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Atomic emission detection for the quantitation of trimethylsilyl derivatives of chemical-warfare-agent related compounds in environmental samples

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Abstract

Quantitation of nerve agent degradation products is needed to develop methods for analysis of environmental samples for verification of the Chemical Weapons Convention. A procedure has been characterized which involves formation of the trimethylsilyl esters of alkylmethylphosphonic acids using 1% trimethylchlorosilane in bis-(trimethylsilyl)trifluoroacetamide as a derivatizing agent. Eight phosphorus-containing acids were extracted from spiked water, wipes, and two soil samples at low ppm levels, prepared using solid-phase extraction with a strong anion-exchange column, and derivatized. A gas chromatograph (GC) interfaced to an atomic emission detector (AED) was used to quantitate the derivatives in order to determine the extraction and derivatization efficiencies for environmental sample preparation. Because elemental response factors for the AED are independent of the type of compound, quantitation can be accomplished using an external standard, for which dimethylmethylphosphonate (DMMP) is used. The derivatization efficiencies ranged from 80% to 110% (six trials, with R.S.D. in the range 2–7%). The extraction efficiencies ranged from 13% to 99% in water, and they were lower from the soil and wipes. Gas chromatography–mass spectrometry of the derivatives was used to provide positive identifications.

1. Introduction

International treaties regarding the use, production, storage and destruction of chemical warfare (CW) agents, as well as current bilateral agreements between the United States and Russia, have created a need for analytical capabilities for inspection and verification [1]. These requirements include capabilities for sampling, sample preparation, and analysis of CW agents, precursors, byproducts, and degradation products. Because of the range of chemical warfare agents that are included in the treaties, chemicals with a wide range of polarities and solubilities must be detected.

One type of specified CW inspection, called a "challenge inspection", is required by the treaty to be carried out in a way to protect the industrial and national security of the installations that are inspected [1]. The best way to achieve this requirement is by the use of instrumentation that can be set up and operated "on-site", or at the location of the site to be inspected. This approach eliminates the need to transport sam-

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ples to a remote laboratory, reducing chain-of-custody requirements and improving the protection of confidentiality. GC–MS equipment is now commercially available for use in on-site analysis that gives analytical data of equivalent quality to laboratory instrumentation [2,3]. In addition to the availability of on-site equipment, however, it is also necessary to develop sample preparation methodologies that can be efficiently carried out in non-laboratory settings. Optimally, the analytical procedures should be as simple and general as possible to facilitate their use on-site as well as to minimize the quantities of solvents, consumables, and extra equipment that must be transported. These methods must be characterized to the greatest extent possible for many different matrices in order to provide results of the highest confidence in legally binding inspections.

Among the CW-related compounds are alkyl methylphosphonic acids, which are degradation products of nerve agents. These chemicals are non-volatile and strongly acidic in water solution. The currently used methods for determination of these compounds on-site involve solid-phase extraction, concentration, derivatization, and analysis of the derivatized products by gas chromatography–mass spectrometry (GC–MS) [4]. The derivatizing agent is 1% trimethylchlorosilane in bis(trimethylsilyl)trifluoroacetamide (BSTFA), which forms the trimethylsilyl (TMS) derivatives of the acids.

The goal of this study is the optimization and validation of these methods in a variety of matrices. The sensitivity of these methods has been targetted for concentrations of 10 ppm or more (by mass) for soil, water, and wipe samples to give identifications with high confidence. The analysis is by GC–MS with a full-scan mass spectrum with library matching to give a positive identification even in the presence of compounds extracted from the matrices that may interfere. This goal has been achieved for distilled water, wipe, sandy loam soil, and sandy clay soil. Distilled water was chosen as a benchmark matrix, since the method involves water extractions from the other matrices which will add impurities to the water. Additional work is in progress to validate the methods in other matrices, including a humic soil, decontamination solutions, and environmental water samples, and for other chemicals, including mustard-gas degradation products. A parallel effort is under way for the analysis of CW agents and other non-polar, volatile compounds in these matrices.

Previously published studies have validated or characterized similar methods for a smaller subset of compounds [5–8]. However, no previously published study has reported a systematic characterization of a particular method for on-site analysis of as wide a range of CW-related compounds.

In order to optimize the methods for on-site analysis, it is advantageous to know the efficiency of each step of the process, particularly the derivatization efficiency and the extraction efficiencies from water, soil and wipe matrices. Quantitation can be accomplished using gas chromatography coupled with phosphorus-specific atomic emission detection (GC–AED). AED has previously been evaluated as a screening method for CW-related samples [9]. The compound-independent nature of the AED response makes it ideal for quantitation [10–12]. An external standard which contains phosphorus can be used to determine a calibration curve for all phosphorus-containing compounds. In addition, AED is better suited for quantitative analysis of TMS derivatives than some other methods. For example, the flame-photometric and nitrogen–phosphorus detectors are fouled from silica deposits which form on the detector when silyl derivatizing agents are used. The deposits result from injection of excess derivatizing reagent into the detector. GC–MS requires standards of each individual derivatized compound for quantitation, even though it is used qualitatively to confirm the identities of the derivatives in the gas chromatograph.

A procedure for the quantitation of the alkyl methylphosphonic acids using phosphorus-specific atomic emission detection is described. The quantitation of the derivatives enables calculation of the derivatization efficiencies of these acids and the extraction efficiencies from the various matrices. The relative standard devia-

tions (R.S.D.s) of these quantities are used to assess the reliability of the methods.

