

CHROM. 21 156

IDENTIFICATION OF TABUN IMPURITIES BY COMBINED CAPILLARY COLUMN GAS CHROMATOGRAPHY–MASS SPECTROMETRY

PAUL A. D'AGOSTINO*, LIONEL R. PROVOST and KAREN M. LOOYE

Defence Research Establishment Suffield, Ralston, Alberta T0J 2N0 (Canada)

(First received September 2nd, 1988; revised manuscript received November 30th, 1988)

SUMMARY

A munitions-grade tabun sample containing a number of sample components was studied by combined capillary column gas chromatography–mass spectrometry under electron-impact and ammonia and deuterated ammonia chemical ionization conditions. Interpretation of the data resulted in the identification of nineteen impurities, including twelve monophosphorus and pyrophosphate compounds previously unreported in tabun. Ammonia and deuterated ammonia chemical ionization was particularly useful as this technique provided molecular ion information for all the identified sample components.

INTRODUCTION

The alleged use of the nerve agent ethyl dimethylphosphoramidocyanidate (tabun) in the Iran–Iraq war emphasizes the need for specific detection and identification procedures for this and other chemical warfare agents^{1–4}. Gas chromatographic–mass spectrometric (GC–MS) techniques have been used extensively for the analysis of these and other organophosphorus compounds. Electron-impact (EI) mass spectra generally provide excellent structural information⁵, but the presence of little or no molecular ion information often hinders the identification of unknown organophosphorus compounds. Chemical ionization mass spectrometry (CI–MS)⁶, a milder ionization technique, has been used with increasing frequency to provide the molecular ion information necessary for the identification of these organophosphorus compounds⁷.

CI–MS using methane, isobutane, ethylene or methanol has been applied to the analysis of organophosphorus chemical warfare agents^{8,9} and pesticides^{10–15}. More recently, the efficacy of ammonia CI–MS¹⁶ has been demonstrated for phosphorus oxyacids¹⁷, several organophosphorus pesticides^{10,14,18} and numerous chemical warfare agents, decomposition products and related impurities^{19–22}.

Previous GC–MS analysis of tabun samples in our laboratory¹⁹ and by others^{3,4} resulted in the detection of several impurities, including diethyl dimethylphosphoramidate, ethyl isopropyl dimethylphosphoramidate, trichthyl phosphate, ethyl tetramethylphosphorodiamidate, tetramethylphosphorodiamidic cyanide and two pyrophosphates. Subsequent analysis of a munitions-grade tabun sample confirmed

the presence of these compounds and a number of other impurities. The identity of these unknown sample components would be valuable for future chemical event verification.

Tabun and nineteen related impurities were detected in the munitions sample during capillary column GC-MS analysis under EI and ammonia and deuterated ammonia CI conditions. Interpretation of the data resulted in the identification and characterization of twelve monophosphorus and pyrophosphate compounds previously unreported in munitions-grade tabun.

EXPERIMENTAL

Standards

All tabun samples were prepared in high-performance liquid chromatographic grade chloroform (Fisher Scientific, Edmonton, Canada) and stored in PTFE-lined screw-capped glass vials prior to analysis. The munitions-grade tabun, used for impurity identification, was taken from a sample which had been in a steel container for at least 30 years.

Synthetic samples of tabun, triisopropyl phosphate and bis(diethyl phosphoric) anhydride were prepared in our Organic Chemistry Laboratory. Anhydrous ammonia (99.99%; Liquid Carbonic, Scarborough, Canada) and deuterated ammonia (99%; MDS Isotopes, Dorval, Canada) were used as CI reagent gases.

Instruments

A Varian (Georgetown, Canada) Model 3700 gas chromatograph with flame ionization detection (FID) was used for all capillary column GC-FID analyses. Data were recorded on a Varian 4270 integrator and/or a Nelson Analytical 6000 data system. GC analyses were performed on 15 m \times 0.32 mm I.D. capillary columns (J & W Scientific, Rancho Cordova, CA, U.S.A.) coated with DB-5 [(95%) methyl-(5%) diphenylpolysiloxane], DB-1701 [(86%) dimethyl-(14%) cyanopropylphenylpolysiloxane] and DBWAX (100% polyethylene glycol) films. An on-column injector of our own design was used for sample introduction²³. Injections were made at 50°C. This temperature was maintained for 2 min and followed by a 10°C/min temperature program. Maximum temperatures of 260, 280 and 230°C were maintained for 5 min for the DB-5, DB-1701 and DBWAX capillary columns, respectively. High-purity helium, at a linear velocity of 35 cm/s (methane injection at 50°C), was used as the carrier gas.

