

# Mass spectrometric identification of products formed during degradation of ethyl dimethylphosphoramidocyanidate (tabun)

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## ABSTRACT

The major sample components in dichloromethane extracts of munitions-grade tabun decontaminated with methanol-potassium hydroxide, including nine compounds not previously associated with tabun, were identified following capillary column gas chromatographic-mass spectrometric analysis. Electron impact fragmentation ions provided valuable structural information for the unknown sample components, but the presence of little or no molecular ion information for many of the components made identification difficult. Ammonia chemical ionization analysis was required to provide the complementary molecular ion information necessary for identification or tentative identification of these compounds. All the major sample components exhibited significant  $(M + H)^+$  and  $(M + NH_4)^+$  pseudo-molecular ions and in some cases structurally significant chemical ionization fragmentation ions during capillary column ammonia chemical ionization gas chromatographic-mass spectrometric analysis.

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## INTRODUCTION

The possible ratification of a United Nations Chemical Weapons Convention has prompted many nations to consider the ramifications of chemical warfare agent destruction. Destruction of organophosphorus chemical warfare agents may be done by chemical and/or thermal means, with chemical degradation often being preferred for small-scale operations. Regardless of the destruction method, it will be critical to both the Chemical Weapons Convention inspectorate and environmental concerns, that adequate analytical methods be available to monitor both the destruction of chemical warfare agents and the resultant reaction products.

Capillary column gas chromatography with flame ionization detection (GC-FID) may be used for the detection of chemical warfare agents [1,2]. However, it is generally agreed that the Chemical Weapons Convention will require confirmation of chemical warfare agents and their degradation

products by mass spectrometry (MS). Electron impact (EI) ionization has been used for the verification of organophosphorus chemical warfare agents, as the EI mass spectra of numerous chemical warfare agents, their decomposition products and related compounds have been published [3–8]. EI mass spectra generally provide excellent structural information [9], but the presence of little or no molecular ion information often hinders the identification of unknown organophosphorus compounds. Chemical ionization mass spectrometry (CI-MS) [10] has been used with increasing frequency to provide molecular ion information for organophosphorus compounds [11] with isobutane and other CI gases [4,12] having been used in the analysis of organophosphorus chemical warfare agents. More recently, the efficacy of ammonia CI-MS [13] has been demonstrated for phosphorous oxyacids [14], for several organophosphorus pesticides [15–17], during tandem MS study [18,19] and for the identification of unknown components of interest to the Chemical Weapons Convention in tabun [5,8] and

VX [7] formulations. Ammonia CI-MS was particularly valuable in the formulation analyses and was therefore used in this project for the identification of unknown organophosphorus degradation products in decontaminated munitions grade tabun.

A small-scale chemical destruction of the organophosphorus chemical warfare agent, ethyl dimethylphosphoramidocyanidate (tabun), was carried out using methanol-potassium hydroxide and the resultant solutions stored awaiting high-temperature incineration at the Defence Research Establishment Suffield. Samples of the decontaminated munitions-grade tabun were extracted with dichloromethane and subjected to capillary column GC-MS analysis to verify complete destruction of the tabun. EI-MS and ammonia CI-MS analysis of the dichloromethane extracts indicated the presence of a number of compounds due to methanolysis that were not previously associated with the munitions grade tabun [8]. The primary objective of this study was the MS identification of these unknown components, as this information would be of value to others involved in the verification of chemical warfare agent destruction.

#### EXPERIMENTAL

Munitions-grade tabun and dichloromethane extracts of the munitions-grade tabun decontaminated with methanol-potassium hydroxide were provided by personnel involved in a project that will rid the Defence Research Establishment Suffield Experimental Proving Grounds of chemical waste. All samples were stored in PTFE-lined screw-capped vials at 4°C prior to GC analysis. Anhydrous-grade ammonia (99.99%) was used during CI-MS analyses (Liquid Carbonic Ltd.).

