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# Detection of alkyl methylphosphonic acids in complex matrices by gas chromatography–tandem mass spectrometry

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## Abstract

A method was developed to detect alkyl methylphosphonic acids in complex matrices using gas chromatography–tandem mass spectrometry. By converting the acids to their trimethylsilyl derivatives and monitoring the collision-induced dissociation of  $m/z$  153 to  $m/z$  75 under electron ionization or methane chemical ionization (CI) conditions, five members of this series (alkyl=ethyl, isopropyl, isobutyl, pinacolyl and cyclohexyl) were selectively detected against backgrounds of diesel fuel and soil extracts containing base–neutral–acid polynuclear aromatic hydrocarbons and pesticides without interference. Detection limits were 200–500 pg injected. Ammonia CI was successfully employed for molecular mass confirmation. Published by Elsevier Science B.V.

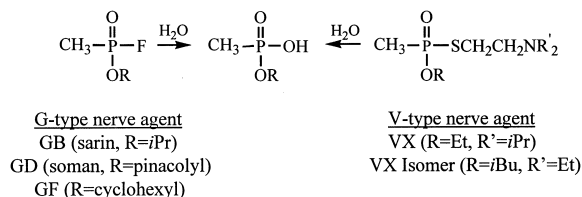
**Keywords:** Soil; Warfare agents; Environmental analysis; Alkyl methylphosphonic acid; Organophosphorus compounds

## 1. Introduction

Detection of organophosphorus nerve agents and their degradation products in the environment is important (1) to monitor destruction of chemical agent stockpiles, (2) to identify and monitor cleanup of sites that have a previous history of nerve agent use, and (3) to verify compliance or noncompliance with the United Nations Chemical Weapons Convention (CWC) [1] treaty banning the development, production, stockpiling and use of scheduled chemical agents which entered into force in April 1997. The alleged use of nerve agents in the Iran–Iraq conflict [2,3] and the Tokyo subway incident [4,5] has been well documented.

Often the only sampling sources available are soil,

water and/or vegetation in the surrounding environment or human biological samples. G-type (alkyl methylphosphonofluoridate) and V-type [O-alkyl S-(2-dialkylamino)ethyl methylphosphonothiolate] organophosphorus classes of nerve agents are unstable under these conditions and hydrolyze to their corresponding alkyl methylphosphonic acids, as shown below for five of the most common nerve agents currently in existence:



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Because organophosphorus compounds containing

the C–P bond have little industrial use, detection of alkyl methylphosphonic acids provides an indication of possible past presence of nerve agent. The detection of alkyl methylphosphonic acids to verify CWC noncompliance is complicated, however, because each of the above classes as defined by the CWC is not listed in the schedule as distinct compounds but as families of compounds including all permutations where  $R \leq C_{10}$  alkyl and cycloalkyl. This results in 879 alkyl and several thousand cycloalkyl methylphosphonic acids for which detection capability is required. Since analytical data currently exists for only a handful of these compounds, a screening method that would detect potential compounds in this family would be useful.

Difficulties encountered detecting organophosphorus acids in complex soil [6] and biological [7–9] matrices have been documented. Alkyl methylphosphonic acids are polar and not amenable to direct capillary column gas chromatography–mass spectrometry (GC–MS) analysis due to low volatility and require derivatization prior to analysis by methylation [10], trimethylsilylation [11], *tert.*-butyldimethylsilylation [12], or pentafluorobenzoylation [7]. Direct detection of alkyl methylphosphonic acids has been reported using ion chromatography [13,14], liquid chromatography–MS with thermospray [15,16] and atmospheric pressure/electrospray [17–19] ionization, and capillary zone electrophoresis [20–22].

The specificity of tandem MS (MS–MS) has recently been demonstrated for the confirmation of organophosphorus chemical warfare agents in matrices similar to those expected under typical battlefield conditions [23,24]. The objective in this study was to investigate the use of GC–MS–MS as a tool for increasing specificity and sensitivity for detection of the alkyl methylphosphonic acid series in the presence of chemical interferences. Spectra were obtained for the trimethylsilyl (TMS) derivatives of five members of this series [alkyl=ethyl, isopropyl, isobutyl, 1,2,2-trimethylpropyl (pinacolyl) and cyclohexyl] under electron ionization (EI) and chemical ionization (CI) conditions. MS–MS collision-induced dissociation (CID) product ion spectra were obtained under optimal conditions for the most abundant fragment ions common to all five compounds and the method tested for the capability to

selectively detect the five compounds in complex matrices, including (1) diesel fuel and (2) methylene chloride, water and TMS derivatizing agent extracts of soil containing base–neutral–acid (BNA) polynuclear aromatic hydrocarbons and pesticides. The use of ammonia CI was investigated as a soft ionization technique for confirmation of the molecular mass of detected acids.

## 2. Experimental

### 2.1. Materials

Ethyl methylphosphonic acid, isopropyl methylphosphonic acid, isobutyl methylphosphonic acid, cyclohexyl methylphosphonic acid, and pinacolyl methylphosphonic acid were synthesized in the laboratory by hydrolysis of the corresponding high purity alkyl methylphosphonofluoridates obtained through the Chemical Agent Standard Analytical Reference Material program. Bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) was obtained from Supelco (Bellefonte, PA, USA). Tetrahydrofuran (THF), 99.9% anhydrous, was purchased from Aldrich (Milwaukee, WI, USA). GC–MS grade methylene chloride was purchased from Burdick and Jackson (Muskegon, MI, USA).