Capillary column GC-MS analyses were performed with a VG Micromass 70/70E double-focusing mass spectrometer (VG Analytical, Wythenshawe, U.K.) interfaced with a Varian 3700 gas chromatograph. The EI operating parameters were as follows: source pressure, $2 \cdot 10^{-6}$ Torr; source temperature, 200°C; electron energy, 70 eV; and electron emission, 100 μ A. The ammonia and deuterated ammonia CI operating conditions were as follows: source pressure, $5 \cdot 10^{-5}$ - $6 \cdot 10^{-5}$ Torr; electron energy, 50 eV; and electron emission, 500 μ A. The CI source temperature was initially 120°C and gradually increased to 140°C by the end of each GC-MS analysis owing to heating by the filament. Details of ammonia CI optimization have been reported²⁰. All EI and CI mass spectra were obtained at a resolution of 1000 (10% valley definition) and an accelerating voltage of 6 kV. Data were collected from 500 to 35 u (exponential down) at a scan rate of 1 s per decade.

RESULTS AND DISCUSSION

Capillary column GC-FID analysis of a munitions-grade tabun sample indicated that impurities accounted for 28% of the volatile organic content. Samples of the tabun were analysed by capillary column GC-MS under EI, ammonia CI ($\text{NH}_3\text{-CI}$) and deuterated ammonia CI ($\text{N}^2\text{H}_3\text{-CI}$) conditions in an effort to acquire the molecular and fragmentation ion information necessary for sample component identification. Comparison of acquired EI mass spectral data with previously published data confirmed the presence of several monophosphorus compounds including triethyl phosphate, diethyl dimethylphosphoramidate, ethyl isopropyl dimethylphosphoramidate, ethyl tetramethylphosphorodiamidate and tetramethylphosphorodiamidic cyanide¹⁹. Triisopropyl phosphate and the pyrophosphate bis-(diethyl phosphoric) anhydride were confirmed by comparison of acquired EI data with that obtained for synthesized standards.

The remaining monophosphorus and pyrophosphate compounds were identified on the basis of mass spectral interpretation. Characteristic fragmentation ions and in some instances molecular ions were obtained under EI ionization conditions. Pseudo-molecular $(\text{M} + \text{X})^+$ and/or $(\text{M} + \text{NX}_4)^+$ ions (where $\text{X} = \text{H}$ during $\text{NH}_3\text{-CI}$ and $\text{X} = {}^2\text{H}$ during $\text{N}^2\text{H}_3\text{-CI}$), together with a limited number of fragmentation ions, were observed for all sample components during CI operation.

Most in-house CI-MS analyses of organophosphorus compounds have been conducted with ammonia reagent gas, as this technique provides excellent molecular ion information at trace levels. Deuterated ammonia CI-MS was investigated as a complementary technique in this study because of the demonstrated usefulness of labelled reagent gases for structural studies (*e.g.*, determination of active hydrogen sites by isotope exchange) and for the elucidation of fragmentation pathways²⁴⁻²⁹. In addition, situations may arise where it may be possible to improve signal-to-noise ratios by monitoring $(\text{M} + {}^2\text{H})^+$ and/or $(\text{M} + \text{N}^2\text{H}_4)^+$ when $(\text{M} + \text{H})^+$ and/or $(\text{M} + \text{NH}_4)^+$ ions are interfered with by background chemical noise in complex environmental or biological samples.

Table I lists the identities of the monophosphorus and pyrophosphate compounds detected during capillary column GC-MS analysis of the munitions-grade tabun sample. Several different capillary columns were used to resolve the sample components, the best chromatographic separations being obtained with the more polar DB-1701 and DBWAX films. Fig. 1 illustrates a typical EI total ion current chromatogram for the tabun sample using the DBWAX film.

Monophosphorus compounds

The EI and $\text{NH}_3\text{-CI}$ mass spectra of tabun, diethyl dimethylphosphoramidate, ethyl isopropyl dimethylphosphoramidate, triethyl phosphate, ethyl tetramethylphosphorodiamidate and tetramethylphosphorodiamidic cyanide were the same as previously recorded¹⁹. $\text{N}^2\text{H}_3\text{-CI}$ mass spectra for these six compounds, listed in Table II, were dominated by $(\text{M} + {}^2\text{H})^+$ and/or $(\text{M} + \text{N}^2\text{H}_4)^+$ pseudo-molecular ions and exhibited pseudo-molecular relative ion intensities similar to those observed during $\text{NH}_3\text{-CI}$ operation.

Isotope-exchange during $\text{N}^2\text{H}_3\text{-CI}$ was observed for compounds with CI fragmentation ions containing active hydrogen sites. For example, the triethyl

TABLE I
 COMPOUNDS IDENTIFIED (OR TENTATIVELY IDENTIFIED) IN MUNITIONS GRADE
 TABUN

Me = Methyl, Et = ethyl; *i*Pr = isopropyl.

