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Mass spectral data of alkyl and cycloalkyl methylphosphonofluoridates

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Titel	Mass spectral data of alkyl and cycloalkyl methylphosphonofluoridates
Auteurs	E.R.J. Wils en A.L. de Jong
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Binnen de A-opdracht "Monstername en identificatie van chemische strijdmiddelen" (A93 KL 424) is het opnemen van spectra voor referentiedoeleinden sinds het begin van de opdracht een belangrijk aandachtspunt geweest. Deze spectra worden opgenomen in het NATO SICA AEP-10 handboek in de vorm van een atlas en digitaal in de NATO SICA database. De belangrijkste reden voor het aanleggen van deze verzameling van spectra is dat daarmee een chemisch strijdmiddel of een verwante verbinding (ontledingsprodukt, uitgangsstof en dergelijke) snel geïdentificeerd kan worden. De ervaring leert dat de identificatie van een onbekende verbinding, zelfs als deze verwantschap vertoont met bekende verbindingen, relatief veel tijd kost.

De opbouw van een verzameling referentiespectra is eveneens voor de A-opdracht "Wapenbeheersing" (A93 D 402) van belang. De laatste jaren vindt steeds meer de gedachte terrein dat adequate verificatie van een verbod op chemische wapens alleen kan plaatsvinden door spectrometrische analyse, bij voorkeur met de combinatie gaschromatografie-massaspectrometrie (GC-MS), van ter plekke genomen monsters. De lijst-1 verbindingen welke genoemd worden in het Chemisch Wapen Verdrag zijn veelal homologe reeksen, zoals de alkyl en cycloalkyl methylfosfonfluoridaten (alkyl/cycloalkyl ≤ C10). Sommige van deze verbindingen zijn beter bekend onder hun triviale naam zoals sarin (GB), soman (GD) en cyclohexylsarin (GF). Zoals uit de laatste naamgeving blijkt, wordt de naam sarin tevens als stamnaam gebruikt voor andere homologen.

In monsters geanalyseerd tijdens de inspecties door de Verenigde Naties (UNSCOM) in 1991 in Irak, werden naast de bekende chemische strijdmiddelen sarin en cyclohexylsarin andere sarinen gevonden. Mede op grond van deze vondst werd besloten van de sarin familie electronen ionisatie (EI) massaspectra te verzamelen van zoveel mogelijk verbindingen en deze op te nemen in de databases van het TNO Prins Maurits Laboratorium (TNO-PML). Aangezien synthese van de sarin homologen tijd- en geldrovend is, werden de stoffen in situ gemaakt door het mengen van een alcohol met de uitgangsstof methylfosfondifluoride gevolgd door GC-MS analyse van het reactiemengsel. De gekozen alcoholen werden beperkt tot primaire en secondaire alcoholen, die bovendien relatief goedkoop waren. Op deze manier werden ongeveer 60 massaspectra opgenomen. Door bestudering van de fragmentatiepatronen uit de verkregen massaspectra werden enkele algemene regels afgeleid. Deze kunnen mogelijk dienen voor de identificatie van die sarin homologen, waarvan geen massaspectra werden opgenomen.

De uitgevoerde studie heeft een grote hoeveelheid informatie opgeleverd, welke het mogelijk maakt alkyl/cycloalkyl sarinen snel te kunnen identificeren indien deze zouden voorkomen in te analyseren monsters.

De verkregen massaspectra werden opgenomen in de NATO SICA database en tevens ter beschikking gesteld aan de OPCW ("Organisation for the Prohibition of Chemical Weapons") als onderdeel van het Nederlandse bod, waarin toegang tot de databases met chromatografische en spectrometrische gegevens van het TNO-PML werd toegezegd.

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A-1

CONTENTS

1 INTRODUCTION

The Schedule-1 list of the Chemical Weapon Convention (CWC) contains homologue series of alkyl and cycloalkyl methylphosphonofluoridates (alkyl/cycloalkyl ≤ C10) [1]. Some of these compounds are well-known chemical warfare (CW) agents such as sarin (alkyl : isopropyl) and soman (alkyl : 1,2,2-trimethylpropyl). The trivial name sarin is sometimes used as the reference compound name, i.e. cyclohexyl sarin instead of cyclohexyl methylphosphonofluoridate. All compounds are commonly named G-agents.

The second Round Robin international verification exercise carried out in 1990 [2], and also the analysis of Iraqi samples during the United Nations (UNSCOM) inspections in 1991, made it clear that there are other G-agents than the ones incorporated in the NATO/SICA AEP-10 Handbook [3]. In the second Round Robin exercise, octyl methylphosphonofluoridate (octyl sarin) isomers were used as examples of unknown G-agents. In the samples taken at Muthanna (Iraq), compounds such as secondary and n-butyl sarin were found.

In order to perform a rapid identification of these compounds, data have to be gathered of as many homologues as possible. Ideally, this may be done by preparing a large number of sarin homologues, followed by the recording of the spectral data. As this would be a long and costly programme, an alternative was developed. By mixing an alcohol with the precursor methylphosphonodifluoride in methylene chloride, some conversion to a corresponding sarin will take place. Mass spectra of the sarin homologues can easily be obtained after analysing this mixture by gas chromatography-mass spectrometry (GC-MS).

In a search of the availability of aliphatic and cyclic alcohols, over 300 were identified, which could be purchased as fine chemicals [4]. The alcohols chosen for this study were restricted to primary and secondary alcohols as well as to relatively inexpensive ones. Tertiary alcohols react rather slowly. Furthermore, it is unlikely that a G-agent will be produced for a chemical weapon system starting from expensive alcohol.

In this report, the electron impact (EI) mass spectra of the G-agents prepared with the selected alcohols are presented and discussed.

2 EXPERIMENTAL PART

Approximately 100 mg of methylphosphonodifluoride was dissolved in 2 ml of methylene chloride. From this solution, 0.2 ml was transferred to a septum capped vial (4 ml) and 1 µl of an alcohol was added to it (see Annex A, purchased from Aldrich or ICN). The solution was allowed to stand for at least 30 minutes at room temperature. Before the GC-MS analysis, the solution was diluted 10 times with methylene chloride.

0.5 µl of the reaction mixture was injected onto a fused silica capillary column (50 m x 0.3 mm ID, df 0.25 µm) coated with CPSil5CB or CPSil8CB (Chrompack), by means of a Carlo-Erba on-column injector installed on an HP 5890A gas chromatograph. The column was directly connected to the ion source of a VG70-250S (Fisons Instruments) double focusing magnetic sector mass spectrometer. The temperature of the interface was 250 °C. The helium flow rate was around 1.5 ml/min. Generally, the following temperature programme was used: 40 °C (1 min), 8 °C/min to 280 °C (5 min).
The following source conditions (typical for EI ionisation) were chosen:

- ionisation energy 70 eV;
- emission current 200 µA;
- temperature : 200 °C;
- vacuum : 5×10^{-6} mbar.

Mass spectra were recorded under low resolution conditions (resolving power around 1000, 10% valley) using continuous scanning over the mass range m/z 25-500 every second.

Both the mass scale and the relatively intensity (RI) scale were regularly checked as part of the mass spectrometer quality control programme. Mass scale calibration was performed with perfluorokerosene (PFK), and decafluorotriphenylphosphine (DFTPP) was used for checking the RI-scale according to the criteria proposed by Donnelly et al [5].

Generally, mass spectra were selected at the right side of the slightly tailing GC-peaks, giving a rather constant ion current during the scan. The mass spectral background ions arising from air and column bleed were removed by background subtraction. Spectra were stored in the TNO Prins Maurits Laboratory (PML) mass spectral library (PMLLIB), which resides on the VG11-250J data system of the mass spectrometer. They were also transferred to a PC according to the procedure previous described [6].

3 RESULTS AND DISCUSSION

3.1 Recording of mass spectra

As an example, the result of a GC-MS analysis of the reaction mixture obtained after mixing n-butanol with methylphosphonodifluoride is presented in Figure 1. The very volatile precursor methylphosphonodifluoride co-elutes with the solvent methylene chloride. The conversion was rather small as can be deduced from the ratio between the alcohol peak and that of the corresponding sarin. Despite this low conversion, good quality mass spectra of the sarin homologues could generally be obtained (see for example Figure 2). Attempts to produce sarin homologues from tertiary alcohols as well in this way were unsuccessful due to the very low conversion.
Multiple GC-peaks may be observed due to the presence of stereoisomers. A good example of such a splitting was obtained for 1,2-dimethylbutyl sarin, which contains three chiral centres. No differences were noticed in the EI mass spectra of the stereoisomers of the compounds analysed.
All alcohols used during this study are compiled in Annex A, whereas the recorded EI mass spectra of the sarin homologues are presented in Annex B (Tables 1 - 7). The abbreviations of the alkyl chains are added to the tables. Mass spectra of the known CW agents sarin (1MEt), soman (122TMPr) and cyclohexyl sarin (C6) have been included for comparison as well.