2. Experimental

2.1. Chemicals and matrices

The following standard chemicals were obtained from the Edgewood Research, Development, and Engineering Center (Aberdeen Proving Ground, MD, USA): ethylmethylphosphonic acid (EMPA), isopropylmethylphosphonic acid (IPMPA), pinacolylmethylphosphonic acid (PMPA), cyclohexylmethylphosphonic acid (CMPA), isobutylmethylphosphonic acid (IBMPA), ethylmethylphosphonothioic acid (EMPTA), and isobutylmethylphosphonothioic acid (IBMPTA). Purity of the chemicals was determined by NMR. Methylphosphonic acid (MPA, 98%) was obtained from Johnson Matthey (Ward Hill, MA, USA). Hexane (HPLC grade, 97% *n*-hexane) and acetonitrile (99.9%) were from J.T. Baker (Phillipsburg, NJ, USA). Dichloromethane (99.9%), methanol (99.9+%), ammonium hydroxide (ACS reagent), 2-propanol (99.9%), and DMMP (97%) were obtained from Sigma–Aldrich Chemical Co. (Milwaukee, WI, USA). The derivatizing agent, Sylon-BFT [1% trimethylchlorosilane in bis-(trimethylsilyl)trifluoroacetamide, BSTFA], was obtained from Supelco (Bellefonte, PA, USA). Distilled/deionized water (18 MΩ) was generated internally using a Barnstead (Dubuque, IA, USA) Nanopure system.

Cotton wipe material was purchased from VWR Scientific (Bridgeport, NJ, USA). Wipes are used for collecting samples by wiping off solid surfaces, possibly after wetting the surface with solvent. This particular material was characterized in order to be consistent with previous international field trials.

The first soil type was a sandy soil from California. It has been characterized in detail by Kingery et al. [13]. In brief, it is neutral (6.6) in pH and 88% sand. It has a fairly high phosphate content (47 mg/kg), possibly because of modification with fertilizer. It was obtained from farmlands near Lawrence Livermore National Laboratory, California. Sorption of alkyl methylphosphonic acids was measured to be low (53 μg/g for MPA, 3.3 μg/g for IPMPA, and 1.1 μg/g for EMPA). Degradation of EMPA on the soil was observed in about 350 h, which was attributed to biological activity, but this time scale was much longer than the present measurements. Degradation of IPMPA was first order and much slower, indicating that no biological degradation was involved.

The second soil type was a sandy clay, also from California. It was characterized [13] to be 46% sand, 28% silt, and 26% clay. The pH was 7.9, more basic than the sandy soil. Phosphate content was also high (76 mg/kg), and there was higher potassium (156 mg/kg) and calcium (2280 mg/kg) than the sandy soil. Sorption of MPA, IPMPA, and EMPA was low and very similar to the sandy soil. EMPA decomposed after 150 h, probably also due to biological activity, but IPMPA degradation was again first order and slow.

2.2. Equipment and chromatographic conditions

A Hewlett-Packard Model 5890 Series II gas chromatograph interfaced to a Hewlett-Packard Model 5921A atomic emission detector was used for all analyses. The gas chromatograph was fitted with a 30 m × 0.25 mm I.D. HP-5 (cross-linked 5% phenyl methyl silicone) fused-silica capillary column, film thickness 0.25 μm. Helium was used as a carrier gas at linear velocity of 32 cm/s. The oven temperature was set initially at 60°C, programmed from 60 to 200°C at 10°C/min. Splitless injections of 2 μl were used with a solvent delay of 4.00 min for the analytes and 1.80 min for the external standard. The injector port temperature was set at 275°C, the transfer line temperature at 300°C, and the cavity block temperature in the AED at 300°C. Hydrogen, at high flow, was used as the reagent gas. Peaks were detected by measuring phosphorus emission at 186 nm. Sulfur emission was monitored at 181 nm to help establish retention times for the two thioic acids.

For mass spectral work, a Hewlett-Packard

Model 5890 Series II gas chromatograph and Model 5971 MSD were used. Similar GC conditions were used, although the starting temperature was 60°C, held for 2 min, and ramped at 15°C/min to 250°C. The MSD was operated in scan mode from 50 to 300 amu. The retention times are different for the two instruments, but the elution orders are identical.

2.3. Preparation of standards

DMMP standards were prepared gravimetrically in acetonitrile and run on the AED. A typical calibration curve is shown in Fig. 1. The correlation coefficient of 0.9992 shows good linearity. The curve also includes points for a series of dialkyl methylphosphonates of varying concentrations and molecular masses. The correspondence between the calibration curve for DMMP and the signals of the other compounds is good.

Individual standards of the alkyl methylphosphonic and thioic acids were prepared in acetonitrile and hexane due to limited solubility in hexane. An amount of 300 μl of the standards was added to 200 μl of Sylon-BFT. The samples were sealed and heated at 60°C for 15 min. The derivatized acids were analyzed by GC–AED to determine the efficiency of the derivatization for each of the acids under these conditions, and five trials were averaged (except for CMPA, for which three trials were done). Measurements indicated that there was no significant difference in derivatization efficiency between hexane and acetonitrile as solvents.

Standard solutions of a mixture of MPA and the other acids were prepared in isopropanol and were used to spike the soils, water, and wipes.