<i>Compound No.^a</i>	<i>Mol. wt.</i>	<i>Compound</i>	<i>Structure</i>
1	209	Diisopropyl dimethylphosphoramidate ^b	$\begin{array}{c} \text{O} \\ \parallel \\ \textit{i}\text{-PrO}-\text{P}-\text{NMe}_2 \\ \\ \text{O}\textit{i}\text{-Pr} \end{array}$
2	195	Ethyl isopropyl dimethylphosphoramidate ^c	$\begin{array}{c} \text{O} \\ \parallel \\ \textit{i}\text{-PrO}-\text{P}-\text{NMe}_2 \\ \\ \text{OEt} \end{array}$
3	224	Triisopropyl phosphate	$\begin{array}{c} \text{O} \\ \parallel \\ \textit{i}\text{-PrO}-\text{P}-\text{O}\textit{i}\text{-Pr} \\ \\ \text{O}\textit{i}\text{-Pr} \end{array}$
4	181	Diethyl dimethylphosphoramidate ^c	$\begin{array}{c} \text{O} \\ \parallel \\ \text{EtO}-\text{P}-\text{NMe}_2 \\ \\ \text{OEt} \end{array}$
5	210	Diisopropyl ethyl phosphate ^b	$\begin{array}{c} \text{O} \\ \parallel \\ \textit{i}\text{-PrO}-\text{P}-\text{OEt} \\ \\ \text{O}\textit{i}\text{-Pr} \end{array}$
6	196	Diethyl isopropyl phosphate ^b	$\begin{array}{c} \text{O} \\ \parallel \\ \textit{i}\text{-PrO}-\text{P}-\text{OEt} \\ \\ \text{OEt} \end{array}$
7	182	Triethyl phosphate ^c	$\begin{array}{c} \text{O} \\ \parallel \\ \text{EtO}-\text{P}-\text{OEt} \\ \\ \text{OEt} \end{array}$

TABLE I (continued)

Compound No. ^a	Mol. wt.	Compound	Structure
8	194	Isopropyl tetramethylphosphoramidate ^b	$ \begin{array}{c} \text{O} \\ \parallel \\ i\text{-PrO}-\text{P}-\text{NMe}_2 \\ \\ \text{NMe}_2 \end{array} $
9	180	Ethyl tetramethylphosphoramidate ^c	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{EtO}-\text{P}-\text{NMe}_2 \\ \\ \text{NMe}_2 \end{array} $
10	176	Isopropyl dimethylphosphoramidocyanidate ^b	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{CN}-\text{P}-\text{NMe}_2 \\ \\ \text{O}i\text{-Pr} \end{array} $
11	162	Ethyl dimethylphosphoramidocyanidate (tabun)	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{CN}-\text{P}-\text{NMe}_2 \\ \\ \text{OEt} \end{array} $
12	161	Tetramethylphosphorodiamidic cyanide ^c	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{CN}-\text{P}-\text{NMe}_2 \\ \\ \text{NMe}_2 \end{array} $
13	318	Diethyl phosphoric diisopropyl phosphoric anhydride ^b	$ \begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{O}i\text{-Pr} \\ \quad \quad \quad \\ \text{OEt} \quad \quad \text{O}i\text{-Pr} \end{array} $
14	317	Diisopropyl phosphoric ethyl dimethylphosphoramidic anhydride ^b	$ \begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{O}i\text{-Pr} \\ \quad \quad \quad \\ \text{NMe}_2 \quad \quad \text{O}i\text{-Pr} \end{array} $

(Continued on p. 276)

TABLE I (continued)

Compound No. ^a	Mol. wt.	Compound	Structure
15	304	Diethyl phosphoric ethyl isopropyl phosphoric anhydride ^b	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{OEt} \\ \quad \quad \\ \text{OEt} \quad \text{O}_i\text{-Pr} \end{array}$
16	303	Diethyl phosphoric isopropyl dimethylphosphoramidic anhydride ^b	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{NMe}_2 \\ \quad \quad \\ \text{OEt} \quad \text{O}_i\text{-Pr} \end{array}$
17, 19	288	Bis(ethyl dimethylphosphoramidic) anhydride	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{Me}_2\text{N}-\text{P}-\text{O}-\text{P}-\text{NMe}_2 \\ \quad \quad \\ \text{OEt} \quad \text{OEt} \end{array}$
18	290	Bis(diethyl phosphoric) anhydride	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{OEt} \\ \quad \quad \\ \text{OEt} \quad \text{OEt} \end{array}$
20	289	Diethyl phosphoric ethyl dimethylphosphoramidic anhydride ^b	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{EtO}-\text{P}-\text{O}-\text{P}-\text{NMe}_2 \\ \quad \quad \\ \text{OEt} \quad \text{OEt} \end{array}$
21	287	Ethyl dimethylphosphoramidic tetramethylphosphorodiamidic anhydride	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{Me}_2\text{N}-\text{P}-\text{O}-\text{P}-\text{NMe}_2 \\ \quad \quad \\ \text{OEt} \quad \text{NMe}_2 \end{array}$

^a See Fig. 1.^b Tentative identification based on interpretation of acquired EI and CI mass spectral data.^c Compounds previously reported as tabun impurities.

phosphate N²H₃-CI fragmentation ion at *m/z* 157 may be rationalized by the neutral loss of C₂H₄ from the (M + ²H)⁺ ion followed by hydrogen-deuterium exchange of the hydroxyl hydrogen. Under NH₃-CI conditions an ion due to loss of C₂H₄ from the (M + H)⁺ ion with a relative intensity similar to *m/z* 157 was observed at *m/z* 155.

