Journal of Chromatography, 637 (1993) 71–80
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 933

Application of headspace analysis, solvent extraction, thermal desorption and gas chromatography–mass spectrometry to the analysis of chemical warfare samples containing sulphur mustard and related compounds

Robin M. Black*, Raymond J. Clarke, David B. Cooper, Robert W. Read and David Utley

Chemical and Biological Defence Establishment, Porton Down, Salisbury, Wiltshire SP4 0JQ (UK)

(First received November 27th, 1992; revised manuscript received February 2nd, 1993)

ABSTRACT

Samples of soil, munition fragments and wool, associated with a chemical warfare incident involving sulphur mustard, were analysed using headspace, solvent extraction and thermal desorption techniques combined with full scanning gas chromatography–mass spectrometry. Quantitative analysis was undertaken for sulphur mustard, mustard sulphoxide and thiodiglycol, using solvent extraction and gas chromatography–mass spectrometry with selected ion monitoring. In a soil sample contaminated at ppm (w/w) levels all methods gave positive results for mustard and related compounds. Selected ion monitoring and thermal desorption were the more useful techniques at low ppb (w/w) levels. Cyclic decomposition products 1,4-thioxane and 1,4-dithiane appear to be useful indicators of mustard contamination when using thermal desorption analysis. The hydrolysis product thiodiglycol and hydrolysis/elimination product 2-(vinylthio)ethanol appear to be useful indicators of mustard contamination in soil samples when employing extraction methods.

INTRODUCTION

Allegations concerning the use of chemical weapons have increased over the past decade, particularly during the period of the Iraq–Iran war [1]. In August 1988 chemical weapons were reported to have been used against the Kurdish population in the mountainous region of northern Iraq close to the borders of Turkey and Iran. In November of that year an investigative journalist [2] entered the area and collected samples from the hillside site of an impacted bomb. The ruptured, thin-walled metal bomb was embedded in the ground. Samples of soil, bomb casing, and what appeared to be sheep's wool, were collected from the site and brought back to the UK for analysis. Headspace analysis of two of these samples, undertaken in a commercial laboratory, identified three decomposition products of sulphur mustard as 1,4-dithiane, 1,4-thioxane and divinyl sulphide (1,1-thiobis-ethene) [2]. A more extensive analysis for volatile and extractable material was subsequently undertaken at the Chemical and Biological Defence Establishment (CBDE). Headspace sampling, solvent extraction and thermal desorption were applied to the samples, each coupled with analysis by full scanning gas chromatography–mass spectrometry (GC–MS). In addition, samples were

* Corresponding author.

0021-9673/93/$06.00

analysed quantitatively for sulphur mustard and its more stable oxidation and hydrolysis products, mustard sulphoxide and thiodiglycol, using solvent extraction combined with GC–MS-selected ion monitoring. A summary of the results of these analyses has appeared in the literature [2] but with few details of the methods employed. In this paper we report the results of our analyses in full and discuss the relative advantages of the analytical methods employed.

EXPERIMENTAL

Samples

The samples were received in a cold box at CBDE on 9 December 1988 and were stored at −20°C for 5 days prior to analysis. They consisted of the following.

(a) A brown plastic jar, labelled sample 1, containing *ca.* 410 g of soil which had been excavated from beneath the munition.

(b) A similar plastic jar, labelled sample 2, containing some coarse white wool-like material, possibly sheep's wool, plus a few residual soil-like particles at the bottom of the jar.

(c) Two similar samples wrapped in metal foil, each containing a thin, shiny metal fragment *ca.* 5 × 8 cm, together with soil which had been in contact with the fragments; these two samples were numbered 4A and 4B, repectively, at CBDE. Sample 4A contained 34 g of soil, sample 4B contained 17 g of soil.