Munitions-grade tabun and dichloromethane extracts of decontaminated munitions-grade tabun samples were analysed by capillary column GC-MS under both EI and ammonia CI conditions. Analyses were carried out with a VG 70/70E mass spectrometer equipped with a Varian 3700 gas chromatograph. All GC injections were cool on-column onto 15 m × 0.32 mm I.D. J&W capillary columns coated with either DBWAX or DB-1701 films (0.25 μm) with the following temperature programme: 50°C (2 min), then 10°C/min to 230°C. Helium was used as the carrier gas with a linear velocity of ap-

proximately 100 cm/s. EI conditions were as follows: electron energy, 70 eV; source temperature, 200°C; emission, 100 μA and source pressure,  $5 \cdot 10^{-7}$  Torr. Ammonia CI conditions were as follows: electron energy, 50 eV; source temperature, 130°C; emission, 500 μA and source pressure,  $9 \cdot 10^{-5}$  Torr. All EI and CI full scanning data were obtained over 400 to 35 u at 1 s/decade with an accelerating voltage of 6 kV.

#### RESULTS AND DISCUSSION

Twenty-four organophosphorus compounds were detected during capillary column GC-MS analysis of the munitions-grade tabun and dichloromethane extracts of the decontaminated munitions-grade tabun (Table 1). Fig. 1 illustrates a typical chromatogram obtained for munitions-grade tabun using the DBWAX column. Following methanol-potassium hydroxide decontamination of the munitions-grade tabun, a number of new sample components were resolved through the use of both DBWAX (Fig. 2) and DB-1701 (Fig. 3) columns. Tabun and two other cyano substituted organophosphorus compounds, observed in munitions-grade tabun [8], were not detected in samples decontaminated with methanol-potassium hydroxide. Electron impact mass spectra provided valuable structural information for the unknown compounds, but the presence of little or no molecular ion information hindered identification.

Ammonia CI-MS, a technique being used with increasing frequency to provide the complementary molecular ion information for organophosphorus chemical warfare agents, greatly aided the identification of the decontamination products of munitions-grade tabun. All the compounds identified during chromatographic analysis of munitions-grade tabun and the decontamination products of the munitions-grade tabun exhibited pseudo-molecular ions during ammonia CI-MS and in many cases structurally significant CI fragmentation ions due to the neutral loss of  $C_xH_{x+2}$  (where  $x = 2$  or 3) from the largest alkoxy ( $OC_xH_{x+2}$ ) substituent.

Figs. 4 and 5 illustrate the EI and ammonia CI mass spectra of organophosphorus compounds not previously reported in munitions-grade tabun [8]. Five of the compounds, isopropyl methyl ethylphosphonate (Fig. 4a), diisopropyl ethylphospho-

TABLE I

## COMPOUNDS IDENTIFIED IN MUNITIONS-GRADE TABUN AND DECONTAMINATED MUNITIONS-GRADE TABUN

Peak Nos. refer to chromatograms in Figs. 1, 2 and 3. Asterisks indicate presence in munitions (M)-grade tabun or in decontaminated (D) munitions-grade tabun.

Peak No.	Mol. wt.	M	D	Compound
1	166	*	*	Isopropyl methyl ethylphosphonate
2	194	*	*	Diisopropyl ethylphosphonate
3	209	*	*	Diisopropyl dimethylphosphoramidate <sup>a</sup>
4	140	—	*	Trimethyl phosphate
5	153	—	*	Dimethyl dimethylphosphoramidate
6	181	—	*	Isopropyl methyl dimethylphosphoramidate
7	195	*	*	Ethyl isopropyl dimethylphosphoramidate <sup>a</sup>
8	167	—	*	Ethyl methyl dimethylphosphoramidate
9	224	*	*	Triisopropyl phosphate <sup>a</sup>
10		—	*	Unknown <sup>b</sup>
11	181	*	*	Diethyl dimethylphosphoramidate <sup>a</sup>
12	182	—	*	Ethyl isopropyl methyl phosphate
13	210	*	*	Diisopropyl ethyl phosphate <sup>a</sup>
14	168	—	*	Diethyl methyl phosphate
15	196	*	*	Diethyl isopropyl phosphate <sup>a</sup>
16	182	*	*	Triethyl phosphate <sup>a</sup>
17	194	*	*	Methyl pinacolyl methylphosphonate
18	194	*	*	Isopropyl tetramethylphosphorodiamidate <sup>a</sup>
19	166	—	*	Methyl tetramethylphosphorodiamidate
20	180	*	*	Ethyl tetramethylphosphorodiamidate <sup>a</sup>
21	176	*	—	Isopropyl dimethylphosphoramidocyanidate <sup>a</sup>
22	162	*	—	Ethyl dimethylphosphoramidocyanidate (Tabun) <sup>a</sup>
23	161	*	—	Tetramethylphosphorodiamidic cyanide <sup>a</sup>
24	154	—	*	Dimethyl ethyl phosphate