2.4. Sample preparation method

Samples were made by spiking the matrix with stock solution, allowing the solvent to dry, and extracting, all within a few hours. The samples were then prepared in accordance with the current standard method [4]. For water samples or extracts, a volume of 10 ml aqueous solution was concentrated using a strong anion-exchange (SAX) solid-phase extraction cartridge (Baker-bond Quaternary Amine, J.T. Baker, Phillipsburg, NJ, USA). Analytes retained on the cartridge were eluted with 1.0% (v/v) ammonium hydroxide in methanol. The eluent was evaporated to dryness at 60°C under nitrogen. The sample residue was derivatized using a mixture of 200 μl of Sylon-BFT and 300 μl of

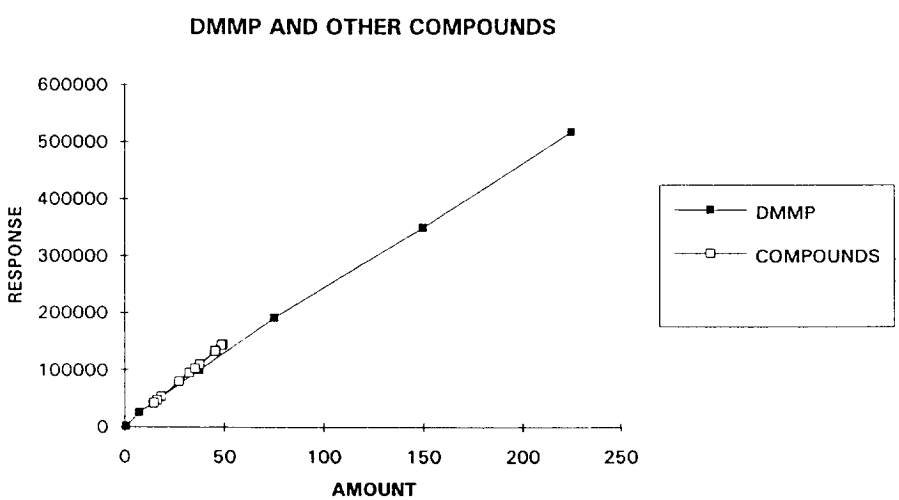

Fig. 1. Calibration curve of the GC–AED using standard DMMP solutions (solid squares). Points for other phosphonates are also shown to indicate that the signal is compound independent. Twelve compounds that were used of the type $CH_3PO_3R_1R_2$, for R_1 and R_2 selected from methyl, ethyl, isopropyl, *n*-propyl, pinacolyl (1,2,2-trimethylpropyl), hexyl, 2-methoxyethyl, 2-butoxyethyl, and cyclohexyl. Amount is in nanograms of P.

hexane, immediately sealed in an autosampler vial, and heated at 60°C for 15 min. The derivatized samples were analyzed by GC–AED or GC–MSD usually on the same day and always within a few days.

Soil (5 g sample weight) and wipe (1 g weight) samples were extracted twice with approximately 10 ml each of water. The water was filtered and analyzed following the same procedure as the aqueous samples. Soil, water, and wipe samples were spiked with the standard solutions of the acids in isopropanol to 10 ppm by mass: wipes at 10 μg/1 g of sample, water at 100 μg/10 ml of sample, and soil at 50 μg/5 g of sample. Three repetitions were done for each.

3. Results and discussion

Past studies have used several different types of derivatives to analyze alkylmethylphosphonic acids, including trimethylsilyl (TMS) [6], *tert.*-butyldimethylsilyl (TBDMS) [5,7], methyl [8,15–17], and perfluorobenzyl [14]. Each type of derivative has some advantages.

Methylation of alkylmethylphosphonic acids using diazomethane has been reported [15], but the use of diazomethane is inappropriate for field work due to its hazardous and difficult preparation and its lack of stability [16,17]. Methylation using trimethylphenylammonium hydroxide by co-injecting the underivatized acid and the hydroxide into a heated GC injector port has been done [8]. However, results indicate that the derivatization efficiency using this method is not good, especially for low concentrations of acid, and detection of MPA is difficult for solution concentrations below 150 ppm [18]. In addition, this method requires a GC injector port that is heated to 300°C, which can be difficult to achieve on some fieldable instruments due to limited power. This technique requires additional development work.

Perfluorobenzyl derivatives may provide greater sensitivity in negative chemical ionization MS detection [14], although currently negative-ion detection is not available on fieldable instrumentation. These derivatives may be valuable with additional field-instrument development.

Use of TBDMS derivatives of alkylmethylphosphonic acids [5,7] has been reported to give some advantages compared to TMS derivatives in terms of hydrolytic stability and ease of MS detection [7], although a direct comparison of sensitivity or stability has not been done. It has also been reported that, for some inorganic oxygen-containing anions, the TMS derivatives degrade rapidly at room temperature even in the derivatization solution, while TBDMS derivatives are stable [19], although this degradation was not observed for phosphate. To see whether this type of degradation was a problem for alkylmethylphosphonic acids, solutions of the acid derivatives still in BSTFA solution were analyzed after being stored in sealed vials for seven months at room temperature. It was still possible to detect and positively identify all the derivatives, although some degradation may have occurred. In fact, EMPA, IPMPA, PMPA, and MPA derivatives could be positively identified in BSTFA solutions prepared from wipe and soil extracts at spiking levels of 5 ppm after seven months of storage. Thus, degradation of these TMS derivatives does not appear to be a problem.