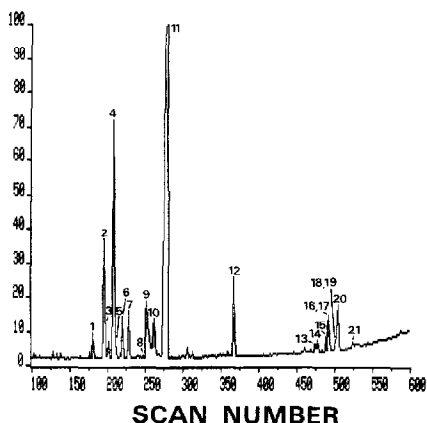


Fig. 1. Capillary column GC-MS total ion current (500–35 u) chromatogram of 1 μg of munitions-grade tabun obtained under EI conditions (15 m \times 0.32 mm I.D. DBWAX; one MS scan = 1.6 s). Numbered peaks are identified in Table I.

TABLE II

 $\text{N}^2\text{H}_3\text{-Cl}$ DATA FOR MONOPHOSPHORUS COMPOUNDS

Compound	m/z (relative intensity, %)							
	$(M + ^2H)^+$	$(M + \text{N}^2\text{H}_4)^+$	Other ions					
Diisopropyl dimethylphosphoramidate	211 (100)	231 (2)	213 (2)	212 (10)	210 (11)	170 (5)	169 (5)	128 (4)
Ethyl isopropyl dimethylphosphoramidate	197 (100)	217 (3)	198 (10)	196 (12)	195 (3)	156 (9)	155 (8)	126 (3)
Triisopropyl phosphate	226 (100)	246 (3)	227 (11)	225 (6)	205 (4)	185 (9)	164 (4)	143 (3)
Diethyl dimethylphosphoramidate	183 (100)	203 (3)	185 (2)	184 (8)	182 (13)	181 (2)	153 (2)	126 (4)
Diisopropyl ethyl phosphate	212 (100)	232 (7)	213 (12)	211 (6)	191 (3)	171 (11)	150 (7)	130 (7)
Diethyl isopropyl phosphate	198 (100)	218 (7)	200 (2)	199 (11)	197 (3)	177 (4)	157 (11)	156 (4)
Triethyl phosphate	184 (100)	204 (11)	186 (2)	185 (10)	183 (12)	157 (7)	130 (2)	74 (2)
Isopropyl tetramethylphosphorodiamidate	196 (100)	—	197 (11)	195 (8)	194 (6)	156 (5)	155 (6)	140 (9)
Ethyl tetramethylphosphorodiamidate	182 (100)	—	184 (2)	183 (9)	181 (11)	180 (5)	138 (3)	50 (2)
Isopropyl dimethylphosphoramidocyanidate	178 (16)	198 (100)	199 (9)	197 (29)	196 (4)	179 (1)	177 (2)	157 (2)
Ethyl dimethylphosphoramidocyanidate	164 (21)	184 (100)	185 (8)	183 (31)	182 (4)	165 (1)	163 (3)	156 (4)
Tetramethylphosphorodiamidic cyanide	163 (100)	183 (73)	184 (6)	182 (14)	164 (8)	162 (8)	155 (4)	135 (5)

Fragmentation ions for compounds containing isopropoxy substituents also exhibited isotopic exchange following the neutral loss of C_3H_6 . Exchanges of this nature within the ion source for these and other compounds are reasonable as a sample ion may suffer many collisions with neutral gas molecules prior to exiting the source. This CI

