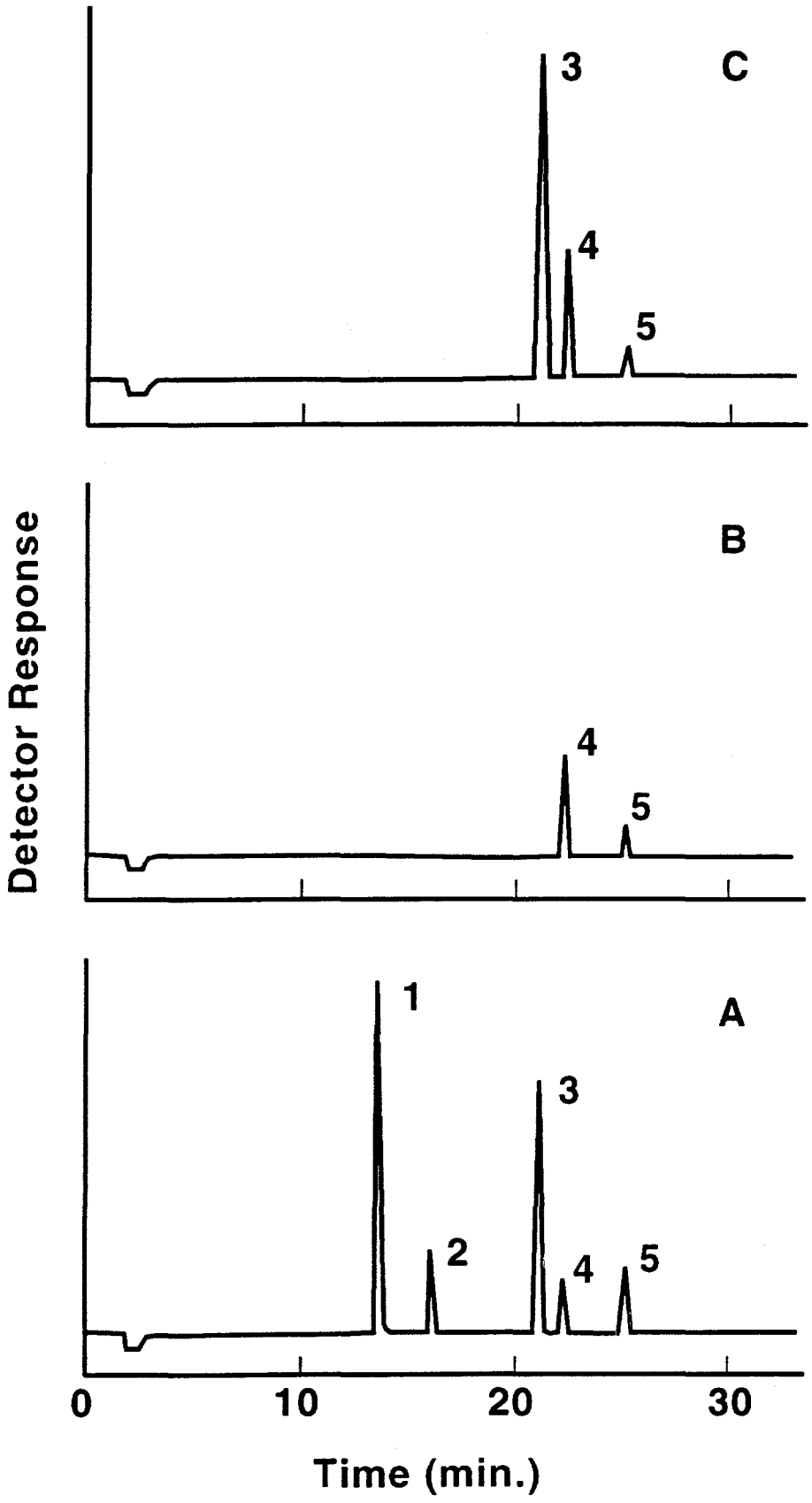
FIGURE CAPTION

FIG. 1. Representative chromatograms from the determination of organophosphonates in groundwater.

A = Standard containing 5 µg/mL for all compounds except DEEP (2.5 µg/mL). Legend: 1 = DMMP; 2 = TMP; 3 = DIMP; 4 = DEEP; 5 = TEP.

B = Synthetic groundwater blank fortified with 25 µg/L TEP surrogate (peak 5). Extract contains 25 µg DEEP (peak 4), added post-extraction.

C = Extract from site D. Diluted aqueous sample fortified with 25 µg/L TEP (peak 5) surrogate. Extract contains 25 µg DEEP (peak 4), added post-extraction.


C
3
4
5
B
4
5
A
1
2
3
4
5
Detector Response
0
10
20
30
Time (min.)