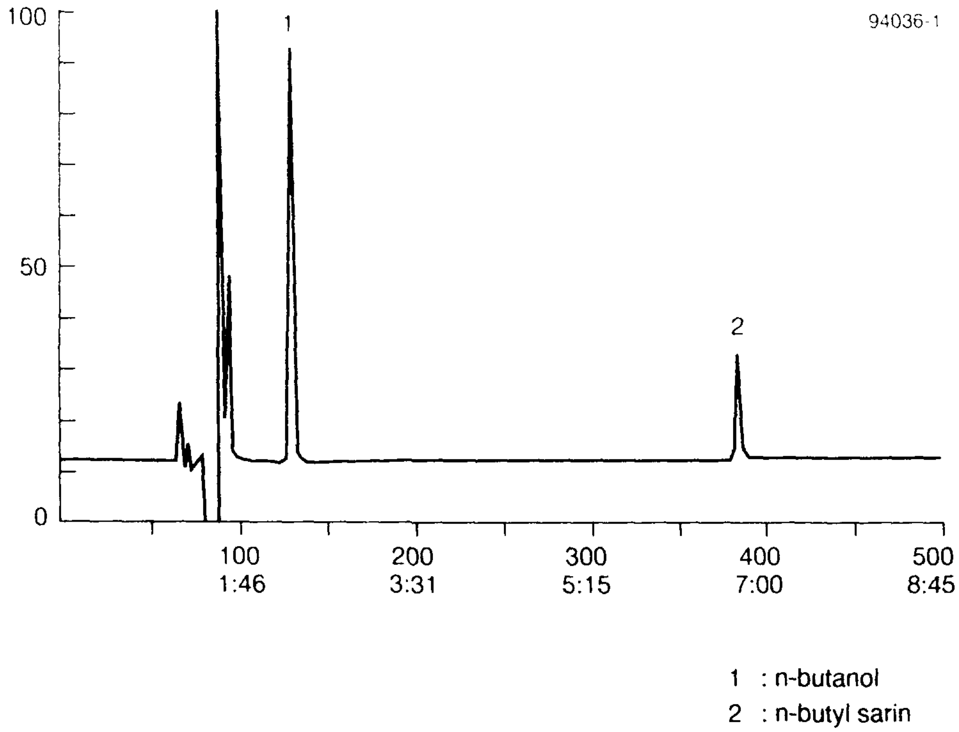


Figure 1 *Resulting gas chromatogram obtained after analysing the reaction mixture between methylphosphonodifluoride and n-butanol in methylene chloride*

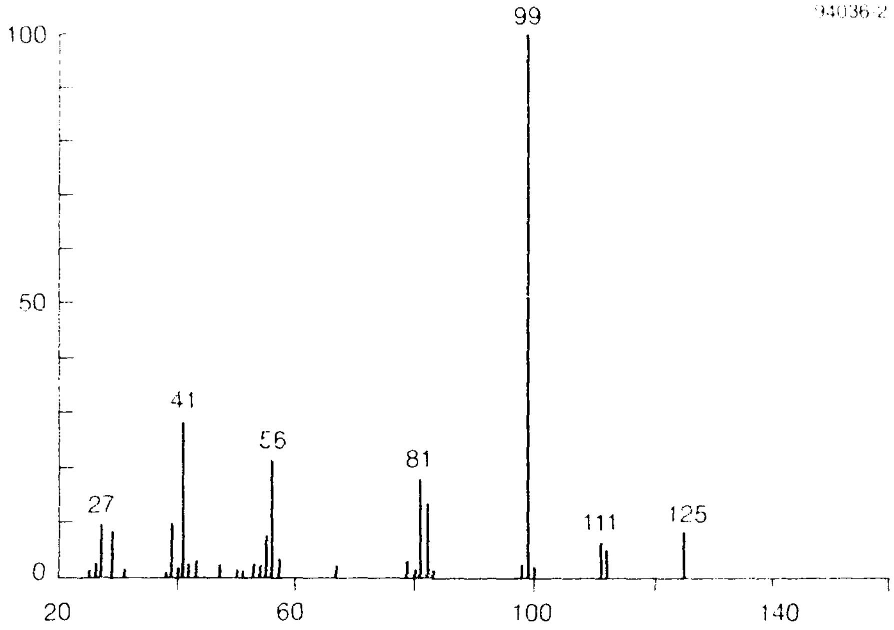


Figure 2 *Resulting mass spectrum of n-butyl sarin (MW 154)*

3.2 Mass spectral fragmentation

Because methyl sarin (MW 112) cannot lose an alkene/alkenyl group, it is to be expected that its mass spectrum (see Annex B, Table 1) is different from the other alkyl sarins. A loss of formaldehyde from the molecular ion leads to the base peak at m/z 82 with the elemental composition CH_4OPF. Methyl sarin is the only compound which produces a molecular ion. All other compounds analysed, even ethyl sarin, did not produce a molecular ion. Consequently, full characterization of the sarin homologues by chemical ionization has to be carried out as well, in case they are found in real samples. This can either be carried out under positive ion conditions leading to protonated molecular ions ($[M + H]^+$) or under negative ion conditions resulting in a loss of a proton ($[M - H]^-$).

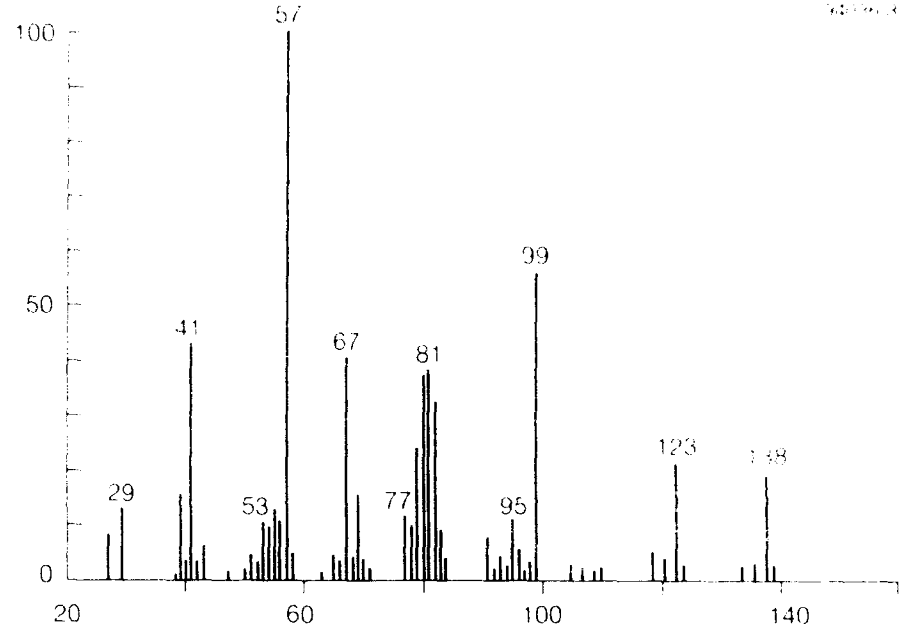
Fragmentation of the sarin homologues is rather straightforward and has been described previously for sarin and soman [7, 8]. All compounds analysed in this study give rise to the phosphorus-containing ion at m/z 99 (CH_5O_2PF), which is either the base peak or relatively abundant. This ion results from the loss of an alkenyl/cycloalkenyl group from the molecular ion and is very characteristic of mass spectra of sarin homologues. In addition to that particular ion, the mass spectra consist of fragments due to the alkyl/cycloalkyl moiety as well as of other phosphorus-containing fragments. Unfortunately, as the number of C-atoms in the alkyl cycloalkyl moiety exceeds six, several of these fragments have the same nominal mass (Table 1). The difference between the exact masses of both fragments is greater than 70 mmu and may quite easily be measured using a higher resolving power (≥ 5000, 10% valley) of the mass spectrometer. Even under the low resolution conditions used, splitting of the mass fragments is normally observed. However, as a common practice in mass spectrometry, the fragments with the same nominal masses have been summed in the low resolution mass spectra (see Annex B).

Table 1 *Alkyl cycloalkyl and phosphorus-containing fragments with the same nominal mass*

Nominal mass	Exact mass	Elemental composition
m/z 81	80.9906	CH_3OPF
m/z 81	81.0704	C_6H_9
m/z 82	81.9984	CH_4OPF
m/z 82	82.0782	C_6H_{10}
m/z 98	97.9932	CH_4O_2PF
m/z 98	98.1096	C_7H_{14}
m/z 99	99.0011	CH_5O_2PF
m/z 99	99.1174	C_7H_{15}
m/z 111	111.0011	$C_2H_5O_2PF$
m/z 111	111.1174	C_8H_{15}
m/z 112	112.0089	$C_2H_6O_2PF$
m/z 112	112.1252	C_8H_{16}
m/z 125	125.0168	$C_3H_7O_2P$
m/z 125	125.1330	C_9H_{17}
m/z 126	126.0246	$C_3H_8O_2PF$
m/z 126	126.1409	C_9H_{18}
m/z 139	139.0324	$C_4H_9O_2PF$
m/z 139	139.1487	$C_{10}H_{19}$
m/z 140	140.0402	$C_4H_{10}O_2PF$
m/z 140	140.1565	$C_{10}H_{20}$

The mass spectra of the lower members of the sarin homologues are the most informative for considering the fragmentation processes. When the alkyl and cycloalkyl chains become longer, the mass spectra tend to correspond more and more to those of the corresponding alkenes/cycloalkenes. This is illustrated in Figure 3, where the mass spectra of 4-t-butylcyclohexyl sarin and

4-t-butylcyclohexene are presented. Apart from m/z 99 (CH$_3$O$_3$PH$_5$), both spectra are very similar.