Contaminated soil containing a high concentration of BNA polynuclear aromatic hydrocarbons and pesticides typical of that obtained from a superfund site in the western USA was obtained as a certified reference material from Resource Technology (Laramie, WY, USA; catalog no. CRM105-100, lot no. C5105RTC). Reported concentrations of selected contaminants were 16  $\mu\text{g/g}$  naphthalene, 27  $\mu\text{g/g}$  2-methylnaphthalene, 17  $\mu\text{g/g}$  acenaphthalene, 640  $\mu\text{g/g}$  acenaphthene, 256  $\mu\text{g/g}$  dibenzofuran, 368  $\mu\text{g/g}$  fluorene, 1153  $\mu\text{g/g}$  phenanthrene, 415  $\mu\text{g/g}$  anthracene, 1410  $\mu\text{g/g}$  fluoranthene, 1060  $\mu\text{g/g}$  pyrene, 251  $\mu\text{g/g}$  benzo[*a*]anthracene, 316  $\mu\text{g/g}$  chrysene, 100  $\mu\text{g/g}$  benzo[*b*]fluoranthene, 65  $\mu\text{g/g}$  benzo[*k*]fluoranthene, 84  $\mu\text{g/g}$  benzo[*a*]pyrene, 1203  $\mu\text{g/g}$  pentachlorophenol, 22  $\mu\text{g/g}$  indeno[1,2,3-*cd*]pyrene, 23  $\mu\text{g/g}$  benzo[*ghi*]perylene, and 4–20  $\mu\text{g/g}$  each of the pesticides

$\gamma$ -benzene hexachloride, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, endosulfan I and II and endrin.

## 2.2. Sample preparation

Since the objective of this study was to test the sensitivity and selectivity of methylphosphonic acid detection rather than extraction efficiency, extracts were spiked with a known concentration of derivatized acids. A stock solution of derivatized methylphosphonic acids was prepared by combining 40  $\mu\text{g}$  of each acid from individual stock solutions in methanol (total volume 0.174 ml), evaporating to dryness under a gentle stream of nitrogen, derivatizing with 100  $\mu\text{l}$  BSTFA–1% TMCS at 60°C for 20 min and diluting with methylene chloride to give a solution containing 100 ng/ $\mu\text{l}$  of each derivatized acid. The diesel fuel contaminated sample was prepared by combining 50  $\mu\text{l}$  of the derivatized acid stock solution with 2.5 mg of diesel fuel and diluting to 250  $\mu\text{l}$  with methylene chloride to give a solution containing 20 ng/ $\mu\text{l}$  of each derivatized acid and 10  $\mu\text{g}/\mu\text{l}$  diesel fuel. The methylene chloride extract of the BNA–pesticide soil was obtained by extracting 5 g of soil with 2 $\times$ 5 ml methylene chloride using 1 min of shaking/inverting and 5 min of sonication. The combined extracts were filtered through a 0.45  $\mu\text{m}$  nylon filter and concentrated to 1 ml under a gentle stream of nitrogen. A 100  $\mu\text{l}$  volume of this extract was combined with 50  $\mu\text{l}$  of the derivatized acid stock solution and 100  $\mu\text{l}$  methylene chloride to give a solution containing 20 ng/ $\mu\text{l}$  of each derivatized acid.

The derivatized water extract of the soil was obtained by extracting a fresh 1 g soil sample with 2 $\times$ 1 ml of deionized–distilled water as above. The combined extract was concentrated to 1 ml. After evaporation of 100  $\mu\text{l}$  of this extract to dryness, the residue was dissolved in 20  $\mu\text{l}$  BSTFA–1% TMCS, 20  $\mu\text{l}$  of the 100 ng/ $\mu\text{l}$  derivatized acid stock solution and 60  $\mu\text{l}$  THF and heated at 60°C for 20 min to give an extract containing 20 ng/ $\mu\text{l}$  of each derivatized acid.

The soil was derivatized directly by taking 1 g of dried soil that had been previously extracted with 2 $\times$ 1 ml methylene chloride as above and heating the soil with 100  $\mu\text{l}$  BSTFA–1% TMCS, 100  $\mu\text{l}$  THF and 1 ml methylene chloride at 60°C for 20 min. The

extract was filtered through a 0.45  $\mu\text{m}$  nylon filter, concentrated to 400  $\mu\text{l}$  and combined with 100  $\mu\text{l}$  of the derivatized acid stock solution to give an extract containing 20 ng/ $\mu\text{l}$  of each derivatized acid. For most analyses, the injection volume was 0.2  $\mu\text{l}$  resulting in 4 ng of each derivatized acid injected.

Solutions containing 2 ng/ $\mu\text{l}$  of each derivatized alkyl methylphosphonic acid were prepared by a 1 to 10 dilution of both the spiked diesel fuel solution and BNA–pesticide soil methylene chloride extract in order to determine detection sensitivity. Injection of 0.1  $\mu\text{l}$ , 0.2  $\mu\text{l}$  and 0.25  $\mu\text{l}$  of these extracts represents the injection of 200 pg, 400 pg and 500 pg of each derivatized acid, respectively.