<sup>a</sup> Compound previously identified in munitions-grade tabun (ref. 8)

<sup>b</sup> EI data were not interpretable and no ammonia CI data were obtained.

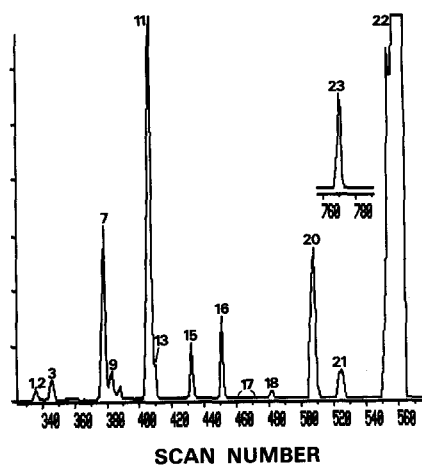


Fig. 1. Capillary column GC-MS total ion current chromatogram of munitions-grade tabun obtained under electron impact ionization conditions. Sample components are identified in Table I. Conditions: 15 m × 0.32 mm I.D. J&W DBWAX; 50°C (2 min), 10°C/min to 230°C (5 min); 1 MS Scan = 1.3 s).

nate (Fig. 4b), dimethyl dimethylphosphoramidate (Fig. 4c), ethyl methyl dimethylphosphoramidate (Fig. 4e) and methyl pinacolyl methylphosphonate (Fig. 5c), exhibited EI mass spectra similar to those published by the Finnish Research Project for Chemical Warfare Verification [3,20], and tentative identification was possible on this basis. Further evidence, particularly for the three compounds which do provide molecular ion information under EI conditions (isopropyl methyl ethylphosphonate, diisopropyl ethylphosphonate and methyl pinacolyl methylphosphonate) was obtained during ammonia CI analysis.  $(M+H)^+$  and  $(M+NH_4)^+$  pseudo-molecular ions were observed for these three compounds as well as for the other two compounds that exhibit molecular ions under EI conditions. Background subtraction, performed on all the ammonia CI mass spectra presented, was not always effective

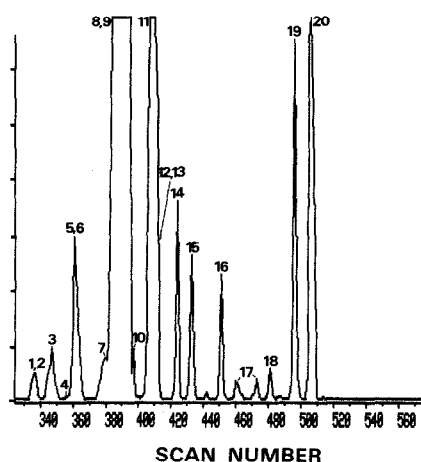


Fig. 2. Capillary column GC-MS total ion current chromatogram of dichloromethane extract of methanol-potassium hydroxide decontaminated munitions-grade tabun obtained under electron impact ionization conditions. Sample components are identified in Table I. Component 9 was minor compared to component 8. Conditions: 15 m  $\times$  0.32 mm I.D. J&W DBWAX; 50°C (2 min), 10°C/min to 230°C (5 min); 1 MS Scan = 1.3 s.