For the methods used in the current study, TMS derivatization was chosen on the basis of cost and availability of reagents and consistency with established recommended operating procedures [20]. The current results indicate that TMS derivatives are adequate for this purpose. Bauer and Vogt [21] have reported that BSTFA has a high hydrolytic sensitivity, requiring the use of special vials for derivatization. In our experience, Sylon-BFT can be routinely exposed to air with no significant degradation. The reagent is added to autosampler vials and sealed with crimp-type caps with no further precautions. Bauer and Vogt also reported that a variety of alkylphosphonic acids did not dissolve in BSTFA without the use of methanol as a solvent, which reacted vigorously to the BSTFA [21]. The alkylmethylphosphonic acids in this study are reproducibly derivatized without using polar solvent. However, the acids that were

spiked were all in the form of free acids rather than salts. Some studies have indicated that inorganic sodium or potassium salts are difficult to derivatize with BSTFA because they do not dissolve, although ammonium salts can be derivatized when dissolved in dimethylformamide [21,22]. This point will be addressed in more detail later.

Hexane and acetonitrile were compared as solvents for diluting the BSTFA. No significant difference was observed for the derivatization efficiency in hexane compared to acetonitrile. Hexane was found to give much better chromatography, since the GC peaks from solutions in acetonitrile can give broad, poorly defined peaks [7]. It is suspected that this problem is caused by poor solvent focusing on the non-polar GC column. The use of an uncoated precolumn or the initiation of the GC run at 90–100°C, above the acetonitrile boiling point, improved the chromatography.

Using the described methods, the spiked samples were prepared, derivatized, and analyzed. The peaks in the gas chromatogram were positively identified by using GC–MS. Fig. 2 shows a total ion chromatogram, top panel, along with extracted ion chromatograms for the ions of mass 153, 169, and 225. MPA, which is doubly substituted with TMS, has a base peak of 225 corresponding to the $[M-15]^+$ ion [23]. The other alkylmethylphosphonic acid derivatives have a base peak for the fragment ion at 153, corresponding to the $[CH_3PO_3HSi(CH_3)_2]^+$ ion, making this ion very characteristic of TMS derivatives of these compounds. This ion mass is also fairly uncommon as the base peak in mass spectra of other compounds, so it is a preferred extracted ion for locating the derivatives in a complex spectrum. The alkylmethylphosphonic derivatives also give an ion of mass 169, corresponding to $[CH_3PO_3H_2Si(CH_3)_3]^+$. The alkylmethylphosphonothioic acids have analogous ions at 169 and 185, due to the substitution of S for O. A custom library database was

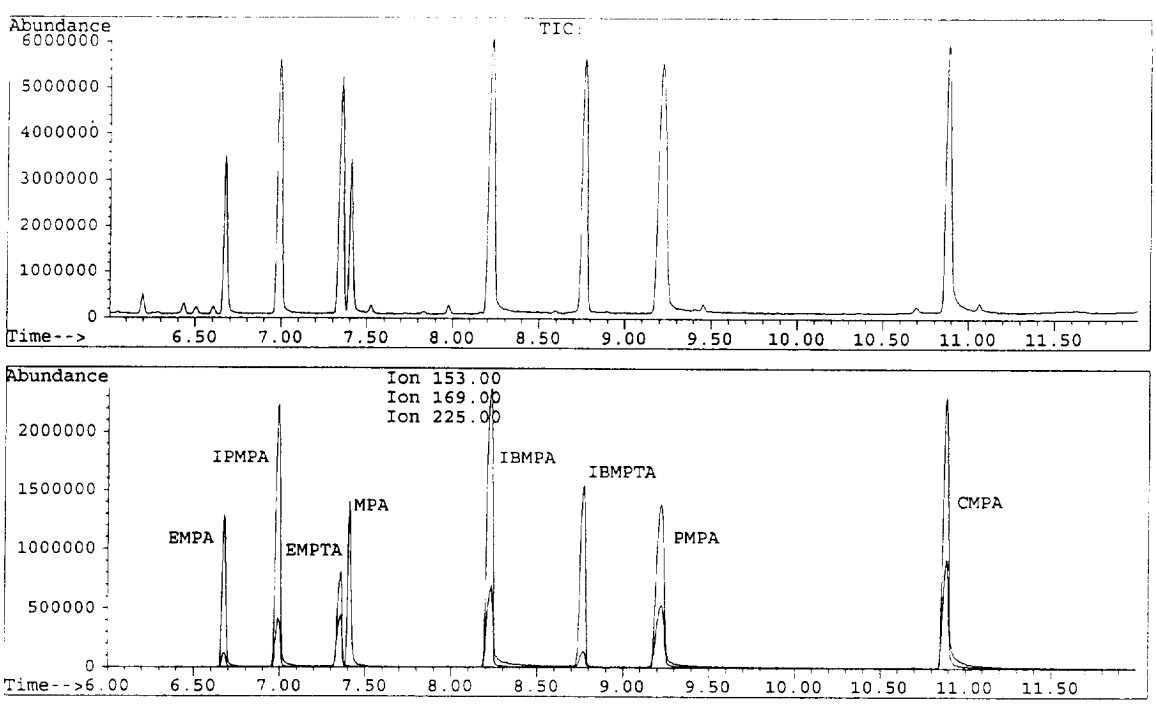

Fig. 2. GC–MS chromatograms for analysis of a mixture of alkylmethylphosphonic acids. Top panel: total-ion chromatogram. Bottom panel: extracted ion chromatograms for ions of mass 153, 169, and 225. The peaks corresponding to the TMS derivatives of the acids are labelled according to the abbreviations in the text.

assembled from mass spectra taken of separate standard solutions of each compound. The mass spectrum for each peak of the prepared samples was searched in the library and a positive identification was obtained. The elution order of the derivatives was determined.