## 2.3. Instrumental

Capillary column GC–MS and GC–MS–MS in the EI and methane CI modes were performed using a Finnigan MAT (division of ThermoQuest, San Jose, CA, USA) TSQ-7000 triple-stage quadrupole mass spectrometer equipped with a Varian (Walnut Creek, CA, USA) gas chromatograph and a 30 m $\times$ 0.25 mm I.D. DB-5 (95% dimethyl, 5% diphenyl polysiloxane, film thickness 0.25  $\mu\text{m}$ ) column (J&W Scientific, Folsom, CA, USA). The carrier gas was ultra-high-purity helium with a flow-rate of 1 ml/min. The oven temperature was ramped from 60–270°C at 15°C/min with a 5 min hold at 270°C. The injection temperature was 220°C, interface temperature 250°C, source temperature 150°C, electron energy 70 eV for EI and 200 eV for CI, emission current 400  $\mu\text{A}$  for EI and 300  $\mu\text{A}$  for CI, and the mass range was scanned from 45–450 u (EI) or 60–450 u (CI) at 0.7 s/scan. The methane CI source pressure was 470 Pa. All MS–MS CID experiments were performed using Argon as the collision gas with a collision pressure of 160 mPa and a collision voltage of –15 V.

Ammonia CI spectra were obtained using a Finnigan 5100 single quadrupole GC–MS equipped with a Finnigan model 9611 gas chromatograph and a 15 m $\times$ 0.25 mm I.D. Rtx-5 (95% dimethyl, 5% diphenyl polysiloxane, film thickness 0.25  $\mu\text{m}$ ) column (Restek, Bellefonte, PA, USA). The carrier gas was ultra-high-purity helium at a flow-rate of 1 ml/min.

The oven temperature was ramped from 60–270°C

at 10°C/min with a 5 min hold at 270°C. The injection temperature was 200°C, interface temperature 230°C, electron energy 70 eV, emission current 750  $\mu$ A and the mass range was scanned from 45–450 u at 1 s/scan. The ammonia pressure was 70 Pa.

### 3. Results and discussion

#### 3.1. EI and methane CI mass spectra

Five alkyl methylphosphonic acids,  $\text{MeP}[\text{O}][\text{OR}]\text{OH}$ , were selected for this study (R = ethyl, isopropyl, isobutyl, pinacolyl and cyclohexyl) as being typical/probable compounds encountered from the  $\text{C}_1$ – $\text{C}_{10}$  alkyl and cycloalkyl family defined by the CWC. All are degradation products of known nerve agents. Peak numbers noted in chromatograms, molecular masses ( $M_r$ ) and GC retention times ( $t_R$ ) of the TMS derivatives,  $\text{MeP}[\text{O}][\text{OR}]\text{OTMS}$ , of each acid are listed in Table 1. EI spectra are shown in Fig. 1. The base peak observed in all five spectra is the fragment ion at  $m/z$  153, which likely corresponds to the structure  $\text{MeP}[\text{O}][\text{OH}][^+\text{O}=\text{Si}(\text{Me})_2]$ , resulting from loss of the R group and a TMS methyl group. The assignment of this structure is supported by the CID product ion spectrum of  $m/z$  153, given in Fig. 2, which shows fragmentation goes primarily to  $m/z$  75  $[\text{Me}_2\text{Si}=\text{OH}]^+$ . The assignment of these structures as fragment ions has also been reported in the mass spectra of *tert*-butyldimethylsilyl derivatives of alkyl methylphosphonic acids [25]. All five compounds also fragment to a common ion at  $m/z$  169 (10–50% of base peak), which corresponds to a

Table 1

Molecular masses ( $M_r$ ) and GC retention times ( $t_R$ , 30 m $\times$ 0.25 mm DB-5, 60–270°C at 15°C/min) of alkyl methylphosphonic acid, TMS esters  $[\text{MeP}(\text{O})(\text{OTMS})\text{OR}]$  used in screening studies

| Peak No. <sup>a</sup> | R Group                                         | $M_r$ | $t_R$<br>(min) |
|-----------------------|-------------------------------------------------|-------|----------------|
| 1                     | $\text{CH}_2\text{CH}_3$                        | 196   | 4:32           |
| 2                     | $\text{CH}(\text{CH}_3)_2$                      | 210   | 4:48           |
| 3                     | $\text{CH}_2\text{CH}(\text{CH}_3)_2$           | 224   | 5:56           |
| 4                     | $\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)_3$ | 252   | 6:54           |
| 5                     | Cyclohexyl                                      | 250   | 8:32           |

<sup>a</sup> Peak numbers listed in Figs. 5–10.