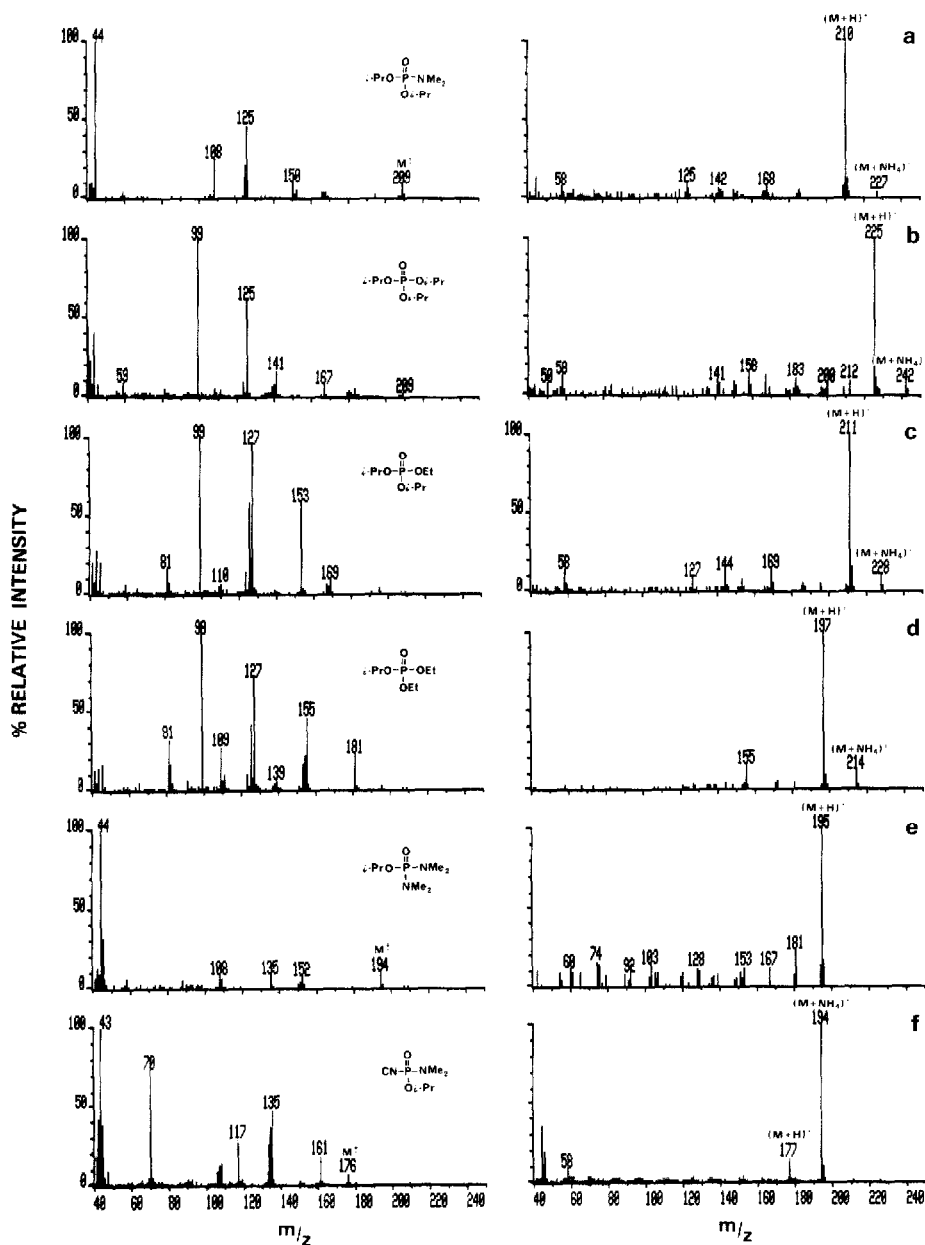


Fig. 2. EI and ammonia CI mass spectra of (a) diisopropyl dimethylphosphoramidate, (b) triisopropyl phosphate, (c) diisopropyl ethyl phosphate, (d) diethyl isopropyl phosphate, (e) isopropyl tetramethylphosphorodiamidate and (f) isopropyl dimethylphosphoramidocyanate.

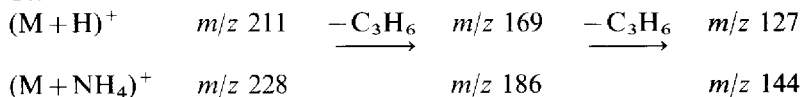
fragmentation ion information, together with the molecular ion data, was particularly useful for the identification of unknown isopropoxy-substituted monophosphorus compounds.

The EI mass spectra of diisopropyl dimethylphosphoramidate, triisopropyl phosphate, diisopropyl ethyl phosphate, diethyl isopropyl phosphate, isopropyl tetramethylphosphorodiamidate and the isopropyl analogue of tabun, isopropyl dimethylphosphoramidocyanidate, illustrated in Fig. 2, were rich in EI fragmentation ion information but contained little or no molecular ion data. Ions due to losses of CH_3 , OC_3H_5 , OC_3H_7 , C_3H_5 , C_3H_6 and/or C_3H_7 from the molecular ion were observed for these isopropoxy-containing compounds. Ethoxy or cyano substitution was often indicated by a subsequent loss of C_2H_4 and HCN , respectively. In addition, an intense $[\text{P}(\text{OH})_4]^+$ ion at m/z 99 indicated the presence of a phosphate structure and the presence of an ion at m/z 44 or 43 suggested dimethylamine substitution.

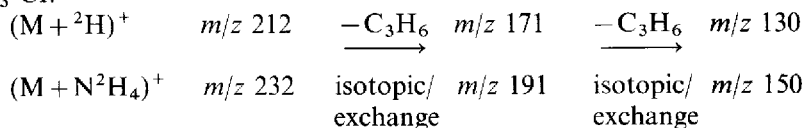
Triisopropyl phosphate was synthesized to support the identification of these isopropoxy compounds. EI fragmentation ions characteristic of only isopropoxy substitution at m/z 209, 183, 167, 141, 125 and 99, due to $(\text{M}-\text{CH}_3)^+$, $(\text{M}-\text{C}_3\text{H}_5)^+$, $(\text{M}-\text{OC}_3\text{H}_5)^+$, $(\text{M}-\text{C}_3\text{H}_5-\text{C}_3\text{H}_6)^+$, $(\text{M}-\text{OC}_3\text{H}_5-\text{C}_3\text{H}_6)^+$ and $[\text{P}(\text{OH})_4]^+$, respectively, were observed during GC-MS analysis.