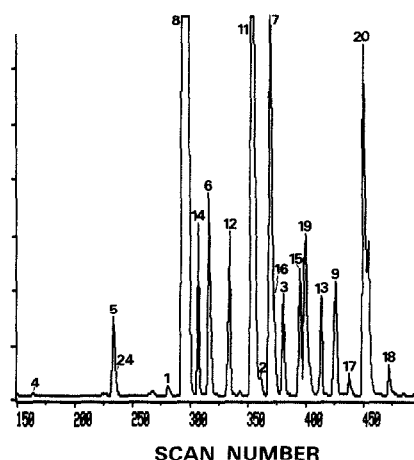


Fig. 3. Capillary column GC-MS total ion current chromatogram of dichloromethane extract of methanol-potassium hydroxide decontaminated munitions-grade tabun obtained under electron impact ionization conditions. Sample components are identified in Table I. Conditions: 15 m  $\times$  0.32 mm I.D. J&W DB-1701; 50°C (2 min), 10°C/min to 250°C (5 min); 1 MS Scan = 1.3 s.

in completely reducing the low mass CI background ions ( $< m/z$  100) for several minor components (*i.e.*, Figs. 4a and b).

The remaining five compounds were identified on the basis of interpretation of both the EI and ammonia CI data acquired. Isopropyl methyl dimethylphosphoramidate (Fig. 4d) exhibited EI ions at  $m/z$  181, 166, 139, 122 and 108, likely due to  $M^+$ ,  $(M-CH_3)^+$ ,  $(M-C_3H_6)^+$ ,  $(M-OC_3H_7)^+$  and  $[N(CH_3)_2P(O)OH]^+$ , respectively. The base ion at  $m/z$  44, due to  $[N(CH_3)_2]^+$ , was typically observed as the base ion during prior analysis of other dimethylphosphoramidates [5,8]. The  $m/z$  181 ion was confirmed as the molecular ion during ammonia CI by the presence of  $(M+H)^+$  and  $(M+NH_4)^+$  pseudo-molecular ions at  $m/z$  182 and 199 respectively.

Ethyl isopropyl methyl phosphate was characterized by EI fragmentation ions at  $m/z$  167, 141, 139, 113 and 95, likely due to  $(M-CH_3)^+$ ,  $(M-C_3H_5)^+$ ,  $(M-C_3H_7)^+$ ,  $[(OH)_3P(OCH_3)]^+$  and  $[(OH)P(O)(OCH_3)]^+$ , respectively. Molecular ion information, absent in the EI data, was provided during ammonia CI analysis. Pseudo-molecular ions at  $m/z$  183 and 200, due to  $(M+H)^+$  and  $(M+NH_4)^+$ , respectively, and CI fragmentation

ions due to the loss of  $C_3H_6$  from both pseudo-molecular ions ( $m/z$  141 and 158) were observed (Fig. 5a).

Diethyl methyl phosphate exhibited a weak EI molecular ion at  $m/z$  168 and several diagnostic EI fragmentation ions at  $m/z$  153, 141, 113, 95 and 81, likely due to  $(M-CH_3)^+$ ,  $(M-C_2H_3)^+$ ,  $[(OH)_3P(OCH_3)]^+$ ,  $[(OH)P(O)(OCH_3)]^+$  and  $[(OH)_2P(O)]^+$ , respectively (Fig. 5b). The molecular weight of the compound was confirmed by the presence of pseudo-molecular ions at  $m/z$  169 and 186, due to  $(M+H)^+$  and  $(M+NH_4)^+$ , respectively, and CI fragmentation ions due to the loss of  $C_2H_4$  from both pseudo-molecular ions ( $m/z$  141 and 158) were observed.