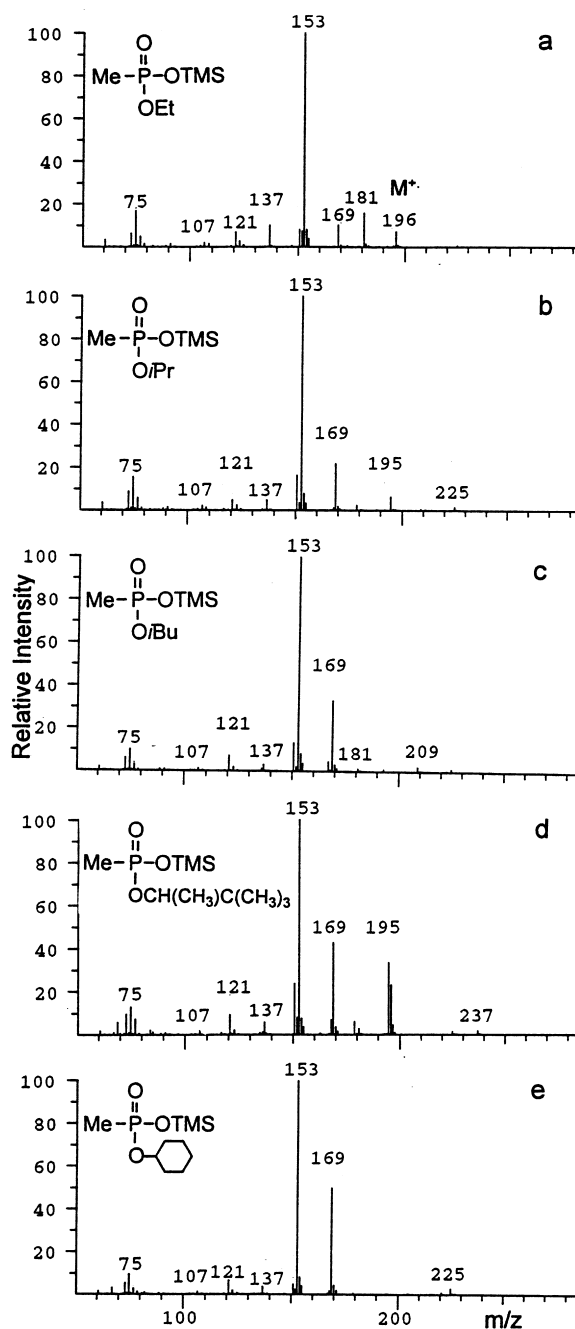


Fig. 1. Electron ionization mass spectra of the TMS esters of alkyl methylphosphonic acids for alkyl=(a) ethyl, (b) isopropyl, (c) isobutyl, (d) pinacolyl and (e) cyclohexyl.

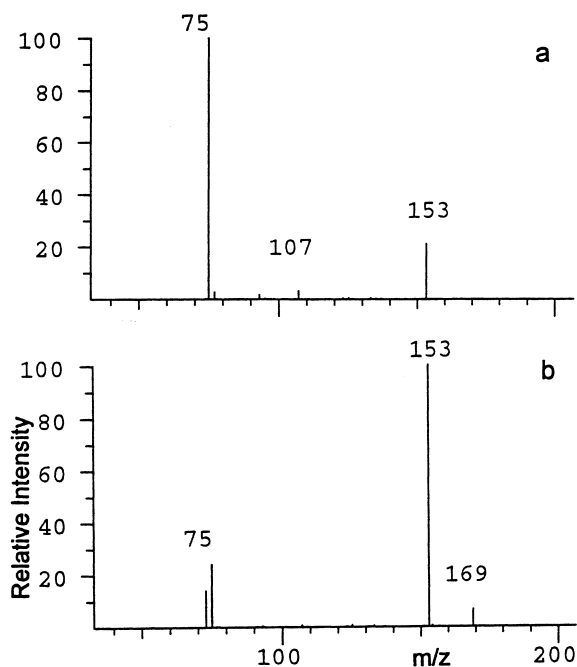


Fig. 2. Electron ionization MS-MS product ion spectra obtained for parent ions  $m/z$  (a) 153 and (b) 169 of the TMS ester of pinacolyl methylphosphonic acid (CID collision gas argon at 160 mPa, CID collision energy  $-15$  V).

protonated form of  $\text{MeP}[\text{O}][\text{OH}]\text{OSi}[\text{Me}]_3$ , resulting from loss of the R group. The CID product ion spectrum of  $m/z$  169 is also shown in Fig. 2. Fragmentation under the conditions in this study occur primarily to the ions at  $m/z$  153 (base peak) and  $m/z$  75 (25% of base peak).

Methane CI mass spectra are provided in Fig. 3. The common ions at  $m/z$  153 and 169 are also observed for all five compounds under methane CI conditions, however both ions are less than 10% of the protonated molecular ion base peak for the ethyl ester. Formation of  $m/z$  169 is generally favored over  $m/z$  153. The common ions at  $m/z$  197 and 211 are methane adduct ions of  $m/z$  169 ( $\text{MeP}[\text{O}][\text{OH}]\text{OSiMe}_3 + \text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_7^+$ , respectively). Formation of a strong  $[\text{M}+\text{H}]^+$  ion is noted for the smaller ethyl, isopropyl and isobutyl R groups but not for the larger pinacolyl (12% of base peak) and cyclohexyl (40% of base peak) R groups. Methane CI detection offers sufficient fragmentation to make MS-MS screening feasible (using  $m/z$  169 or 153 as the parent ion) and still provides molecular