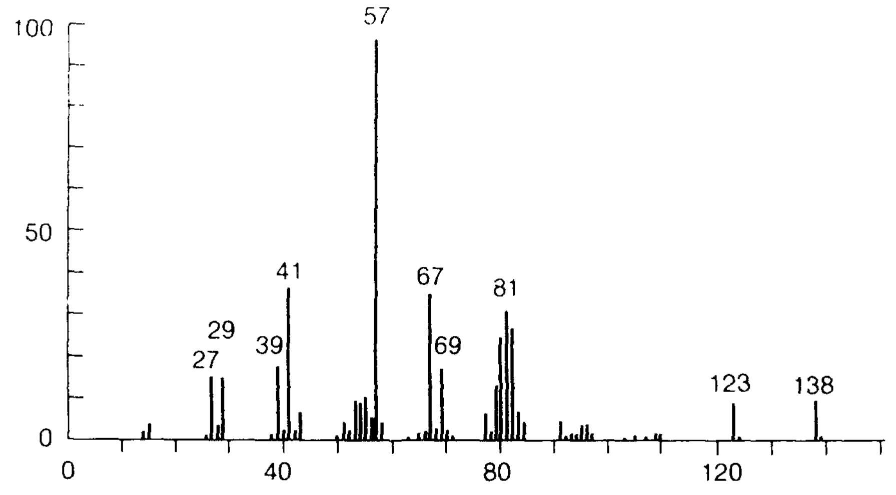


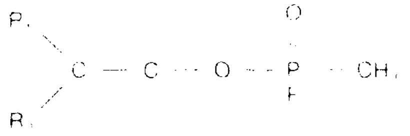
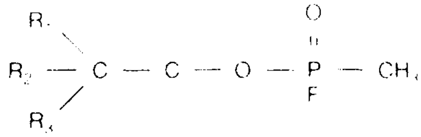
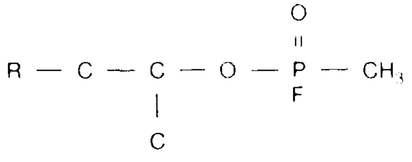
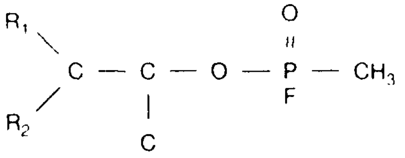
Figure 3 *Mass spectra of 4-t-butylcyclohexyl sarin (top) and 4-t-butylcyclohexene (bottom, taken from the NIST/EPA/MSDC database [9])*

in the spectra of the n-alkyl sarin homologues, phosphorus containing fragments at m/z 111, 112, 125 and 139 were found. When the alkyl chain becomes longer (C > 5), these fragments become less abundant (RI ≤ 2%). The only differences between the spectra of the longer n-alkyl sarin homologues (C > 5) are the shifts in the fragments originating from the alkyl chain.

Branching of the alkyl chain may lead to significantly high mass fragments either due to the loss of alkyl (M-CH_3, M-C_2H_5 etc.) or alkene groups. The loss of an alkene in particular produces information on the branching of the alkyl chain. From the recorded spectra, a number of characteristic fragments could be derived, which are presented in Table 2. When the point of branching of the alkyl chain is further away from the phosphorus atom, the spectra resemble more the spectra of the unbranched sarin homologues. For instance, the main difference between the mass spectra of n-hexyl sarin (MW 182) and 4-methylpentyl sarin (MW 182) is the loss of the isopropyl group (M-C_3H_7) terminating the alkyl chain in the latter compound (see Annex B, Table 2). This loss is observed in similar sarin homologues with a terminating branched alkyl chain.

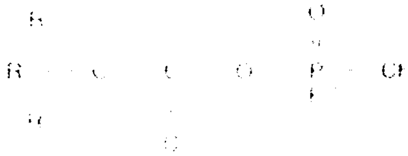
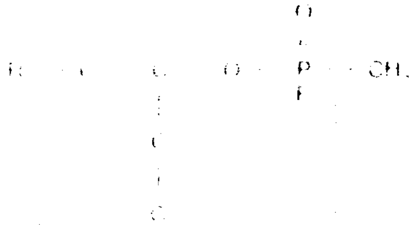
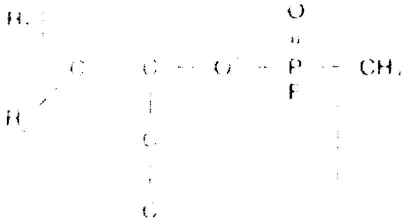
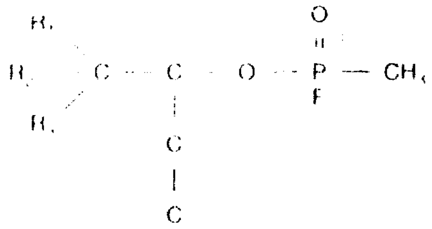
In contrast with the mass spectra of the alkyl sarin homologues, the spectra recorded of the cycloalkyl ones show less details. Changes in the relative intensities were generally the only differences between the various isomers, as can be seen in Annex B, Table 6 for the three methylcyclohexyl sarin isomers.

Table 2 Some characteristic phosphorus containing fragments of branched alkyl sarin homologues

Structure	Fragments	Alkyl chain	Annex B, Table
	m/z 112 strong, loss of R_1, R_2 small or absent	2-methylpropyl 2-methylbutyl 2-methylpentyl 2-ethylbutyl 2,3-dimethylpentyl	1, 2MPr 1, 2MBu 2, 2MPe 2, 2EBu 3, 23DMPe
	m/z 112 base peak, loss of R_1, R_2, R_3 small or absent	2,2-dimethylpropyl 2,2-dimethylhexyl	2, 22DMPr 4, 22DMHx
	m/z 125 strong, no intensive even P-fragments	1-methylpropyl 1-methylbutyl 1-methylpentyl 1,3-dimethylbutyl 1-methylhexyl 1,4-dimethylpentyl	1, 1MPr 1, 1MBu 2, 1MPe 3, 13DMBu 3, 1MHx 3, 14DMPe
	m/z 126 strong, m/z 125 strong	1,2-dimethylpropyl 1,2-dimethylbutyl	2, 12DMPr 2, 12DMBu

R, R_1, R_2, R_3 alkyl groups

Table 2 (continued)

Structure	Fragments	Alkyl chain	Annex B, Table
	m/z 126 strong, m/z 125 small or absent	1,2,2-trimethylpropyl	3, 122TMPr
	m/z 139 strong, no intensive even P-fragments, loss of C_2H_5	1-ethylpropyl 1-ethylbutyl 1-ethylpentyl	2, 1EPr 2, 1EBu 3, 1EPe
	m/z 139 strong, m/z 140 present, loss of C_2H_5	1-ethyl-2-methylpropyl	3, 1E2MPr
	m/z 140 strong, m/z 139 small or absent	1-ethyl-2,2-dimethylpropyl	4, 1E22DMPr

R, R_1, R_2, R_3 = alkyl groups

As an example of the fragmentation of a highly branched alkyl sarin, the mass spectrum of 2,2-dimethylpropyl sarin (MW 168), prepared from methylphosphonic difluoride and 2,2-dimethylpropanol (neopentyl alcohol), is presented in Figure 4. Due to the three methyl groups substituted at the C-2 position, isobutene is lost from the molecular ion resulting in m/z 112 as the base peak. The relative intensity of the characteristic phosphorus-containing ion at m/z 99 (CH_5O_2PF) is less than 40%. Searching for this spectrum against the NATO/SICA database did not lead to a match with a G-agent. This is a good example of the starting point of this study, demonstrating that data on the various sarin homologues are needed in order to perform a rapid identification.

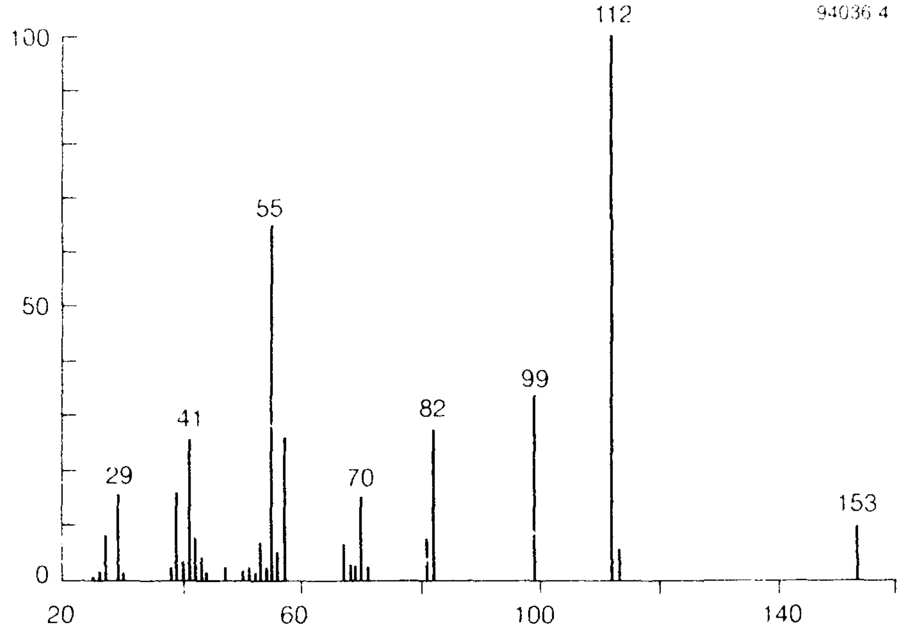


Figure 4 *Mass spectrum of 2,2-dimethylpropyl sarin (MW 168)*

3.3 Data transfer

All recorded mass spectra were taken up in the TNO-PML mass spectral library as well as in the NATO/SICA database. In order to transfer the data of the sarin homologues to other NATO nations, the recorded mass spectra were converted to a PC in the ASCII format used by the NIST/EPA/MSDC database [9]. An example of such a format is presented in Table 3. Each mass spectrum is accompanied by the following general compound information: systematic and trivial name(s), CAS registry number (if available), Wiswesser line notation, elemental composition and molecular weight. Furthermore, the source of the mass spectrum as well as the most important recording conditions were noted. The spectra and this general information may be added to the NIST/EPA/MSDC database under "user spectra", allowing a fast search of the data.