In addition to EI mass spectra, chemical ionization mass spectra were collected of selected samples to confirm the identifications. Methane or ammonia were used as chemical ionization reagents. Both reagents gave parent ion signals for the TMS derivatives, although the methane spectra showed more fragmentation than the ammonia spectra for the acids with the larger alkyl groups. These results will be published separately.

A GC–AED chromatogram showing the separation of the derivatized alkylmethylphosphonic and thioic acids is shown in Fig. 3. The compounds are baseline resolved with the exception of EMPTA and MPA, which overlap slightly.

Table 1
Derivatization efficiencies of the alkyl methylphosphonic acids

Compound	Derivatization efficiency (%)	N	%R.S.D.
EMPA	99	6	6.5
IPMPA	84	6	4.0
EMPTA	93	6	6.0
MPA	80	6	7.4
IBMPA	110	6	3.1
IBMPTA	86	6	4.2
PMPA	107	6	3.4
CMPA	109	3	1.8

The peak shapes are good. The separation time is under 10 min.

The average derivatization efficiencies that were determined are listed in Table 1. They range from 80% for MPA to 110% for IBMPA. The R.S.D.s are in the range of 2–7%. The

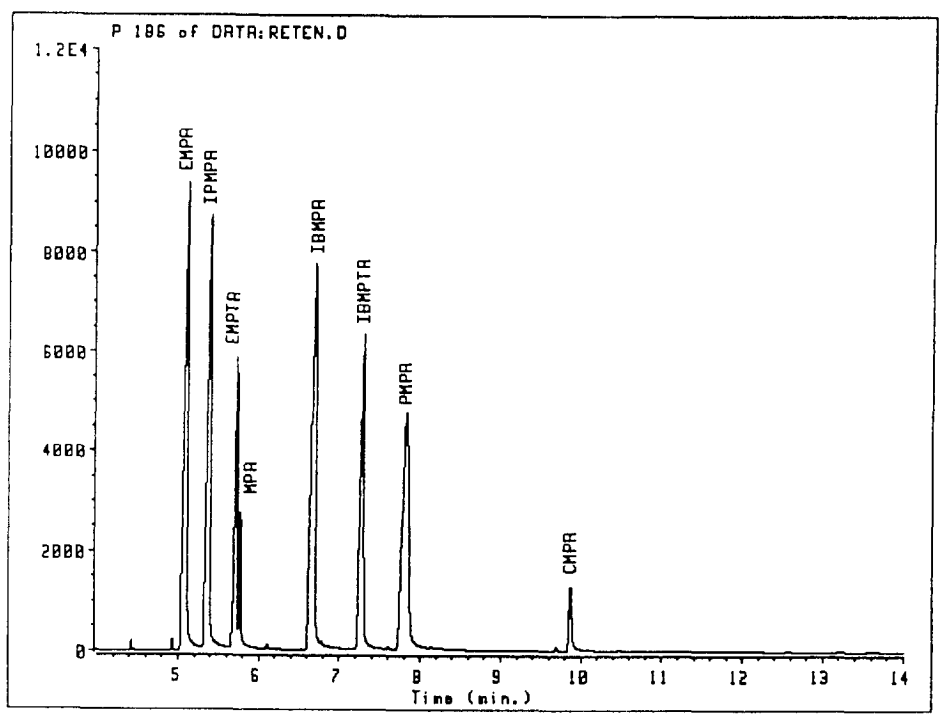

Fig. 3. GC–AED chromatogram with phosphorus detection of a sample spiked with seven alkylmethylphosphonic acids and derivatized in hexane. MPA was present as an impurity from the other seven acids. GC conditions were 60°C (no hold) to 200°C at 10°C/min. The peaks correspond with the abbreviations in the text.

efficiencies for IBMPA, PMPA, and CMPA, which are above 100%, are high by more than two standard deviations, suggesting that there may be a small systematic error in determining the concentrations. The volume change from mixing the BSTFA and acetonitrile solvents was measured and corrected for. In all cases, the derivatization efficiencies are high enough to give good recoveries of these compounds.

The efficiencies for recovery of the eight acids from three matrices are listed in Table 2. The recoveries are corrected for the derivatization efficiencies. The recoveries for water range from 13 to 99% for the acids at a concentration of 10 μg/ml.