Methyl tetramethylphosphorodiamidate was characterized by an intense molecular ion at  $m/z$  166, an EI fragmentation ion due to loss of  $N(CH_3)_2$  from the molecular ion ( $m/z$  122) and the ion diagnostic of dimethylphosphoramidates at  $m/z$  44 due to  $[N(CH_3)_2]^+$  (Fig. 5d). The ammonia CI mass spectrum contained pseudo-molecular ions at  $m/z$  167 and 184 due to  $(M+H)^+$  and  $(M+NH_4)^+$ , respectively.

Dimethyl ethyl phosphate exhibited EI fragmen-

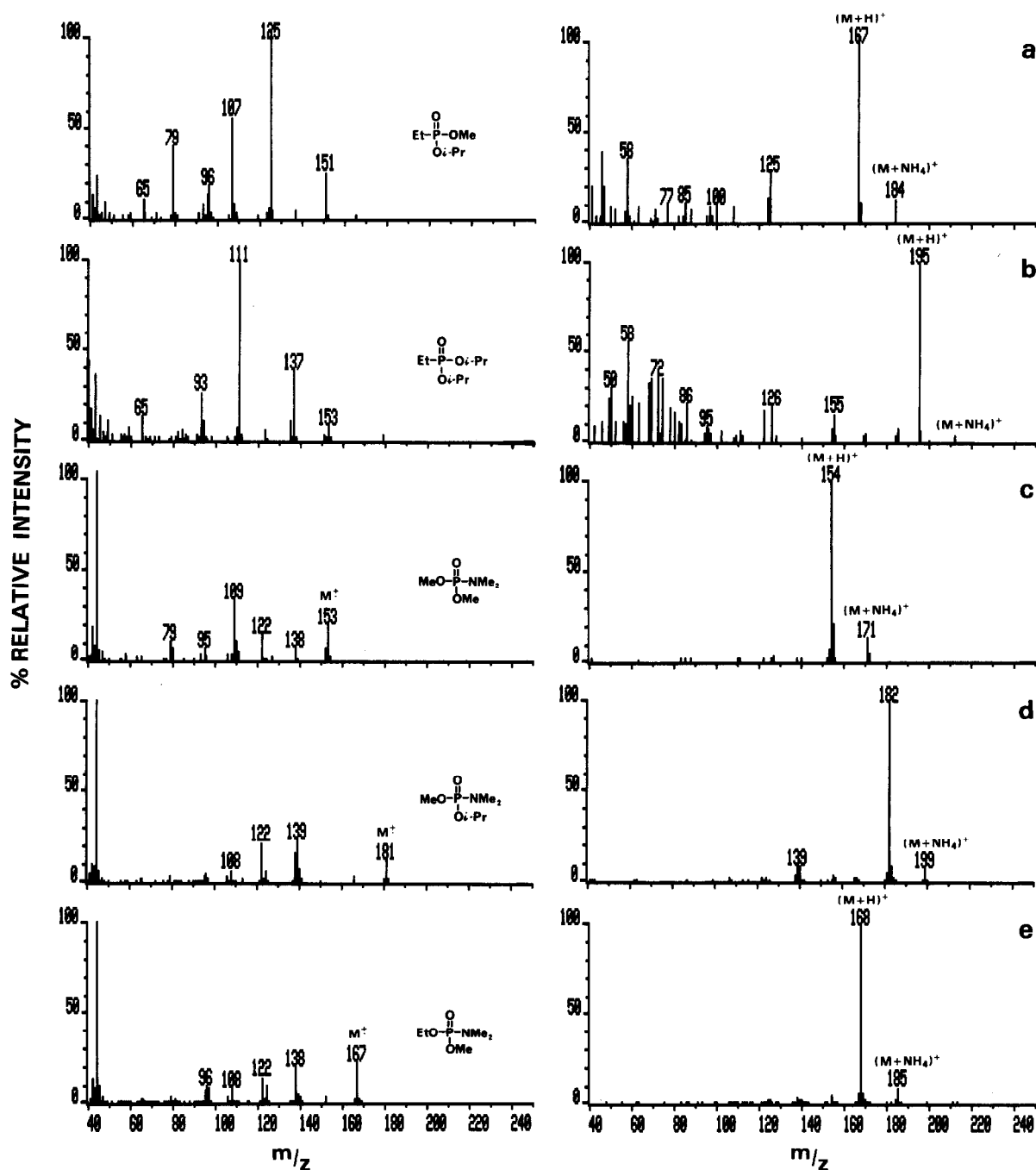


Fig. 4. Electron impact (left) and ammonia chemical ionization (right) mass spectra obtained for (a) isopropyl methyl ethylphosphonate, (b) diisopropyl ethylphosphonate, (c) dimethyl dimethylphosphoramidate, (d) isopropyl methyl dimethylphosphoramidate and (e) ethyl methyl dimethylphosphoramidate. Et = Ethyl; *i*-Pr = isopropyl; Me = methyl.