The mass spectra of the sarin homologues were also transferred to the Organisation for the Prohibition of Chemical Weapons (OPCW) as part of the Netherlands bid to give access to the TNO-PML chromatographic and spectrometric databases. The data may be used for the creation of the OPCW analytical database [10].

Table 3 Mass spectra of soman added as "user spectrum" to the NIST EPA MSDC database

NAME	1,2,2-trimethylpropyl methylphosphonofluoridate GD (NATO) soman pinacolyl methylphosphonofluoridate| CAS 96-64-0 OPF1&OY1&X1&1&1
COMMENT	TNO-Prins Maurits Laboratory (NL) VG70-250S magnetic sector source: 70 eV, 200 µA, 200 °C CPSil5CB cap. column / range: 25-500 amu
FORMULA	$C_7H_{16}F_1O_2P_1$
MW	182
ID	3
Num Peaks:	34

27	48;	29	77;	39	83;	40	16;	41	349;
42	27;	43	76;	45	19;	47	18;	51	7;
53	35;	54	8;	55	62;	56	22;	57	162;
58	8;	65	7;	67	26;	68	9;	69	481;
70	28;	78	11;	79	10;	81	70;	82	381;
83	99;	84	119;	85	74;	98	46;	99	782;
100	7;	125	33;	126	999;	127	38.		

4 AUTHENTICATION

E.R.J. Wils
(author project manager)

A.L. de Jong
(author)

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9 The National Institute for Standards and Technology (NIST), Environmental Protection Agency (EPA) and Mass Spectrometry Data Centre (MSDC) database is supplied in Europe by The Royal Society of Chemistry, University of Nottingham, UK.

10 Preparatory Commission for the Organisation for the Prohibition of Chemical Weapons, Expert Group on Equipment, Second Interim Report, PC-V/B/WP.7, 26 October 1993.

ANNEX A ALCOHOLS USED

Aliphatic alcohols

CH_3OH	Methanol
C_2H_5OH	Ethanol
C_3H_7OH	Propanol-1
C_4H_9OH	Butanol-1
	Butanol-2 (sec butanol)
	2-Methylpropanol-1 (isobutanol)
$C_5H_{11}OH$	Pentanol-1
	Pentanol-2
	Pentanol-3
	2-Methylbutanol-1
	3-Methylbutanol-1
	3-Methylbutanol-2
	2,2-Dimethylpropanol-1 (neopentyl alcohol)
$C_6H_{13}OH$	Hexanol-1
	Hexanol-2
	Hexanol-3
	2-Methylpentanol-1
	3-Methylpentanol-1
	4-Methylpentanol-1
	3-Methylpentanol-2
	4-Methylpentanol-2
	2-Methylpentanol-3
	2-Ethylbutanol-1
	3,3-Dimethylbutanol-1
$C_7H_{15}OH$	Heptanol-1
	Heptanol-2
	Heptanol-3
	5-Methylhexanol-2
	2-Methylhexanol-3
	2,3-Dimethylpentanol-1
	2,2-Dimethylpentanol-3
	2,4-Dimethylpentanol-3
$C_8H_{17}OH$	Octanol-1
	Octanol-2
	Octanol-3
	6-Methylheptanol-2
	2,2-Dimethylhexanol-1
	2-Ethylhexanol-1
	2,4,4-Trimethylpentanol-1
$C_9H_{19}OH$	Nonanol-1
	Nonanol-2
	2,6-Dimethylheptanol-4
	3,5,5-Trimethylhexanol-1
$C_{10}H_{21}OH$	Decanol-1
	Decanol-2
	Decanol-4
	3,7-Dimethyloctanol-1

Cyclic alcohols

C_5H_9OH	Cyclopentanol
$C_7H_{13}OH$	Cycloheptanol
	Cyclohexylmethanol
	2-Methylcyclohexanol
	3-Methylcyclohexanol
	4-Methylcyclohexanol
$C_8H_{15}OH$	Cyclooctanol
	2-(Cyclohexyl)ethanol-1
	2-Ethylcyclohexanol
	4-Ethylcyclohexanol
	2,2-Dimethylcyclohexanol
	2,6-Dimethylcyclohexanol
	3,5-Dimethylcyclohexanol
$C_9H_{17}OH$	3-(Cyclohexyl)propanol-1
$C_{10}H_{19}OH$	2-Isopropyl-5-methylcyclohexanol (menthyl alcohol)
	4-t-Butylcyclohexanol

ANNEX B MASS SPECTRAL DATA

Table 1 Mass spectral data (m/z, relative intensity) of alkyl-methylphosphonofluoridates

Alkyl	Me	Et	Pr	1MEt	Bu	1MPr	2MPr	Pe	1MBu	2MBu	3MBu
MW	112	126	140	140	154	154	154	168	168	168	168
m/z											
26	0.8	3.2	1.5	1.1	2.2	2.8	1.6	0.6	1.9	1.2	1
27	-	7.5	7.3	7.3	9.8	12	8.7	5	12.4	13.2	6.3
29	5.6	12.6	4.7	2.3	8.8	12.6	9.7	5.7	13.1	22.2	5.1
30	1.2	0.8	0.6	-	0.8	-	1.2	-	-	-	0.7
31	4.8	1.9	5.2	1.1	1.5	0.7	1.4	-	0.6	1	-
37	-	-	0.8	2	-	0.8	0.9	-	0.7	-	-
38	0.7	-	1.5	2.3	1	-	2	0.8	1.4	1	-
39	-	-	8.2	12.2	10.2	12.9	17	6.6	15	17.1	8.9
40	-	-	2.4	6.4	1.9	2	3.5	1.5	3.2	3.4	2.1
41	-	-	13.5	12.9	28.9	38.1	38.2	12.7	19.2	35.7	13.9
42	-	0.8	12	12.2	2.3	1.6	3.4	15.7	20.9	20.6	9.8
43	0.6	2.5	5	15.9	3.1	2.9	7.8	3.3	12.7	8.1	7.7
45	1.5	4.9	-	-	-	0.8	-	-	-	-	-
47	11	7.2	3.7	2.9	2.6	2.7	3	1.5	2	4.8	2.1
48	0.9	-	-	-	-	-	-	-	-	-	-
50	1.9	1.1	-	-	1.4	2.2	1.7	-	0.8	0.8	0.7
51	0.5	-	-	-	1.3	0.9	1.9	0.6	-	1.1	0.9
52	-	0.6	-	-	0.6	0.9	-	-	0.7	0.6	0.6
53	-	-	-	-	2.4	2.8	2.3	2.6	4.4	4	3.8
54	-	-	-	-	2.4	1.6	1.4	0.8	1.4	1.9	1.7
55	-	-	-	-	7.2	8.8	8.6	19.3	40.5	47.4	38.1
56	-	-	-	-	21.7	22.9	25.4	1	1.7	3.6	2
57	-	-	-	-	2.9	5.9	3.6	0.6	-	10	1
58	-	-	-	1.5	-	-	-	-	-	-	-
59	-	-	2.4	0.8	-	-	-	-	-	-	-
63	1.4	0.6	-	0.5	-	-	-	-	0.6	-	-
65	-	0.7	-	-	-	-	-	-	-	0.6	-
66	1	0.6	-	-	-	-	-	-	0.7	-	-
67	34.5	8.9	4	2.2	2.4	1.3	4.7	3.6	2.2	6.5	4.4
68	-	-	-	-	-	-	-	2.1	1.3	0.7	2.3
69	-	-	-	-	-	-	-	3.3	1.5	3.4	2.7
70	-	-	-	-	-	-	-	10.2	20	59.4	40.3
71	-	-	-	-	-	-	-	0.8	2.9	5.3	2.6
78	-	1.2	-	-	-	-	-	-	-	-	-
79	-	5.1	3.6	2.8	2.6	1.2	2.2	1.7	1.9	2.8	1.6
80	0.8	4.4	1.2	1.6	1	0.8	0.9	0.6	0.7	1.2	0.7