The recovery for MPA is the lowest at 13%. The pH of the 18-MΩ water used in this study is approximately 6. At this pH, the MPA is singly ionized, which may affect its recovery. However, the optimal pH for recovery of MPA from the solution can only be determined experimentally. Preliminary results indicate that MPA is not observed from basic solutions, even though it would be doubly ionized. It is possible that the MPA forms a salt when the solution is dried and the salt does not dissolve and derivatize in the BSTFA, similar to salts of inorganic anions [21,22]. This is consistent with results of Black et al. [5], who reported that treating aqueous extract by passing it through a cation-exchange column (H^+ form) increased their sensitivity to MPA substantially. Use of a cation-exchange column would make the solution acidic, rather than basic, and it would remove metal ions that could form salts with the MPA. However, we have also found in preliminary work that basic water solutions and basic extractions of the soil improve the recoveries of the other alkylmethylphosphonic acids. Since the recovery at neutral pH is high enough to detect all the acids by GC–MS, no changes to the sample preparation method have been instituted. However, further research on the effects of pH and metal-ion concentration is under way. If it is found that improved recovery is required, it may be necessary to determine the optimal pH and change the method accordingly, although it may not be possible to optimize for both MPA and the mono-esters under the same conditions.

The R.S.D.s for the recoveries from water solution are in the range of 15–20%. The source of the error is not well characterized. In the sample preparation procedure, it is necessary to use a strong anion-exchange column in order to trap the strongly acidic species, which are in anionic form in pH 7 water. Non-polar cartridges such as C_{18} cartridges would be adequate for the alkylmethylphosphonic acids with large alkyl groups [14], but they will not trap smaller acids such as MPA. In order to elute the acids off the SAX cartridges, it is necessary to use a strong base. This solution can also strip some of the bonded phase and dissolve silicates from the cartridge. These species appear to react with the derivatizing agent, causing background in the chromatograms and decreasing the amount of

Table 2
Recovery efficiencies of each of the alkyl methylphosphonic acids from three matrices, along with the relative standard deviations from three trials

Compound	Water rec. (%)	%R.S.D.	Sandy soil rec. (%)	%R.S.D.	Swipes rec. (%)	%R.S.D.
EMPA	36	19	18	21	9	59
IPMPA	59	18	39	14	18	30
EMPTA	64	19	48	7	23	15
MPA	13	21	4	1	2	37
IBMPA	95	18	35	44	40	17
IBMPTA	64	14	41	11	42	15
PMPA	99	13	54	12	48	6
CMPA	79	15	2	10	29	14

Table 3
Recovery efficiencies of the alkyl methylphosphonic acids from sandy clay soil, using two different extraction conditions

Compound	Recovery (%) Case 1[a]	Recovery (%) Case 2[b]
EMPA	14.5	52
IPMPA	15	47
EMPTA	15	48
IBMPA	29	74
IBMPTA	15	46
PMPA	22.5	53
CMPA	3	7

[a] Case 1: two sequential extractions of 10 ml each of water. Average of two trials.
[b] Case 2: two sequential extractions, first 10 ml, second 20 ml. Fractions combined and then prepared the same as Case 1. One trial.

reagent that is available to react with the analytes. This may give rise to some of the variations in the recovery efficiencies.

Previously, a procedure was used which called for elution of the column with 10% ammonium hydroxide in methanol. This method gave even poorer R.S.D.s for the recoveries. Indeed, in some cases some of the acids were entirely missing from the chromatograms. This was attributed to loss of derivatizing agent due to reaction with chemicals that were stripped from the cartridges. Measurement showed that twice as much material by mass (silicates, etc.) was eluted from the columns using 10% NH_4OH compared to 1% NH_4OH. Reduction of the ammonium hydroxide concentration to 1% improved the R.S.D.s. Lower levels than 1% hydroxide were not effective in eluting the acids from the column.

The recoveries for the soils and wipe samples are in general lower than that for the water samples, as expected since the wipe and soil samples involve the extra step of water extraction from the two media. This extraction introduces an additional efficiency factor for each acid, since each may have a different affinity for the solid material. The wipes have the lowest recovery values, indicating some affinity of the

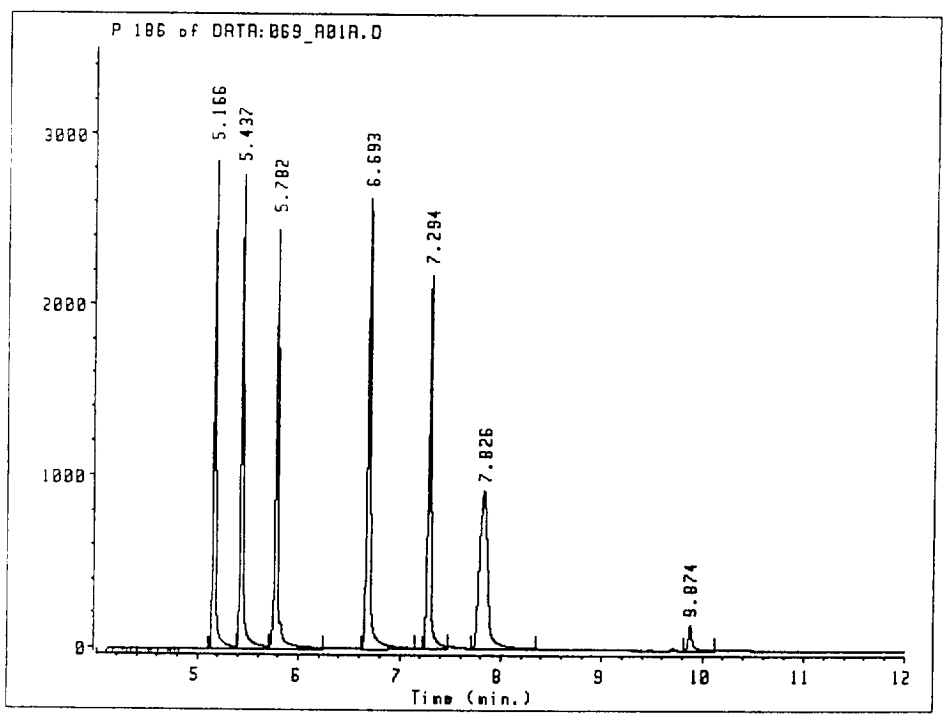

Fig. 4. GC–AED chromatogram with phosphorus detection of an extract from the sandy clay soil.