$(\text{M}+\text{X})^+$ and/or $(\text{M}+\text{NX}_4)^+$ pseudo-molecular ions dominated the NH_3 -CI (Fig. 2) and N^2H_3 -CI (Table II) mass spectra of the isopropoxy compounds previously unreported in tabun. Neutral loss of C_3H_6 from the $(\text{M}+\text{X})^+$ and/or $(\text{M}+\text{NX}_4)^+$ pseudo-molecular ions was usually observed with isotopic exchange during N^2H_3 -CI analysis. For example, diisopropyl ethyl phosphate exhibited successive losses of C_3H_6 from both the $(\text{M}+\text{X})^+$ and $(\text{M}+\text{NX}_4)^+$ ions. The following scheme illustrates these losses and supports the presence of a structure with two isopropoxy substituents:

NH_3 -CI:



N^2H_3 -CI:



The acquired NH_3 -CI mass spectrum of triisopropyl phosphate was similar to published data¹⁷, with the major exception being less CI fragmentation and the observation of an $(\text{M}+\text{NH}_4)^+$ ion (and ions due to losses of C_3H_6 from this ion) during this study. Successive losses of C_3H_6 from the $(\text{M}+\text{H})^+$ and $(\text{M}+\text{NH}_4)^+$ pseudo-molecular ions at m/z 183 and 141 and at m/z 200 and 158, respectively, were observed. Differences in source design or ionization conditions could easily account for these subtle spectral differences.

Pyrophosphate compounds

A previous tabun analysis¹⁹ indicated the presence of two pyrophosphate

compounds. Compounds of this type, probably formed by "dimerization" of two monophosphorus compounds containing ethoxy and/or isopropoxy substituents, accounted for 3% of the volatile organic content. Eight compounds of this general structural type were identified during this capillary column GC-MS study.

Fig. 3 illustrates the EI mass spectra acquired for the pyrophosphates diethyl phosphoric diisopropyl phosphoric anhydride, diisopropyl phosphoric ethyl dimethylphosphoramidic anhydride, diethyl phosphoric ethyl isopropyl phosphoric anhydride, diethyl phosphoric isopropyl dimethylphosphoramidic anhydride, bis-(ethyl dimethylphosphoramidic) anhydride, bis(diethyl phosphoric) anhydride, diethyl phosphoric ethyl dimethylphosphoramidic anhydride and ethyl dimethyl-