Table I *(continued)*

Alkyl	Me	Et	Pr	1MEt	Bu	1MPr	2MPr	Pe	1MBu	2MBu	3MBu
MW	112	126	140	140	154	154	154	168	168	168	168
m/z											
81	22.3	49.4	32.8	11.4	18	8.6	12.9	10.4	7.5	21.1	12
82	100	24.3	13.3	1.4	13.6	1.2	54.3	5.8	2.8	61	5.2
83	3.3	6.3	2.7	0.5	1.4	0.6	2.4	0.7	0.8	2.6	0.7
93	0.9	-	-	-	-	-	-	-	-	-	-
97	10.3	-	-	-	-	-	-	-	-	-	-
98	-	6.1	2.5	2.7	1.9	1.6	1.3	1.1	1.6	1.9	1.8
99	-	100	100	100	100	100	100	100	100	100	100
100	-	1.7	1.3	1.6	1.5	1.3	1.1	1.4	1.1	1.4	1.5
111	2.6	36.1	22.5	-	6.2	-	2.4	2.6	-	1.9	1.7
112	5.2	0.6	1.7	-	4.9	-	77.9	2.6	-	94.6	2.9
113	-	-	1.2	-	0.9	-	3.8	-	-	5.4	-
124	-	-	-	-	-	1.1	-	-	1.7	-	-
125	-	5.2	4.9	36.4	8.3	50.8	-	3	49.2	-	9.8
126	-	-	-	1.7	-	1.6	-	-	1.7	-	5.6
139	-	-	-	0.7	-	5.8	2.7	2.2	-	4.3	-
153	-	-	-	-	-	-	-	-	3.5	-	-

Me : methyl
Et : ethyl
Pr : propyl
1MEt : 1-methylethyl (isopropyl
Bu : butyl
1MPr : 1-methylpropyl
2MPr : 2-methylpropyl
Pe : pentyl
1MBu : 1-methylbutyl
2MBu : 2-methylbutyl
3MBu : 3-methylbutyl

Table 2 *Mass spectral data (m/z, relative intensity) of alkyl-methylphosphonofluoridates*

Alkyl	1EPr	12 DMPr	22 DMPr	He	1MPe	2MPe	3MPe	4MPe	1EBu	2EBu	12 DMBu
MW	168	168	168	182	182	182	182	182	182	182	182
m/z											
26	0.9	1.9	1.5	-	-	0.6	1.7	-	-	-	0.8
27	6.8	16.4	8.4	5.4	5.8	11.9	18.3	3.5	5.7	6.3	11.8
29	7.4	13.1	15.4	6.4	5.4	11.1	25.7	2.5	5.3	7.7	16
30	-	-	1.5	-	-	-	0.9	-	-	-	-
31	-	1.4	-	-	-	0.6	1.1	-	-	-	-
37	-	-	0.8	-	-	-	-	-	-	-	-
38	-	2.1	1.6	-	0.6	-	0.7	-	-	-	0.9
39	6.4	19.7	15.9	5.1	5.3	12.7	16.5	4.1	5.2	6.5	11.6
40	1.1	2.8	3.3	0.7	1	2.6	3.2	1	0.8	1	1.8
41	19.5	26.2	25.3	13.8	13.8	31.4	37.8	18.6	14.2	17	37
42	7.4	13.9	7.5	8	9.4	15.8	12.2	5.5	6.2	7.9	4.7
43	5	26.2	4.1	9.6	8.8	29.9	15.4	10	6.8	19.9	17
44	0.7	1.5	1.2	-	-	1.8	-	-	-	0.6	-
45	-	6.8	-	-	0.7	-	-	-	-	-	-
46	-	-	-	-	-	-	-	-	-	-	-
47	2.3	6.6	2	1.6	1.6	2.7	5.4	1.3	1.5	1.9	3.1
48	-	-	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-	-	-
50	-	1.6	1.6	-	-	-	0.5	-	-	-	0.7
51	-	2.2	2.2	-	-	0.7	1.4	-	-	0.7	1.6
52	-	0.9	1	-	-	-	0.7	-	-	-	0.6
53	1.5	6.6	6.6	1.4	1.5	2.8	6.9	1	1.5	2.8	4.8
54	0.9	2.1	1.9	1.8	1.5	1.9	7	-	1.5	2.6	2.1
55	14.6	61.4	65.2	14.3	14.7	23.4	39.8	4.4	17.8	27.2	20.5
56	0.9	3.5	4.9	14.5	10.1	34.1	32.3	17	6.2	16.4	14.1
57	1.1	-	25.4	1.2	1.7	2.2	7.5	1.1	0.8	0.9	7.4
58	-	-	1	-	-	-	-	-	-	-	-
65	-	0.8	0.6	-	-	-	0.8	-	-	-	0.6
66	-	2.1	0.6	-	-	-	-	-	-	-	-
67	1.6	6.6	6.2	1.5	1.9	2.9	7.4	1.6	1.5	3.6	4.7
68	-	0.9	2.8	-	-	0.8	1.4	0.6	-	-	-
69	0.9	4.3	2.2	5.7	10.2	31.2	47	17.3	4.2	35.6	50.5
70	7.7	56.3	15	-	0.6	2.1	5.2	0.9	-	2.1	3
71	2.1	12.1	2.2	-	-	2.5	-	-	-	2.1	-
78	-	1.3	-	-	-	-	-	-	-	-	-
79	1.2	2.8	0.9	0.7	1.2	1.3	2.5	1	1.2	1.7	2
80	-	3.2	0.6	-	-	0.7	1.6	-	-	0.8	1.1
81	6.2	16.6	8	7.9	6.1	11.4	16.6	7.1	5.3	13	10.8
82	1	45.7	27.5	3	2.8	35.3	6.9	1.9	0.8	38.5	53.8

Table 2 (continued)

Alkyl	1EPr	12 DMPr	22 DMPr	He	1MPe	2MPe	3MPe	4MPe	1EBu	2EBu	12 DMBu
MW	168	168	168	182	182	182	182	182	182	182	182
m/z											
83	0.6	8.7	1	-	0.7	1.4	3.7	1.2		2.4	11.5
84	-	-	-	2.3	9.9	26.9	35.5	5.3	5.3	41	52.4
85	-	-	-	-	1.8	2.6	5	0.7	1.4	5.5	10.6
98	-	10.7	0.7	0.9	1.6	0.9	2.7	1.2	1	1.2	6
99	100	100	33.8	100	100	100	100	100	[illegible]	94.1	100
100	1	1.6	-	1	1.3	1.3	2.9	1.3			1.2
101	-	0.6	-	-	-		1				
111	-	1	0.6	1.2	-	1.2	2.1	[illegible]		[illegible]	0.6
112	-	-	100	1.1	-	76.9	2.2	96.6		100	
113	-	-	5.4	-	-	2.6				4.4	
124	-	7.5	-	-	1.7	-					3
125	-	79.1	-	1	44.4	-	4.4	0.7	0.6		42.5
126	-	45.9	-	-	2	-	4.6	-			74.5
127	-	4.6	-	-	-	-	-				4.5
138	1.9	-	-	-	-	-	-	-	1.2	-	
139	39.4	-	-	0.9	-	1.1	-	4.7	18.8	-	-
140	1.7	-	-	-	-	-	-	0.7	0.9	-	-
153	-	4.2	9.4	-	-	-	1.1	-	15.3	2.3	-
154	-	-	-	-	-	-	-	-	1.1	-	-
167	-	-	-	-	2.6	-	-	-	-	-	-

1EPr : 1-ethylpropyl
12DMPr : 1,2-dimethylpropyl
22DMPr : 2,2-dimethylpropyl
He : hexyl
1MPe : 1-methylpentyl
2MPe : 2-methylpentyl
3MPe : 3-methylpentyl
4MPe : 4-methylpentyl
1EBu : 1-ethylbutyl
2EBu : 2-ethylbutyl
12DMBu : 1,2-dimethylbutyl

Table 3 *Mass spectral data (m/z, relative intensity) of alkyl-methylphosphonofluoridates*