acids for the wipe material. However, the wipe samples also have the smallest quantity of spiked chemical, which decreases the signal level and is likely to be responsible for the high %R.S.D. On the other hand, the R.S.D.s for some of the sandy soil recoveries are smaller than the R.S.D.s for the water extractions, which is likely to be fortuitous.

Table 3 shows the recoveries of the mono-esters from the sandy clay soil with two slightly different extraction conditions. In the first case (two trials), the previously described method was done with two extractions of 10 ml of water. In the second case (one trial), the first extraction was 10 ml and the second was 20 ml. In both cases, extracts were combined before passing through the solid-phase extraction cartridge, and the rest of the preparation was identical. The second case shows a marked improvement in the recoveries for all the acids. However, the first case was adequate for positive identifications, and it is advantageous to keep the volume of water used for the extraction at a minimum. MPA was not spiked on these samples and was not quantified, since it is being analyzed as a separate set of runs, although a small amount was present as a contaminant in some of the mono-esters.

For these matrices, there are no interfering compounds that prevent the identification of the analytes of interest. The wipes contain some extractable fatty acids which are derivatized and can cause congestion in the chromatogram, but which do not interfere in the identifications. The sandy soil was quite clean.

The sandy clay soil had some extracted contaminants, but they did not present a problem. Fig. 4 shows the GC–AED of one of the extracts of the sandy clay soil. There are no major phosphorus signals besides the acids of interest. The EMPTA and MPA peaks, at retention times of 5.782, were not resolved, since the EMPTA has a strong signal and MPA was a minor contaminant. Both were identified in the GC–MS run in the extracted ion chromatogram of the same sample, shown in Fig. 5. The TIC in the

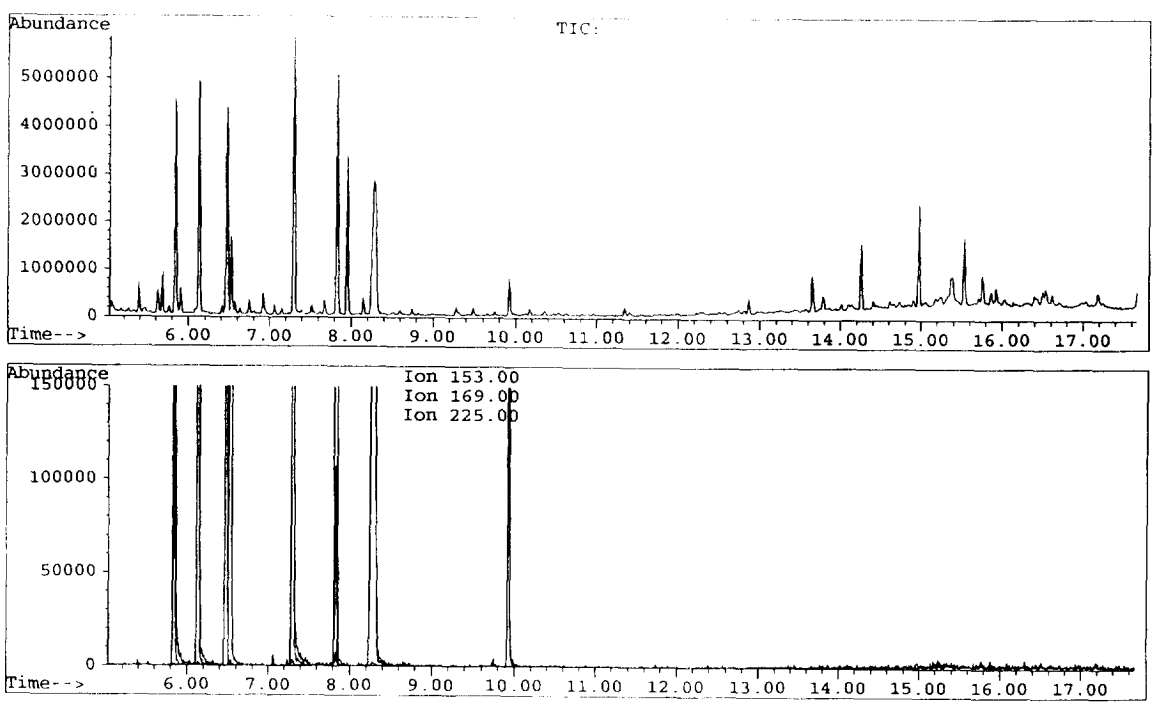

Fig. 5. GC–MS chromatogram of an extract from the sandy clay soil. Top panel: total-ion chromatogram. Bottom panel: extracted ion chromatogram of the ions of mass 153, 169, and 225, with the scale expanded to show the baseline.

top panel shows that many peaks are present from contaminants. However, the extracted ion chromatogram in the bottom panel shows that the ions at mass 153, 169, and 225 can be used to identify the peaks for the acid derivatives unambiguously for this matrix. As a result, it is appropriate to use these ions for a single-ion monitoring (SIM) method to screen for these types of compounds, although a SIM method may not be considered to be a positive identification for treaty verification purposes.