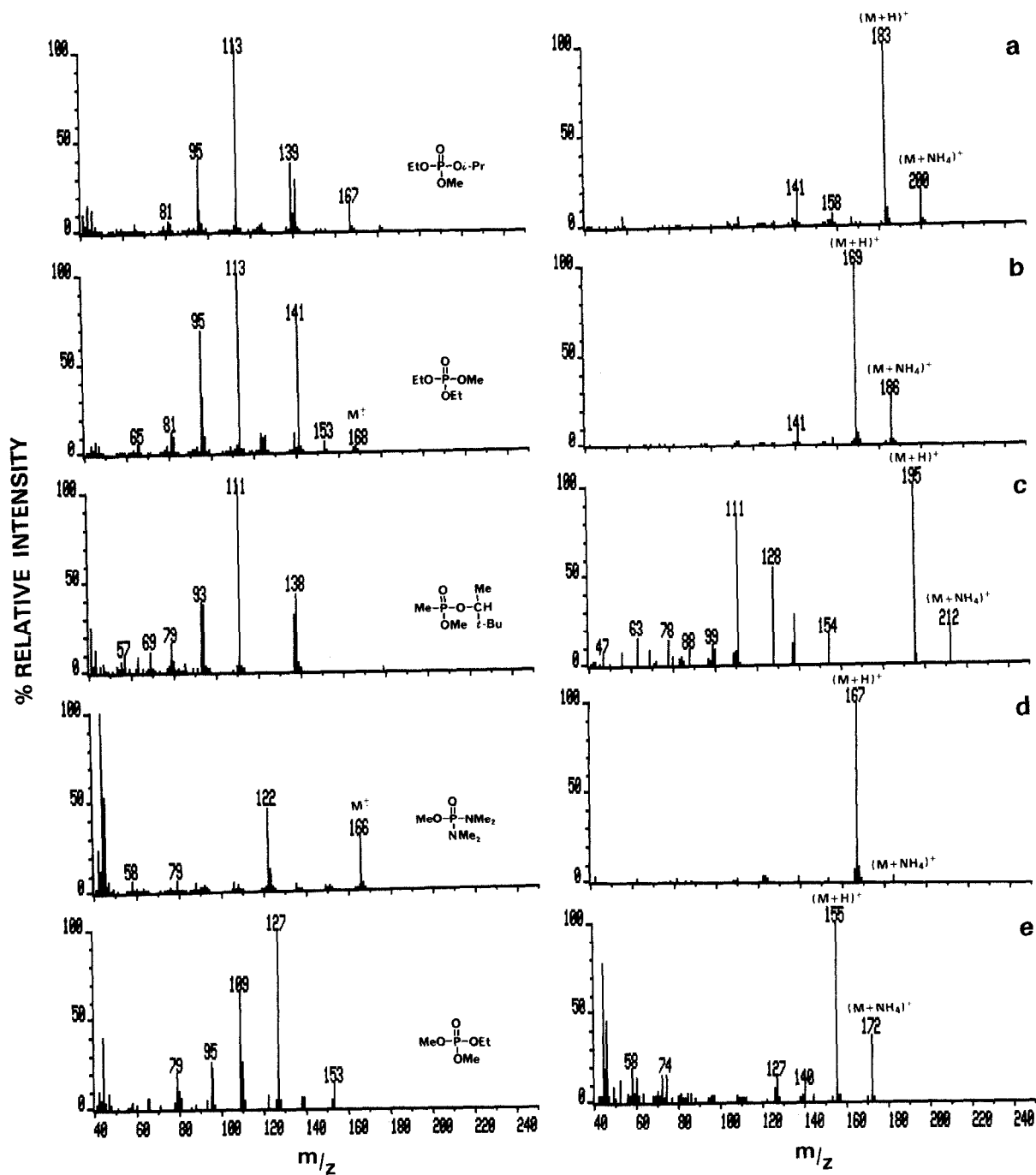


Fig. 5. Electron impact (left) and ammonia chemical ionization (right) mass spectra obtained for (a) ethyl isopropyl methyl phosphate, (b) diethyl methyl phosphate, (c) methyl pinacolyl methylphosphonate, (d) methyl tetramethylphosphorodiamidate and (e) dimethyl ethyl phosphate. *t*-Bu = *tert*-Butyl; other abbreviations as in Fig. 4.

tation ions at  $m/z$  153, 127, 109 and 95 likely due to  $(M-H)^+$ ,  $(M-C_2H_3)^+$ ,  $(M-OC_2H_5)^+$  and  $[(OH)P(O)(OCH_3)]^+$ , respectively (Fig. 5e). Support for a molecular weight of 154 was provided by the presence of pseudo-molecular ions at  $m/z$  155 and 172, due to  $(M+H)^+$  and  $(M+NH_4)^+$ , respectively.

The methanolysis product of tabun, ethyl methyl dimethylphosphoramidate  $[(EtO)(CN)P(O)(N-Me_2)]$ , was the major component identified during GC-MS analysis of the decontaminated munitions-grade tabun (Figs. 2 and 3). Compounds, such as methyl tetramethylphosphorodiamidate and dimethyl dimethylphosphoramidate, could be expected after methanolysis of, for example, the munitions-grade tabun component, tetramethylphosphorodiamidic cyanide. Most of the other methanolysis products could be rationalized in a similar manner. The ammonia CI mass spectrum of trimethyl phosphate acquired was similar to published data [14] and the presence of this minor component was confirmed with a standard. An unusual compound methyl pinacolyl methylphosphonate (two chromatographic peaks due to diastereoisomeric pair) was found in both the munitions-grade tabun and the decontaminated munitions-grade tabun extract. This