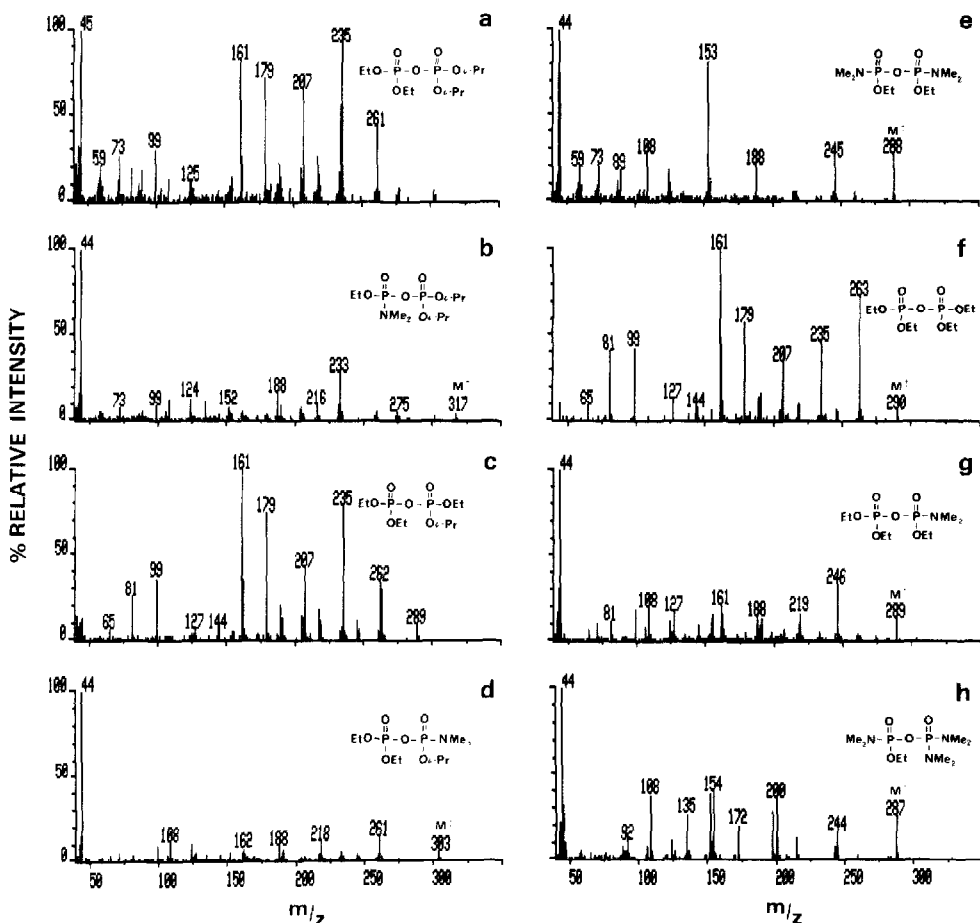


Fig. 3. EI mass spectra of (a) diethyl phosphoric diisopropyl phosphoric anhydride, (b) diisopropyl phosphoric ethyl dimethylphosphoramidic anhydride, (c) diethyl phosphoric ethyl isopropyl phosphoric anhydride, (d) diethyl phosphoric isopropyl dimethylphosphoramidic anhydride, (e) bis(ethyl dimethylphosphoramidic) anhydride, (f) bis(diethyl phosphoric) anhydride, (g) diethyl phosphoric ethyl dimethylphosphoramidic anhydride and (h) ethyl dimethylphosphoramidic tetramethylphosphoramidic anhydride.

phosphoramidic tetramethylphosphorodiamidic anhydride. Pyrophosphates containing only ethoxy and/or isopropoxy substitution exhibited characteristic EI fragmentation ions at m/z 99, 161, 179, 207 and 235 due to $[P(OH)_4]^+$, $[(HO)(O)P-O-P(O)(OH)_2]^+$, $[(HO)_3P-O-P(O)(OH)_2]^+$, $[(EtO)(OH)_2P-O-P(O)(OH)_2]^+$ and $[(EtO)_2(OH)P-O-P(O)(OH)_2]^+$ or $[(EtO)(OH)_2P-O-P(O)(OH)(OEt)]^+$, respectively. Those containing dimethylamine substitution in addition to ethoxy and/or isopropoxy groups all exhibited a base ion at m/z 44 and an ion at m/z 108 due to $[N(CH_3)_2]^+$ and $[N(CH_3)_2-P(O)(OH)]^+$, respectively. Higher mass EI fragmentation ions due to loss of OC_2H_3 , C_3H_6 , $(C_3H_6)_2$, $(OC_3H_7+C_3H_6)$, $[OC_2H_3 + (CH_3)_2]$, $[N(CH_3)_2 + (C_2H_4)_3]$ or $[(N(CH_3)_2)_2 + C_2H_3]$ were also frequently observed.

Bis(ethyl dimethylphosphoramidic) anhydride contains two asymmetric phosphorus atoms, which resulted in the detection of two chromatographic peaks with similar peak areas (compounds 17 and 19), one due to an enantiometric pair and the other to the mesodiastereoisomer. The mass spectra of both diastereoisomers, illustrated in Fig. 3e, were identical and exhibited characteristic EI fragmentation ions due to $(M-OC_2H_3)^+$, $[M-N(CH_3)_2-(C_2H_4)_2]^+$ and $[M-C_2H_4OP(O)N(CH_3)_2]^+$. Most of the other pyrophosphates (compounds 14, 15, 16, 20 and 21) probably possess only one asymmetric phosphorus atom and therefore elute as unresolved enantiomers on the non-chiral GC column. Compound 13 does not possess an asymmetric phosphorus atom and therefore exists as a single species.

The CI data were valuable for molecular ion determination as the mass spectra of all eight pyrophosphates were dominated by $(M+X)^+$ and/or $(M+NX_4)^+$ pseudo-molecular ions. Pseudo-molecular relative ion intensities, listed in Table III, were similar during NH_3 -CI and N^2H_3 -CI analysis. CI fragmentation was minimal above m/z 50 and usually due to neutral loss of C_3H_6 or C_2H_4 , with isotopic exchange being observed during N^2H_3 -CI operation.

TABLE III
 N^2H_3 -CI MOLECULAR ION DATA FOR PYROPHOSPHATE COMPOUNDS

Compound	m/z (relative intensity, %)			
	$(M+H)^+$	$(M+NH_4)^+$	$(M+^2H)^+$	$(M+N^2H_4)^+$
Diethyl phosphoric diisopropyl phosphoric anhydride	319 (100)	236 (21)	320 (100)	340 (30)
Diisopropyl phosphoric ethyl dimethylphosphoramidic anhydride	318 (100)	335 (8)	319 (100)	339 (6)
Diethyl phosphoric ethyl isopropyl phosphoric anhydride	305 (100)	322 (23)	306 (100)	326 (22)
Diethyl phosphoric isopropyl dimethylphosphoramidic anhydride	304 (100)	321 (9)	305 (100)	325 (9)
Bis(ethyl dimethylphosphoramidic) anhydride	289 (100)	306 (7)	290 (100)	310 (5)
Bis(diethyl phosphoric) anhydride	291 (100)	308 (23)	292 (100)	312 (23)
Diethyl phosphoric ethyl dimethylphosphoramidic anhydride	290 (100)	307 (10)	291 (100)	311 (10)
Ethyl dimethylphosphoramidic tetramethylphosphorodiamidic anhydride	288 (100)	—	289 (100)	—

CONCLUSION

Tabun and a number of related organophosphorus impurities were identified during a GC-MS study of munitions-grade tabun. EI fragmentation ions provided valuable structural information for the sample components, but the presence of little or no molecular ion information for many components necessitated the use of CI techniques. Complementary molecular ion information in the form of $(M+X)^+$ and/or $(M+NX_4)^+$ pseudo-molecular ions were obtained for all sample components during CI operation. Interpretation of both the EI and CI mass spectral data acquired during this study led to the identification or tentative identification of nineteen tabun impurities, including twelve organophosphorus and pyrophosphate compounds previously unreported in tabun.