Alkyl	13 DMBu	33 DMBu	1E2MPr	122 TMPr	Hp	1MHx	1EPe	14 DMPe	23 DMPe	1MEBu
MW	182	182	182	182	196	196	196	196	196	196
m/z										
26	-	-	1	-	1.3	0.8	3.4	2.8	-	1.1
27	6.6	2.7	9.5	4.8	10.9	6.1	22.4	30	2.3	16.4
29	4.2	4	7.6	7.7	14.7	7.2	22.2	26.4	4.1	12.6
30	-	-	0.6	-	-	-	-	-	-	-
31	-	-	0.6	-	0.7	-	0.6	1	2.4	-
37	-	-	-	-	-	-	0.8	1.2	-	
38		1.2	1	-	-	1.2	1.6	2.1	-	1
39	7.3	3.9	11.8	8.3	10.1	9.4	24.3	28.8	5.3	15.5
40	1.5	1	1.7	1.6	3	1.8	5.2	5.8	1	2.8
41	24.3	20.9	35.6	34.9	26.8	23.2	56.1	54.3	20.3	34.9
42	5.8	1	4.7	2.7	15.3	7.3	16.3	9.8	2.6	3.9
43	15.8	3	12.7	7.6	11.1	7.2	14	44.4	8.1	11.5
45	0.8	-	-	1.9		0.6	0.9	1.2	-	
47	2	1	1.6	1.8	2.7	1.6	2.2	4	4	4
48	-	-	-	-	-	-	-	-	0.8	-
50	-	-	0.8	-	-	0.9	1.9	1.9	1.1	1.3
51	0.7	-	1	0.7	0.9	1.3	2.9	3.1	0.6	1.6
52	-	-	0.6	-	0.6	0.7	1.7	1.4	0.9	0.7
53	1.9	1.8	3.3	3.5	4.1	3.9	8.1	7.8	2.9	5.3
54	0.6	-	1.8	0.8	5.7	4.7	9.5	7.9	-	4.3
55	5.4	3.5	34.1	6.2	23.4	29.9	51.1	51.9	20	47.5
56	5	3.9	9.8	2.2	23	35.9	59.5	73.9	10.1	28.3
57	2.2	14.1	1.9	16.2	9	8.7	13.1	27.8	-	10.6
58	-	0.6	-	0.8	-	-	0.8	1.3	-	-
59	-	-	3.5	-	-	-	-	-	-	-
63	-	-	-	-	-	-	1	0.6	1	-
65	-	-	0.7	0.7	0.7	0.8	1.7	1.1	0.7	-
66	-	-	-	-	-	-	1	0.7	2.2	1.7
67	2.7	2.2	4.2	2.6	5.5	2.9	6.1	5.7	4.2	5.2
68	0.8	0.9	1	0.9	4.3	2.3	3.9	2	-	2.3
69	52.2	41.9	36.1	48.1	14.5	24.3	39	30.7	43.2	39.6
70	2.7	2.7	2	2.8	15.3	14.6	18.4	17.6	18.4	6.6
71	-	0.6	-	-	1.6	0.9	1.2	1.2	-	1.4
77	-	-	-	-	-	0.7	1.4	1	-	0.9
78	-	-	-	1.1	-	0.6	0.7	-	3.1	1
79	1.3	0.6	1	1	2	2.2	2.2	2	1.2	2.2
80	0.6	-	-	-	1	1.4	1.2	1.2	8.8	3.4
81	6.7	5.6	6.3	7	11.7	7.2	7.2	9.7	11.1	10.3
82	4.4	1.1	6.5	38.1	4.5	2.8	2.1	3	7.1	2.7

Table 3 *(continued)*

Alkyl	13 DMBu	33 DMBu	1E2MPr	122 TMPr	Hp	1MHx	1EPe	14 DMPe	23 DMPe	1MEBu
MW	182	182	182	182	196	196	196	196	196	196
m/z										
83	2	-	2.9	9.9	3.7	8	7	21.8	42.3	11.4
84	33.1	5.2	31.1	11.9	-	-	-	1.5	1.9	
85	5.2	-	6.4	7.4	-	-	-		3.3	-
96	-	-	-	-	0.6	0.7	2.7	1.6	1.6	-
97	-	-		-	0.8	0.8	1.1	1.8	1.1	1.1
98	1.9	1.5	2.2	4.6	7.8	34	28.3	14.9	44.3	34.9
99	100	100	100	78.2	100	100	100	100	100	100
100	1.2	1.2	1.1	0.7	3.2	1.7	1.5	2.1	1.7	1.6
101	-	-	-	-	1.1	-		0.7		-
111	-	-	-	-	2.3	-	-	-	1.2	0.8
112	-	1	-		1.7	-	-	-	22.2	
113	-	-	-	-	-	-	-	-	0.9	-
124	1.2	-	-	-		2.5	-			
125	41.5	3.7	11	3.3	1.4	44.4	1.5	18.1	0.6	18.4
126	3.2	28.6	-	100	-	3.1	-	1.2	-	1.1
127	-	1	-	3.8	-	-	-	-	-	-
138	-	-	8	-	-	-	1.1	-	-	-
139	0.8	-	37.9	-	1.1	-	10.3	-	3	-
140	-	-	11.3	-		-	-	-	-	-
141	-	-	0.8	-	-	-	-	-	-	-
152	-	-	0.8	-	-	-	-	-	-	5
153	-	-	9.9	-	-	0.7	-	2.2	-	54.9
154	-	-	0.7	-	-	-	-	-	-	9.5
155	-	-	-	-	-	-	-	-	-	1
167	1.1	-	-	-	-	-	9.5	-	-	-
168	-	-	-	-	-	-	0.6	-	-	-

13DMBu : 1,3-dimethylbutyl
33DMBu : 3,3-dimethylbutyl
1E2MPr : 1-ethyl-2-methylpropyl
122TMPr : 1,2,2-trimethylpropyl (pinacolyl)
Hp : heptyl
1MHx : 1-methylhexyl
1EPe : 1-ethylpentyl
14DMPe : 1,4-dimethylpentyl
23DMPe : 2,3-dimethylpentyl
1MEBu : 1-(1-methylethyl)butyl

Table 4 *Mass spectral data (m/z, relative intensity) of alkyl methylphosphonofluoridates*

Alkyl	1E22 DMPr	1ME2 MPr	Oc	1MHp	1EHx	2EHx	15D MHx	22D MHx	244T MPe
MW	196	196	210	210	210	210	210	210	210
m/z									
26	1	0.7	1.3		1.5	1.9	1	2.4	0.6
27	19.1	13	8.6	6.5	15.2	14.7	13.5	9.2	9.9
29	26.7	13.1	11.6	12.6	20.8	23.6	17	11.5	19.5
30	1		1.1	-	-	1.5		1.1	0.6
31	4	2.2	0.8	4.7	1	-	1.4	2.2	0.8
38	1.3	0.8	0.8		1.4	2	0.7	1.2	0.6
39	29.4	16.1	10.5	11.4	19.7	15.9	14	13.8	13.1
40	5.2	3.4	2.2	3.4	3.4	2.7	3.9	3.9	3.2
41	75.5	27.7	23.2	32.8	57	49	35.6	32.5	37.1
42	7.8	3.9	13.9	15.8	24.9	15.7	14.4	5.3	5.5
43	18	22.5	14.5	12.3	13.2	16.4	23.2	9.2	12.7
45	0.6	-	-	1	-	1.5	1.1	-	-
47	6.3	4.3	1.6	4.7	1.2	12.7	3.3	3.7	2.4
48	1	0.7	-	1	-	2.6	-	0.7	
50	1	0.7	0.8	1	0.9	2.7	-	1.7	
51	2.9	1.5	1.4	1.4	2.2	1.8	1.3	3	1.1
52	1.1	1.7	0.8	1.1	1.3	4.3	0.7	1.7	-
53	10.6	6.9	4.6	5.3	8.7	6.9	6.6	7.5	5.6
54	3.3	4.8	6.5	5.2	8.2	5.9	4.3	3.3	1.8
55	69.2	100	25.5	54.2	69	63.1	41.8	51.3	42.5
56	14.3	27.1	20.6	35.3	45.2	26.6	48.8	21.7	25.6
57	40.8	17.8	7.8	13.5	17.5	22.8	28.3	37.9	45.1
58	0.8	0.7	-	1.2	0.6	0.8	1.9	1.3	4
59	-	-	-	-	0.7	1.8	-	-	-
63	1.4	0.7	-	1.4	0.6	3.3	-	1.1	-
64	-	-		-	-	1.5	-	-	-
65	1.6	2.1	1.3	1.8	1.8	3.1	1	2.5	0.8
66	2.9	2.2	1.1	2.4	1.1	4.8	-	2.8	-
67	13.6	8.6	8.7	9.9	10.5	18.1	6.6	13.7	4.2
68	2.1	2.7	6.8	4.3	6.8	6.3	6.8	5.1	1
69	65.5	5.5	16.7	26.2	35	20.7	35.6	21.1	15.2
70	25.4	5.4	20	45.7	49.5	74.4	31.8	22.2	16.1
71	-	1.9	3.6	5.6	6.5	9	7.5	3	2.9
77	1	0.7	1.9	1.3	1.7	1.6	0.8	4.3	0.8
78	2.8	2	0.9	3.4	-	9.6	1	2.6	-
79	2.1	2.4	3.1	1.9	1.7	2.8	2	2.5	1
80	8.4	4.2	1.5	8.8	1.5	26	3	8	0.8
81	11.2	11.9	8.7	6.3	10.3	20	11.4	13.6	12
82	19.9	7.4	4.3	3.6	5.8	28.2	3	12.8	5

Table 4 *(continued)*

Alkyl	1E22 DMPr	1ME2 MPr	Oc	1MHp	1EHx	2EHx	15D MHx	22D MHx	244T MPe
MW	196	196	210	210	210	210	210	210	210
m/z									
83	93.5	49.4	18.2	39.1	40.7	46	9.8	25.1	3.7
84	6.9	4.9	10.7	13.1	15	14.5	12.5	3.8	1
85			0.8		0.9	0.9	1.1	0.8	
91			1.7		0.9	1		8.9	
92								1.4	
93			1.2			0.7		3.7	
94								0.7	
95			1.9		1.3	2.3	2.2	10.2	0.8
96				1.7			0.6	1.4	0.8
97	1	2.1	1.7	5.1	2.9	2.8	14.5	8.4	41.7
98	48.5	32.6	3.1	17.4	4.2	46.7	7.6	14.5	8.3
99	93.1	92.1	100	100	100	97.6	100	49.1	100
100	1.7	2	2.3	1.2	1.7	2	2.7	0.9	2.8
101		0.7					0.9		0.9
103								0.7	
105								1.2	
106								1.2	-
107					-			0.9	-
108					-			1.5	
110			2.3		1.6	1.5	0.6	5.1	
111			2.1		-	1.8	1.3	0.9	1.2
112	0.6		10	44.5	44	100	15	100	9.8
113			0.8	3.9	3.8	5.1	2.3	7.2	-
124					0.9	-	1	-	-
125	56.4		1.2	19	2.4		14.2	-	-
126	2	0.8		1.4	-	-	1.6		-
138	0.6	0.6		-	1.4	-	-	-	-
139	2.4	16.3	0.9	-	15.8	-	-	-	-
140	100	0.8	-	-	0.8	-	-	-	-
141	7.1	-	-	-	-	-	-	-	-
142	0.7	-	-	-	-	-	-	-	-
152	-	16.8	-	-	-	-	-	1.6	-
153	-	49.7	-	-	-	-	-	6.8	2.7
154	-	15.4	-	-	-	-	-	-	3.6
155	-	1.1	-	-	-	-	-	-	-
167	-	-	-	-	-	-	0.6	-	-
181	-	-	-	-	1.3	-	-	-	-