compound, present at a very low level relative to the other sample components in munitions-grade tabun (Fig. 1), was likely due to contamination of the tabun with a small amount of the organophosphorus chemical warfare agent, soman or a related pinacolyl containing compound. The P-Et compounds, diisopropyl ethylphosphonate and isopropyl methyl ethylphosphonate (peaks 1 and 2), may also be tabun contaminants. Pyrophosphates identified in munitions-grade tabun [8] were not observed in the dichloromethane extracts of the decontaminated tabun.

## CONCLUSIONS

The major sample components in dichloromethane extracts of munitions-grade tabun decontaminated with methanol-potassium hydroxide, including nine compounds not previously associated with tabun, were identified following capillary column GC-MS analysis. Electron impact fragmentation ions provided valuable structural information for the unknown sample components, but the presence of little or no molecular ion information for many of the components made identification difficult. All

the major sample components exhibited significant  $(M+H)^+$  and  $(M+NH_4)^+$  pseudo-molecular ions and in some cases structurally significant CI fragmentation ions during capillary column ammonia chemical ionization GC-MS analysis. Use of the provided EI-MS and ammonia CI-MS data is anticipated during capillary column GC-MS analysis of chemical destruction samples by other laboratories involved in chemical weapons verification and by the United Nations Inspectorate during the destruction of Iraqi tabun stocks.

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