The mass spectral data provided are sufficient for the identification of the tabun and related impurities. Observation of these sample components may provide analysts with information on sample origin or synthetic procedures when dealing with samples contaminated with this chemical warfare agent.

ACKNOWLEDGEMENTS

The authors thank Dr. C. A. Boulet and Mr. A. S. Hansen for preparing the tabun, triisopropyl phosphate and bis(diethylphosphoric) anhydride standards.

REFERENCES

- 1 *Chem. Eng. News*, 62, No. 14 (1984) 4.
- 2 S. Budiansky, *Nature (London)*, 308 (1984) 483.
- 3 *Report of the Specialists Appointed by the Secretary-General to Investigate Allegations by the Islamic Republic of Iran Concerning the Use of Chemical Weapons*, Report S/16433, United Nations, New York, March 26, 1984.
- 4 G. Andersson, *NBC Defence Technol. Int.*, April (1986) 62-65.
- 5 R. G. Gillis and J. L. Occoclowitz, in M. Halman (Editor), *The Mass Spectrometry of Phosphorus Compounds*, Interscience, New York, 1972, pp. 295-331.
- 6 M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, 88 (1966) 2621-2630.
- 7 J. R. Chapman, *Organophosphorus Chem.*, 14 (1983) 278-304.
- 8 *Identification of Potential Organophosphorus Warfare Agents*, Ministry of Foreign Affairs of Finland, Helsinki, 1979.
- 9 S. Sass and T. L. Fisher, *Org. Mass Spectrom.*, 14 (1979) 257-264.
- 10 R. L. Holmstead and J. E. Casida, *J. Assoc. Off. Anal. Chem.*, 57 (1974) 1050-1055.
- 11 H. J. Stan, *Fresenius Z. Anal. Chem.*, 287 (1977) 104-111.
- 12 H. J. Stan, *Z. Lebensm. Unters.-Forsch.*, 164 (1977) 153-159.
- 13 K. L. Busch, M. M. Bursey, J. R. Hass and G. W. Sovocool, *Appl. Spectrosc.*, 32 (1978) 388-399.
- 14 T. Cairns, E. G. Siegmund and R. L. Bong, *Anal. Chem.*, 56 (1984) 2547-2552.
- 15 T. Cairns and E. G. Siegmund, *J. Assoc. Off. Anal. Chem.*, 70 (1987) 858-862.
- 16 J. B. Westmore and M. M. Alauddin, *Mass Spectrom. Rev.*, 5 (1986) 381-465.
- 17 P. A. Cload and D. W. Hutchinson, *Org. Mass Spectrom.*, 18 (1983) 57-59.
- 18 T. Cairns, E. G. Siegmund, G. M. Doose and A. C. Oken, *Anal. Chem.*, 57 (1985) 572A-576A.
- 19 P. A. D'Agostino, A. S. Hansen, P. A. Lockwood and L. R. Provost, *J. Chromatogr.*, 347 (1985) 257-266.
- 20 P. A. D'Agostino and L. R. Provost, *Biomed. Environ. Mass Spectrom.*, 13 (1986) 231-236.
- 21 A. Hesso and R. Kostianen, *Proceedings of the 2nd International Symposium on Protection Against Chemical Warfare, Stockholm, Sweden, 15-19 June 1986*, National Defence Research Institute, Umea, 1986, pp. 257-260.

- 22 P. A. D'Agostino, L. R. Provost and J. Visentini, *J. Chromatogr.*, 402 (1987) 221-232.
- 23 P. A. D'Agostino and L. R. Provost, *J. Chromatogr.*, 331 (1985) 47-54.
- 24 D. F. Hunt, C. N. McEwen and R. A. Upham, *Tetrahedron Lett.*, (1971) 4539-4542.
- 25 D. F. Hunt, C. N. McEwen and R. A. Upham, *Anal. Chem.*, 44 (1972) 1292-1294.
- 26 C. W. Tsang and A. G. Harrison, *J. Am. Chem. Soc.*, 98 (1976) 1301-1308.
- 27 D. F. Hunt and S. K. Sethi, *J. Am. Chem. Soc.*, 102 (1980) 6953-6963.
- 28 M. V. Buchanan, *Anal. Chem.*, 54 (1982) 570-574.
- 29 R. Kostianen and A. Hesso, *Biomed. Environ. Mass Spectrom.*, 15 (1988) 79-87.