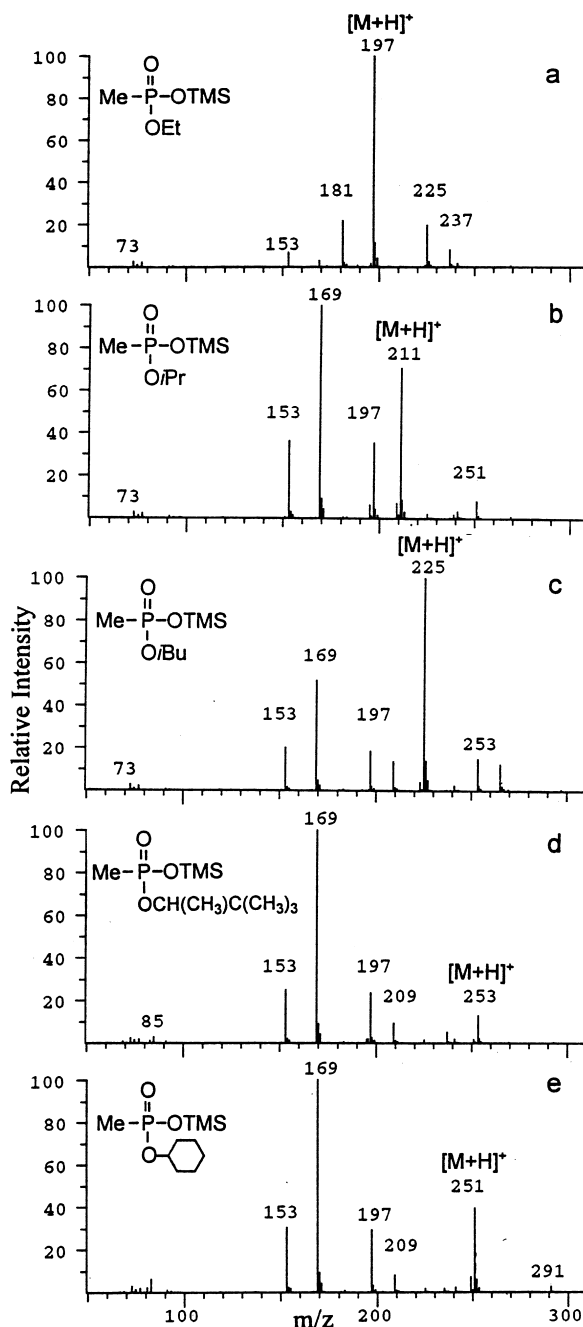


Fig. 3. Methane chemical ionization mass spectra of the TMS esters of alkyl methylphosphonic acids for alkyl=(a) ethyl, (b) isopropyl, (c) isobutyl, (d) pinacolyl and (e) cyclohexyl.

mass information not provided by EI for R groups larger than ethyl.

It is believed that the fragmentation observed here for the five alkyl methylphosphonic acid TMS derivatives to the common ions at  $m/z$  153 and 169 is representative of nearly all members of this compound class. The one notable exception is the smallest member of this series, the TMS derivative of methyl methylphosphonic acid. The EI and methane CI spectra for this compound are shown in Fig. 4. Fragmentation occurs primarily to  $m/z$  167 (loss of a TMS methyl group). Ions at  $m/z$  153 and 169 in both spectra are less than 2% of the base peak and therefore not suitable for use as MS–MS parent ions for detection of this compound at low levels. The O–R bond appears to be more stable under MS conditions for R=Me than it is for larger R groups.

### 3.2. GC–MS–MS detection in complex matrices

Because alkyl methylphosphonic acids fragment to the common ions at  $m/z$  153 and 169, MS–MS is ideal as a screening tool for detecting potential members of this family of compounds with enhanced specificity. The most logical parent ion choice under

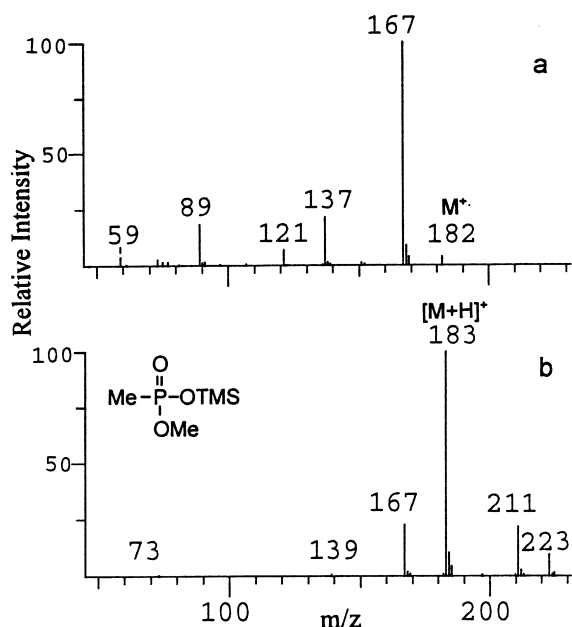


Fig. 4. (a) Electron ionization and (b) methane chemical ionization mass spectra of methyl methylphosphonic acid, TMS derivative.

EI conditions is  $m/z$  153, which is the base peak in all five spectra. Fig. 5 shows MS total ion ( $m/z$  45–450),  $m/z$  153 selected ion monitoring (SIM) and MS–MS  $m/z$  153→75 selected reaction monitoring (SRM) chromatograms obtained for injection of 4 ng of each derivatized acid in a complex BNA–pesticide soil methylene chloride extract similar to that which might be expected from a superfund site in the western USA. The acids were difficult to detect under full scan MS conditions, with the pinacolyl and cyclohexyl esters being undetectable due to chemical interference. SIM alone using  $m/z$  153 did not provide adequate selectivity to distinguish the acids from the background. As shown, by monitoring the MS–MS collision-induced dissociation of  $m/z$  153 to 75, the acids were readily observed with complete elimination of background interference. The detection limit observed under these conditions was 200–500 pg of each derivatized acid injected. All acids except the cyclohexyl ester

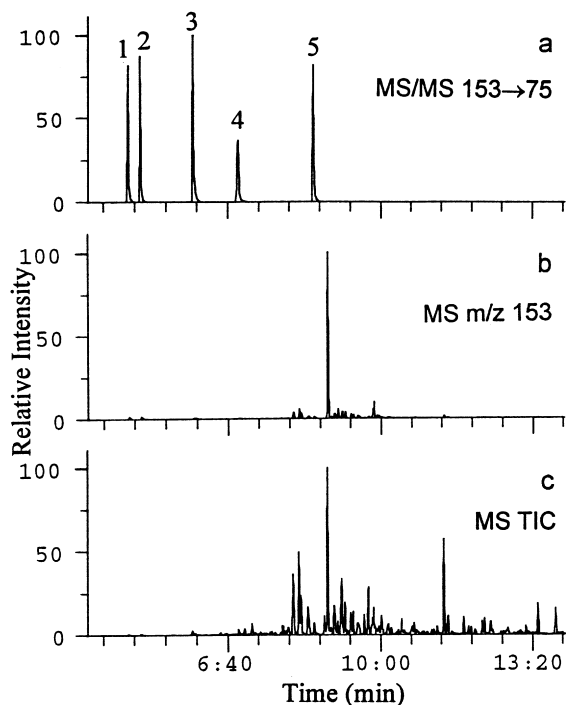


Fig. 5. Electron ionization (a) MS–MS ( $m/z$  153→75), (b) MS selected ion ( $m/z$  153) and (c) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in methylene chloride extract of BNA–pesticide soil.

were detected at 200 ng with a signal/noise ratio of about 8. The cyclohexyl ester could be detected at 500 pg.