The soils contain phosphate, which is also derivatized. The phosphate derivative does not produce a significant peak in the GC–AED chromatogram, possibly because it is obscured by the tail from the acid peaks. It was found in the mass spectra at very low levels by extracting the 299 ion, which is the base peak of the mass spectrum [22–24]. The retention time of the triply derivatized phosphate is different from the alkylmethylphosphonic acids, so it does not interfere with the quantitation. In Fig. 5, it was actually only a small shoulder on the interference peak at 8.0 min.

Further trials are in progress to validate the method for other matrices and, if necessary, refine it further. If possible, the validation for lower detection limits will also be obtained.

4. Conclusions

Gas chromatography coupled to an atomic emission detector is a valuable tool for the quantitation of trimethylsilyl derivatives of alkylmethylphosphonic and thioic acids. The quantitative results helped pinpoint areas for method improvement. The results showed that the derivatization efficiencies for all the acids were sufficiently high for detection by GC–MS. However, the extraction efficiencies, even from water solution, using the solid-phase extraction procedure are substantially lower, and the R.S.D.s are rather high, suggesting that further improvements are still possible. In general, though, this procedure for detecting alkylmethylphosphonic acids in these matrices gives reliable detection at the 10 ppm level, the current goal, so it is adequate for reliable qualitative analysis of environmental samples for treaty verification. Work is in progress to characterize the methods for other matrices, including salt water solutions and decontamination solutions, and for other analytes of interest for CW verification.

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References

[1] Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and their Destruction, United States Control and Disarmament Agency, Washington, DC, 1993.
[2] W.C. McDonald, M.D. Erickson, B.M. Abraham and A. Robbat, Jr., Environ. Sci. Technol., 28 (1994) 336A–343A.
[3] W. Creasy, T.G. Albro, R.L. Cheicante and J.R. Stuff, Spectroscopy, 9(9) (Dec. 1994) 42–47.
[4] J.R. Stuff (Editor), On-Site Sample Preparation Method for Soil, Water, and Wipe Samples for the Qualitative Determination of Chemical Warfare (CW) Related Compounds, U.S. Army Chemical and Biological Defense Command, Aberdeen Proving Ground, MD, in press.
[5] R.M. Black, R.J. Clarke, R.W. Read and M.T.J. Reid, J. Chromatogr. A, 662 (1994) 301–321.
[6] P.A. D'Agostino and L.R. Provost, J. Chromatogr., 589 (1992) 287–294.
[7] J.G. Purdon, J.G. Pagotto and R.K. Miller, J. Chromatogr., 475 (1989) 261–272.
[8] J.A. Tornes and B.A. Johnsen, J. Chromatogr., 467 (1989) 129–138.
[9] T.G. Albro, in Proceedings of the 1994 ERDEC Scientific Conference on Chemical and Biological Defense Research, 15–18 Nov. 1994, Aberdeen Proving Ground, MD, in press.
[10] B.D. Quimby and J.J. Sullivan, J. High Resolut. Chromatogr., 12 (1989) 282–286.
[11] T.G. Albro, P.A. Dreifuss and R.F. Wormsbecher, J. High Resolut. Chromatogr., 16 (1993) 13–17.

[12] S.R. Goode and C. Thomas, Spectroscopy, 9(9) (Dec. 1994) 14–18.
[13] A.F. Kingery, K.P. Lee, S.E. Bufflap and H.E. Allen, Characterization and Fate of Alkyl Methylphosphonates in Standard Soils Used in the Provisional Technical Secretariat Inter-Laboratory Comparison, Final Report to EAI Corporation, 1994. Available on request.
[14] M.L. Shih, J.R. Smith, J.D. McMonagle, T.W. Dolzine and V.C. Gresham, Biol. Mass Spectrom., 20 (1991) 717–723.
[15] A. Verweij, H.L. Boter and C.E.A.M. Degenhardt, Science, 204 (1979) 616–618.
[16] J. Askew, J.H. Ruzicka and B.B. Wheals, J. Chromatogr., 41 (1969) 180–187.
[17] H. Schlenk and J.L. Gellerman, Anal. Chem., 32 (1960) 1412–1414.
[18] T.G. Albro, Evaluation of Trimethylphenylammonium Hydroxide (TMPAH) as a Derivatization Agent for the Methylation of Methylphosphonic Acid (MPA), EAI Report 14/93/002D2, Abingdon, MD, 1993. Available on request.
[19] T.P. Mawhinney, J. Chromatogr., 257 (1983) 37–44.
[20] M. Rautio (Editor), Recommended Operating Procedures for Sampling and Analysis in the Verification of Chemical Disarmament, 1994 Edition, Ministry of Foreign Affairs of Finland, Helsinki, 1994, ROP SP7.
[21] G. Bauer and W. Vogt, Anal. Chem., 53 (1981) 917–919.
[22] W.C. Butts and W.T. Rainey, Jr., Anal. Chem., 43 (1971) 538–542.
[23] D.J. Harvey and M.G. Horning, J. Chromatogr., 79 (1973) 65–74.
[24] M. Zinbo and W.R. Sherman, Tetrahedron Lett., 33 (1969) 2811–2813.