1E22DMPr	1-ethyl-2,2-dimethylpropyl
1ME2MPr	1-(1-methylethyl)-2-methylpropyl
Oc	octyl
1MHp	1-methylheptyl
1EHx	1-ethylhexyl
2EHx	2-ethylhexyl
15DMHx	1,5-dimethylhexyl
22DMHx	2,2-dimethylhexyl
244TMPe	2,4,4-trimethylpentyl

Table 5 *Mass spectral data (m/z, relative intensity) of alkyl-methylphosphonofluoridates*

Alkyl	No	1MOc	355TMHx	2MPr3MBu	De	1MNo	37DMOc	1PrHp
MW	224	224	224	224	238	238	238	238
m/z								
26	1	1	0.6	0.6	1.1	1	1	1.1
27	9	11.9	8.1	7.7	10.4	13	11.4	16.4
29	14.2	17.6	16.4	15.3	17	20.8	17	24.3
30	-	0.6	0.6	-	-	-	0.6	
31	-	1.3	0.6	-	0.6	1.3	0.8	1.4
39	8.3	11.4	10.1	9	9.4	13.1	11	15.5
40	2.2	3	2.6	2.6	2.4	3	3.2	3
41	24.3	30	29.4	26.8	28.7	37.1	35.6	49.1
42	13	18.3	12.2	11.4	14.4	19.8	13	23.2
43	18.3	25	12.7	11.9	22.6	34.7	31.9	32.6
47	1.6	2.7	2	1.7	1.7	2.7	2.2	3.1
51		1	0.9	0.9	0.7	0.9	0.8	1.1
53	3.7	5.6	5.3	5.3	4.4	6.1	6.9	7.2
54	6	6.5	2.7	2.9	7.6	9.2	7	11.2
55	25	35.9	28.2	27.7	29.9	44.6	46.7	68.2
56	21	29.4	9.8	9.5	22.5	39.8	41.1	42.4
57	8.7	11.6	39.1	37.2	12.7	20.2	24.1	16.7
58	-	0.7	3.6	3.2	0.7	0.9	1.6	0.6
65	-	0.9	0.8	0.8	0.8	0.6	1	0.8
66	-	1.1	-	-	1.1	1.6	1.2	2.2
67	6.1	7.9	5.7	5.2	8.4	11.1	9.6	13.1
68	5.2	5.2	2.6	2.6	7	8.1	7.3	7.3
69	14.8	22	33.9	28.1	18.7	33.3	39	40.8
70	14.6	22.6	31.8	26.8	18.4	32.9	58.4	37.3
71	4.3	8.5	8.8	8	4.7	8.2	15.8	8.8
77	-	0.6	0.6	0.7	0.7	0.9	0.8	1.3
78	-	1	-	-	-	1.2	-	1.4
79	0.8	1.2	0.8	1	1.3	1.1	1.2	1
80	0.6	2.9	0.9	0.8	1.1	3	1.5	3.4
81	8.9	8.7	9.5	8.9	9.7	10.6	14.2	9.5
82	5.4	8.8	3.4	2.1	6.9	8.1	6.5	6
83	9.5	16.9	13.9	14.5	13.2	22.2	20.2	22.6
84	8.1	16.7	7	5.3	9.9	18.5	17	20.7
85	1.9	4.5	0.7	-	2.7	6	5	6
95	0.6	0.7	2.2	2.3	1.1	1	2.7	1.2
96	1.1	2.2	-	-	1.8	3.8	3.8	3.7
97	7.2	14.8	1	1.2	8.4	18.3	12.7	30.7
98	8	13.7	4.7	5.4	7.2	19.1	7.6	19.1
99	100	100	100	100	100	100	100	100

Table 8 *(continued)*

Alkyl	No	1MOc	355TMHx	2MPr3MBu	De	1MNo	37DMOc	1PrHp
MW	224	224	224	224	238	238	238	238
m/z								
100	2.9	2.8	2.9	2.8	3.1	2.3	2.8	2
101	1	0.9	0.9	0.9	1	0.7	0.9	0.6
109	-	-	-	0.7	-	-	0.7	-
110	-	-	-	-	0.6	1.2	0.6	1.2
111	1.8	2.2	21.8	20.1	6.5	12.1	13.7	11.9
112	0.7	-	5.6	2.9	5.2	7.4	9.6	6.8
113	-	-	-	-	-	-	0.9	-
124	-	0.7	-	-		-		-
125	0.8	15.5	1.1	1.7	0.7	13.2	6.5	2.2
126	3.3	14.9	4.9	5.7	-	1.1	3.1	-
127	-	1.9	-	-	-	-		-
140	-	-	0.7	-	3.8	17.2	8	23.2
141	-	-	-	-	-	2.2	1.2	2.6
152	-	-	-	-	-	-	-	0.6
153	-	0.6	-	-	-	-	1.1	13.4
154	-	-	-	-	-	-	-	0.9
167	-	-	0.7	-	-	-	-	-
168	-	-	9.6	9.1	-	-	-	-
169	-	-	0.9	1	-	-	-	-

No	: nonyl
1MOc	: 1-methyloctyl
355TMHx	: 3,5,5-trimethylhexyl
2MPr3MBu	: 1-(2-methylpropyl)-3-methylbutyl
De	: decyl
1MNo	: 1-methylnonyl
37DMOc	: 3,7-dimethyloctyl
1PrHp	: 1-propylheptyl

Table 6 *Mass spectral data (m/z, relative intensity) of cycloalkyl methylphosphonofluoridates*

Alkyl	C5	C6	C6M	2MC6	3MC6	4MC6	C7	C6Et	2EtC6	4EtC6
MW	166	180	194	194	194	194	194	208	208	208
m/z										
26	2.1	-	1.7	1.4	1.1	-	1.3	1.3	-	-
27	10.4	4.1	15	17.2	14.7	5.4	11.9	15.8	7.7	7.7
29	8.8	2.5	16	16	13.6	6.1	12.1	17.6	8.3	8.4
31	2.6	-	1.8	2.3	2.4	1.4	3.1	0.8	1.2	-
37	1.1	-		-	-	-	-	-	-	-
38	3.1	-	1.3	1.3	1.2	-	1.3	0.6	-	-
39	23.1	7.6	22.5	26.4	21.9	11	21.4	24.3	9.7	11.4
40	9.9	1.2	6.6	6.3	5.2	2	6.4	4.7	1.8	1.8
41	23.7	11.6	33.5	29.2	25.6	12.5	22.6	48.2	19.4	22
42	8.3	1	5.7	7.4	7	2.6	7	5.5	2.2	2.1
43	2.6	0.8	4.4	3.3	3.9	1.1	2.8	4.6	2.1	3
47	4.7	1	5.6	5.4	5.2	3.5	5.7	4.2	2.7	1.6
48	0.7	-	-	0.6	-	-	1	-	-	-
50	1.9	-	1.2	1.2	1.3	0.6	1.3	0.6	-	-
51	1.9	-	4.1	4.7	4.5	2	3.7	2.5	1.9	1.7
52	2	0.5	3.3	3.5	3.2	1.4	2.8	2.3	1.5	0.7
53	11.4	3.5	14.7	17.8	15.7	7.5	13.7	15.3	7.1	7.8
54	3.1	19.1	33.7	26.4	29.9	22.8	37.9	36.6	8.3	24.4
55	1.6	6.9	48.9	40	37.2	20.9	32.3	35.9	10.8	12.8
56	-	0.6	5.1	3.9	3.7	1.8	3	3.7	1.7	1.8
57	7.5	0.6	1.2	2.8	1.2	2.1	3.3	-	-	0.9
58	1	-	-	-	-	-	-	-	-	-
63	2.3	-	1	1	1.1	0.6	1.3	0.7	-	-
65	5.4	0.6	5.6	5	4.7	2.7	5.2	4.3	1.4	2.5
66	6.2	0.7	11.2	7.5	5.5	3.5	9.4	6.5	3	2.2
67	39.6	33.2	58.2	48.7	31.1	18.8	49.7	71.1	31.4	21.8
68	31.7	1.8	39	40.6	31.7	15.4	31.7	25.6	12.3	8.3
69	11.1	-	5.3	5.1	4.9	2	4.3	15.6	11.3	11.7
70	0.6	-	-	0.6	-	-	0.6	0.9	0.8	1
77	-	-	6.4	6.6	7.1	4.4	4.7	4.4	2.7	3.5
78	1.8	-	1.3	1.5	3.6	1.6	2.8	1.4	-	0.7
79	2.8	2.5	7.5	5.7	9.2	5.2	9.7	10.3	3.6	5.4
80	3.7	0.6	5.4	7.2	7.8	6.4	8.8	9.1	7.2	6.2
81	10.6	9.7	100	100	94.2	56.2	53.6	90.9	100	81.2
82	7.1	11.3	35.1	10.7	10.2	7.4	7.6	65.6	22.2	16
83	3.9	2.9	9.4	6	6.2	5.7	9.2	9	2.1	1.1
85	19.7	-	-	-	-	-	-	-	-	-
86	1.7	-	-	-	-	-	-	-	-	-
91	-	-	3.4	2.8	2.5	1.7	2.2	2.3	1.5	1.3