Because methylphosphonic acids are acidic, water is commonly used as the solvent for extraction of soil samples. The possibility exists that derivatized background compounds present in derivatized water extract may also undergo the  $m/z$  153→75 reaction. To provide a background of BSTFA-derivatized water extract, the BNA-pesticide soil was extracted with water, the water evaporated by nitrogen blow-down, and the residue derivatized with BSTFA-THF. Fig. 6 provides an EI comparison of MS-MS  $m/z$  153→75 SRM and MS total ion chromatograms obtained for injection of 4 ng of each derivatized acid against this background. As expected, because of the high level of organic contamination in this soil, the overall background in the water extract was less than that observed in the methylene chloride extract. No significant background interference was observed from this particular soil sample.

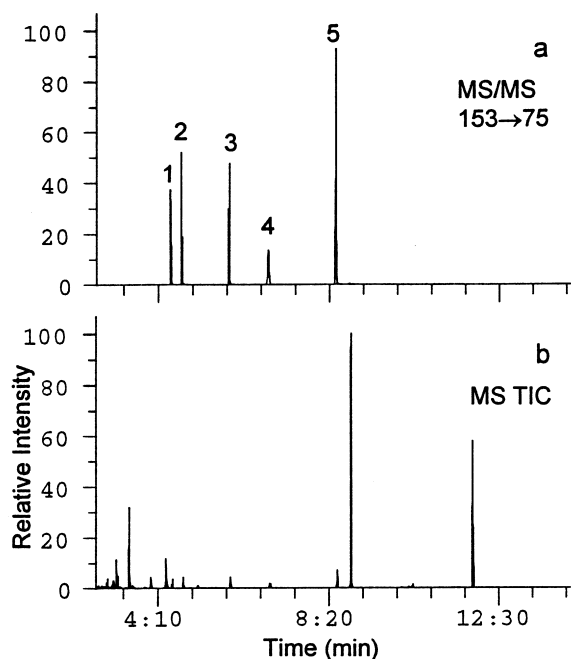


Fig. 6. Electron ionization (a) MS-MS ( $m/z$  153→75) and (b) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in BSTFA-derivatized water extract of BNA-pesticide soil.

Another technique used for detection of alkyl methylphosphonic acids and related compounds is derivatization of the soil directly in a suitable solvent [6]. To see if there might be compounds which adhere to the soil rather than extract into water which may provide potential interference, a sample of the BNA-pesticide soil previously extracted with methylene chloride was derivatized directly in the presence of BSTFA-THF-methylene chloride, followed by filtration to remove the soil. MS-MS  $m/z$  153→75 SRM and MS total ion chromatograms under EI conditions obtained for injection of 4 ng of each derivatized acid against this background are shown in Fig. 7. No significant interference was observed.

Selectivity observed in the BNA-pesticide soil methylene chloride extract matrix using  $m/z$  169 as the parent ion under EI conditions is shown in Fig. 8. Based upon the spectrum in Fig. 2, the CID product ion of choice for SRM to achieve maximum sensitivity would be  $m/z$  153. As shown, this fragmenta-

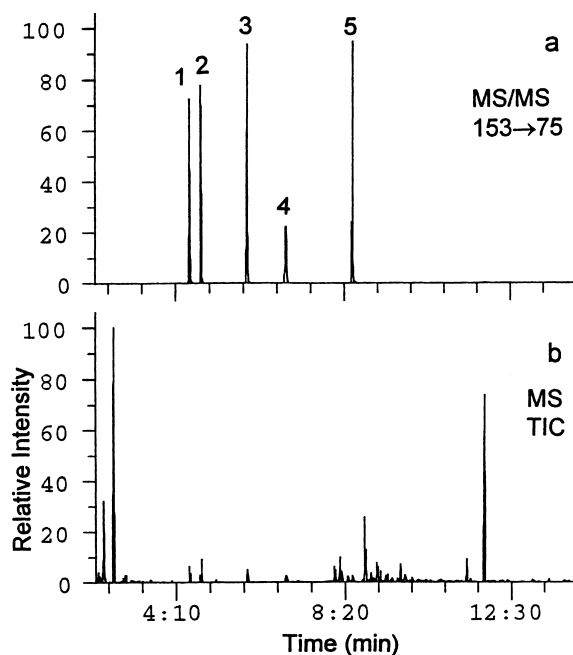


Fig. 7. Electron ionization (a) MS-MS ( $m/z$  153→75) and (b) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in BSTFA-THF-methylene chloride extract of BNA-pesticide soil.