Table 6 *(continued)*

Alkyl	C5	C6	C6M	2MC6	3MC6	4MC6	C7	C6Et	2EtC6	4EtC6
MW	166	180	194	194	194	194	194	208	208	208
m/z										
92	-	-	0.8	-	-	-	-	-	-	-
93	-	-	2.4	1.5	1.7	1.1	1.2	2.5	1	-
94	-	-	2.3	1.4	1.8	1.1	0.8	-	-	
95	-	-	11.8	11.8	13.3	9	7.6	18	13.9	10
96	-	-	48.3	58.3	41.1	24.8	24.8	1.4	-	0.7
97	-	-	9.9	14.1	11.1	6.6	7.7	-	-	-
98	8.5	1.1	4.6	8.3	8.7	8	12.3	2.2	2.5	2.4
99	100	100	72.4	73	100	100	100	100	40.3	100
100	2.8	1	2	1.4	2.4	2.4	2.6	2.1	-	1.7
101	0.9	-	0.7	-	0.8	0.7	0.8	0.7	-	-
108	-	-	-	-	-	-	-	0.9	0.7	0.6
109	0.8	-	-	-	-	-	-	3	1.6	2
110	-	-	-	-	-	-	-	34.1	38.3	23
111	-	-	1.7	-	-	-	-	6.9	6.1	2.9
112	-	-	29.9	-	-	-	-	-	-	-
113	-	-	2.2	-	-	-	1.2	-	-	-
123	0.7	-	-	-	-	-	-	-	-	-
124	2.3	-	-	-	0.6	-	1.1	-	-	-
125	7.4	0.8	-	6.9	3.3	2.1	6	1.6	2.3	0.8
126	-	-	-	-	-	-	-	1.5	-	-
137	11.1	2.6	-	3.5	1.6	1.8	8.2	-	1.2	-
138	3	-	-	0.8	-	2.6	2	-	-	0.6
151	-	-	-	0.6	1.2	-	1	-	-	-

C5 : cyclopentyl
C6 : cyclohexyl
C6M : cyclohexylmethyl
2MC6 : 2-methylcyclohexyl
3MC6 : 3-methylcyclohexyl
4MC6 : 4-methylcyclohexyl
C7 : cycloheptyl
C6Et : 2-(cyclohexyl)ethyl
2EtC6 : 2-ethylcyclohexyl
4EtC6 : 4-ethylcyclohexyl

Table 7 *Mass spectral data (m/z, relative intensity) of cycloalkyl methylphosphonofluoridates*

Alkyl	22DMC6	26DMC6	35DMC6	C8	C6Pr	2iPr5MC6	4tBuC6
MW	208	208	208	208	222	236	236
m/z							
26	-	-	-	1.1	0.7	-	0.9
27	8.6	9.1	7.4	11.9	3	7	8.1
29	8.1	8.9	8.5	11.6	3	6.5	13.2
31	2.3	0.8	4.8	5	-	0.6	0.6
38	0.9	0.6	-	0.9	-	-	1.1
39	20.5	15.8	13.9	28.2	6.9	9.4	15.8
40	4.5	3.5	3.1	4.9	1.4	1.9	3
41	32.8	26.3	24.5	49.1	16.2	23.9	43.1
42	3.8	3.1	3.8	6.1	2.6	2.5	3
43	6.9	2.9	3.3	4.1	1.4	8.5	6.2
47	5.2	2.3	7.2	8.1	1.2	1.2	1.2
48	0.7	-	1.6	1.8	-	-	-
50	1.4	0.6	1.5	1.8	0.6	-	1.9
51	4.8	2.6	2.7	4.1	1.6	2.1	4.6
52	2.7	1.5	1.9	4.9	1.1	1.8	3.3
53	15.9	10.2	9.3	15.7	5.6	8.6	10.6
54	11.4	8.5	3.7	65.9	9.2	4.8	9.6
55	26.5	25	23.4	28.2	23.9	22.5	12.9
56	7.9	3.6	3.2	8.2	1.4	3	10.8
57	1.2	2	1	2.4	0.8	4.7	100
58	-	-	-	-	-	-	4.7
63	1.8	0.7	1.8	2.3	0.6	-	1.1
64	-	-	0.6	0.7	-	-	-
65	7.6	3.6	4	5.6	2.4	3.4	4.1
66	17.5	2.6	4.5	10.7	3	1.7	3.1
67	77	34	31.9	98.2	32.7	32.4	40.5
68	40.9	25.5	42.1	47.7	12.6	12.4	3.9
69	39.1	12.9	19.9	27.7	4.1	9.2	15.4
70	2.1	0.7	1.1	1.5	-	1.5	3.6
71	0.5	0.5	0.9	0.5	-	-	1.8
77	11.8	5.1	6.2	6.6	4.4	5.9	11.6
78	2.7	0.6	5.7	7.3	2.1	1.8	9.7
79	9.6	2.3	2.5	3.1	11.1	9.6	24
80	12.6	4	15.4	24.7	5.8	7	36.7
81	60.3	33.3	28.2	80.5	58.2	67.8	38.2
82	86.1	26.1	15.1	90.6	36.4	25.6	32.3
83	19	4.6	24.1	33.9	19.1	10.4	9.1
84	-	-	-	-	1	0.8	3.8
91	9	3.7	6.2	2.8	4.9	5	7.6

Table 7 *(continued)*

Alkyl	22DMC6	26DMC6	35DMC6	C8	C6Pr	2iPr5MC6	4tBuC6
MW	208	208	208	208	222	236	236
m/z							
92	1.1	0.6	0.9	0.4	1.2	1.2	1.5
93	11.3	3.9	6.2	2.1	3.6	6.4	4.1
94	2.4	1.1	1.2	-	3	10.4	2.2
95	100	100	100	34.6	15.4	100	11.2
96	11.8	12.6	10.7	2.4	49.1	21.5	5.4
97	-	-	-	0.5	3.3	2.7	1.6
98	14.3	3.2	28	34.9	2.2	3.3	3
99	61.4	35	62	100	100	33.6	56.2
100	1	0.5	1.1	1.7	1.4	-	0.7
103	-	-	0.5	-	-	-	0.8
105	0.6	-	0.9	-	1.1	1	2.3
107	0.8	-	0.7	0.5	2.2	1.4	2
108	2	0.7	1.7	1	-	-	-
109	6.4	3.3	7.9	2.5	3.4	8.1	1.6
110	64.8	38.3	44.4	51.5	-	2.5	2
111	14.5	6.6	6.3	9	2.8	-	-
112	0.9	-	-	0.5	-	-	-
115	-	-	0.6	-	0.9	-	0.6
117	-	-	-	-	1.3	-	0.6
118	-	-	-	-	1	-	-
119	-	-	1.5	-	-	0.8	5.1
120	-	-	-	-	1.1	-	0.7
121	-	-	-	-	-	1.6	3.4
122	-	-	-	-	3.5	-	0.7
123	-	-	-	-	1.3	39.7	20.8
124	0.5	-	-	0.8	17.1	3.8	2.2
125	9.7	-	1.9	9.9	1.7	1.3	-
127	-	-	-	0.7	-	-	-
134	-	-	-	-	-	-	1.8
136	-	-	-	-	-	1.1	2.6
137	2.6	-	-	6.9	-	1.2	0.7
138	0.8	0.9	-	2.1	-	44	18.6
139	-	0.5	-	0.5	0.6	5.4	1.9
151	-	0.8	0.7	1.2	-	-	-

22DMC6	: 2,2-dimethylcyclohexyl
26DMC6	: 2,6-dimethylcyclohexyl
35DMC6	: 3,5-dimethylcyclohexyl
C8	: cyclooctyl
C6Pr	: 3-(cyclohexyl)propyl
2iPr5MC6	: 2-isopropyl-5-methylcyclohexyl (menthyl)
4tBuC6	: 4-t-butylcyclohexyl

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Mass spectral data of alkyl and cycloalkyl methylphosphonoflouridates

11. AUTHOR(S)

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15. ABSTRACT (MAXIMUM 200 WORDS (1044 BYTE))

Electron impact (EI) mass spectra of over 60 alkyl and cycloalkyl methylphosphonofluoridates (alkyl cycloalkyl ≤ C10) were recorded and taken up in databases. Each compound was prepared in situ by mixing an alcohol with methylphosphonodifluoride followed by gas chromatographic-mass spectrometric analysis (GC-MS) of the reaction mixture. The choice of the alcohols was restricted to relatively inexpensive, primary and secondary alcohols. The EI mass spectra and a short description of the fragmentation patterns of the methylphosphonofluoridates are presented.

16. DESCRIPTORS	IDENTIFIERS
Databases Gas Chromatography Mass Spectroscopy Alcohols	Mass Spectra Methylphosphonofluoridates

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