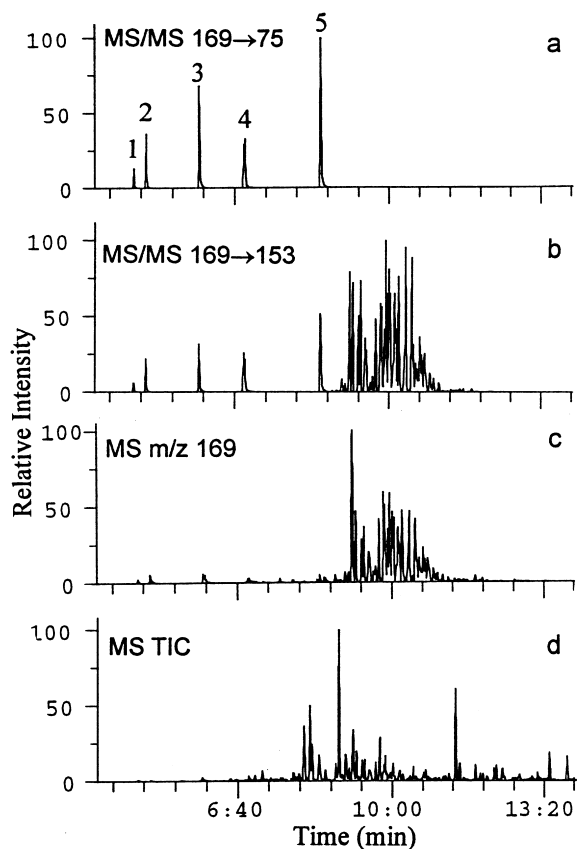


Fig. 8. Electron ionization (a) MS–MS ( $m/z$  169→75), (b) MS–MS ( $m/z$  169→153), (c) MS selected ion ( $m/z$  169) and (d) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in BNA–pesticide soil methylene chloride extract.

tion is also common for many of the contaminants and does not produce the desired selectivity. All five derivatized acids were detected at 4 ng and complete background elimination was obtained by monitoring the CID product ion  $m/z$  75, but with a fivefold reduction in sensitivity compared to monitoring the dissociation of  $m/z$  153 to 75.

Fig. 9 shows selectivity obtained in a diesel fuel background. Each injection contained 4 ng of each derivatized acid and 2  $\mu$ g of diesel fuel. In this case, monitoring the MS–MS dissociation of  $m/z$  153 to 75,  $m/z$  169 to 75, and  $m/z$  169 to 153 all resulted in complete background elimination. Monitoring the  $m/z$  153 to 75 dissociation produced maximum

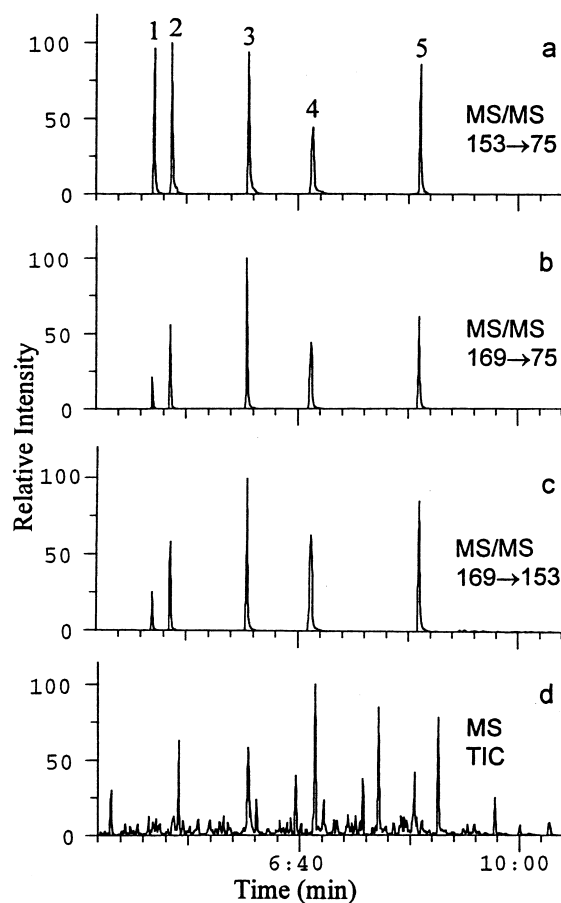


Fig. 9. Electron ionization (a) MS–MS ( $m/z$  153→75), (b) MS–MS ( $m/z$  169→75), (c) MS–MS ( $m/z$  169→153) and (d) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in 2  $\mu$ g of diesel fuel.

selectivity and sensitivity (200–500 pg detection limit) for each of the derivatized acids.

An example of the effectiveness of MS–MS screening in the diesel fuel background under methane CI conditions is shown in Fig. 10. Under full scan MS conditions the derivatized acids were indistinguishable from background. Significant background interference was still observed when monitoring the single  $m/z$  153 ion. All five acids were detected at 4 ng by monitoring the MS–MS dissociation of  $m/z$  153 to 75 with complete elimination of the background, although detection sensitivity was



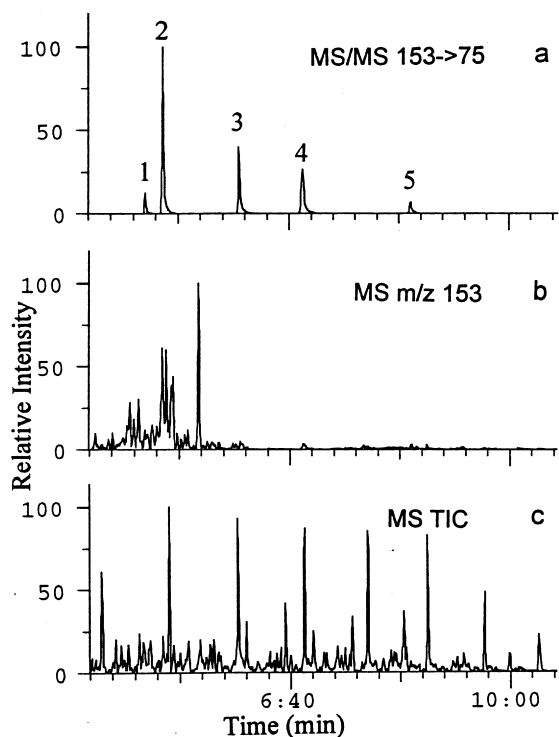


Fig. 10. Methane chemical ionization (a) MS–MS ( $m/z$  153→75), (b) MS selected ion ( $m/z$  153) and (c) MS total ion chromatograms of 4 ng each of MeP(O)(OTMS)OR for R=ethyl (1), isopropyl (2), isobutyl (3), pinacolyl (4) and cyclohexyl (5) in 2  $\mu$ g diesel fuel.

significantly less for the ethyl and cyclohexyl esters than for the isopropyl, isobutyl and pinacolyl esters. Similar results were obtained using  $m/z$  169 as the parent ion. Overall, MS–MS detection sensitivity under methane CI conditions was five- to tenfold less than obtained under EI conditions.

### 3.3. Ammonia CI mass spectra

The decreasing pseudomolecular ion intensity observed with increasing size of the alkyl group under methane CI conditions suggests that a reagent gas which results in softer ionization may be advantageous for molecular mass confirmation of alkyl methylphosphonic acid TMS derivatives containing larger alkyl groups ( $C_7$ – $C_{10}$ ). The use of ammonia as a soft CI reagent gas has been successfully applied

for the analysis of chemical warfare agents [26]. Ammonia CI spectra obtained for the TMS derivatives of the five acids are given in Fig. 11. As shown, the pseudomolecular  $[M+H]^+$  ion is the base peak

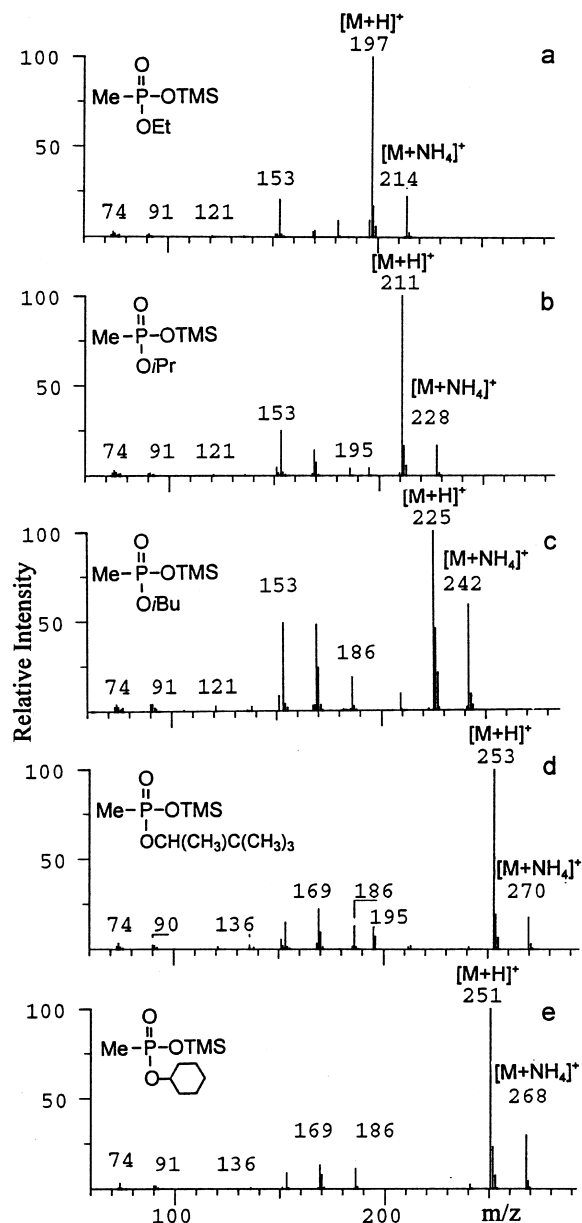


Fig. 11. Ammonia chemical ionization mass spectra of the TMS esters of alkyl methylphosphonic acids for alkyl=(a) ethyl, (b) isopropyl, (c) isobutyl, (d) pinacolyl and (e) cyclohexyl.

for all five compounds. Also indicative of this class of compounds is the presence of the  $[M+NH_4]^+$  adduct ion (20–50% of the base peak).

#### 4. Conclusions

GC–MS–MS has been applied to selectively detect the TMS esters of a series of alkyl methylphosphonic acids (alkyl=ethyl, isopropyl, isobutyl, pinacolyl and cyclohexyl) in complex matrices. Superior specificity and sensitivity were obtained by monitoring the dissociation of the  $m/z$  153 parent ion to the  $m/z$  75 product ion under EI conditions. Complete background elimination was observed in diesel fuel and BNA–pesticide contaminated soil extract matrices with a detection limit of 200–500 pg injected for each derivatized acid. The technique has potential application as a rapid and selective screening tool for detection of members of the family of alkyl methylphosphonic acids for  $alkyl \leq C_{10}$  alkyl and cycloalkyl (with the notable exception of alkyl=methyl) as defined by the CWC schedules. Detection under CI conditions is required for molecular mass confirmation. Methane CI provided molecular mass information for smaller members of the series but decreasing pseudomolecular ion formation was observed with increasing size of the alkyl group. Softer ammonia CI provided superior results with the  $[M+H]^+$  ion observed as the base peak for all five compounds.

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