Headspace analysis (samples 1 and 2)

The headspace in the two plastic containers was sampled immediately on opening by drawing ambient air over the sample at 0.5 l/min for 10 min with the aid of a Cassella pump. Volatiles were adsorbed onto Tenax-GC (50 mg) contained in an ATD50 tube. The trapped volatiles were thermally desorbed and analysed by full scanning GC–MS using a Perkin-Elmer ATD50 thermal desorption system coupled to a Hewlett-Packard 5890 GC/5970B GC–MSD instrument. The thermal desorption system was operated in the two-stage desorption mode with oven temperature 250°C, desorb time 10 min, transfer line 150°C, cold trap low −30°C, cold trap high 300°C, and split flow 13 ml/min. The gas chromatograph was fitted with a Hewlett-Packard Ultra-2 (phenylmethyl silicone) column 25 m × 0.2 mm I.D., film thickness 0.33 μm. Helium at 103 kPa was used as carrier gas. The oven temperature was held at 35°C for 5 min, programmed from 35 to 300°C at 10°C/min, and held at 300°C for 7 min; the GC–MS transfer line was held at 250°C. The mass spectrometer was operated using electron impact ionisation and scanned over the mass range 40–300 u at 1.65 scans/s from 0–10 min, 40–400 u at 1.19 scans/s from 10–20 min, and 40–500 u at 0.93 scans/s from 20–38.5 min.

Extraction with full scanning GC–MS analysis

Aliquots (1–10 g) of soil samples 1, 4A, and 4B were extracted by tumbling in screw-cap vials with dichloromethane (2–10 ml) and dry sodium sulphate (1 g) for 30 min. After filtering, the extracts were concentrated under a stream of nitrogen. Wool sample 2 (0.22 g) was also extracted by tumbling with dichloromethane. GC–MS analysis was performed using a VG 7070EQ instrument coupled to an 11/250 data system. The gas chromatograph was fitted with a DB-5 (J & W) 15 m × 0.25 mm I.D. column, film thickness 0.25 μm; helium at 103 kPa was used as carrier gas. The oven was held at 50°C for 1 min, and then programmed from 50 to 270°C at 15°C/min. On-column injection (0.5 μl) was used. The mass spectrometer was scanned from 45 to 600 u at 1 scan/s with 0.2 s interscan time. Electron impact ionisation at 70 eV or methane chemical ionisation at 150 eV was used. A duplicate analysis was performed using a Hewlett-Packard GC–MSD system employing on column injection and GC–MS conditions as described above.

Thermal desorption analysis

Aliquots of soil from samples 1, 2 (residual soil particles), 4A and 4B, wool sample 2, and metal fragment 4B were heated at 50°C for 30 min, 100°C for 30 min or 250°C for 10 min in ADT50 tubes under a gas flow of 13 ml/min. Volatiles were trapped in a cold trap at −30°C containing Tenax (10 mg) and analysed using a coupled ADT50-GC–MSD system employing GC–MS conditions as described above.

Quantitative trace analysis for mustard and mustard sulphoxide

Aliquots of soil from samples 1, 4A and 4B (*ca.* 0.75 g), and wool sample 2 (0.15 g) were extracted by tumbling for 10 min with dichloromethane (2 ml) and sodium sulphate (0.3 g) in a 3-ml vial. The extract was transferred to a 1-ml vial and concentrated to small volume under a stream of nitrogen at 40°C. The extraction was repeated and the combined extracts concentrated to 100 μl. Remaining dichloromethane was removed by adding ethyl acetate (100 μl), concentrating to 100 μl and repeating the process. Metal fragment 4A was extracted twice with dichloromethane (20 ml then 10 ml) in a beaker. The combined extracts were concentrated on a rotary evaporator and treated as above.

GC–MS analysis was performed using a Finnigan 4600 GC–MS system operated in the selected ion mode. The gas chromatograph was fitted with a 25 m × 0.22 mm I.D. bonded phase column coated with OV1710, film thickness 0.25 μm, inserted directly into the ion source. Helium at 103 kPa was used as carrier gas. The oven was held at 60°C for 2 min, programmed from 60 to 220°C at 10°C/min and held at 220°C for 2 min. Splitless injection (2 μl) was used, 0.5 min delay, injector temp 250°C. The GC–MS interface was held at 240°C. Sulphur mustard was analysed using chemical ionisation with methane as reagent gas [3,4]; electron energy 150 eV, source pressure 80 Pa, source temperature 100°C. Ions monitored were *m/z* 123, 125, 159, and 161, total scan time 1 s. Mustard sulphoxide was analysed similarly but using ammonia as reagent gas, source pressure 80 Pa. Ions monitored were *m/z* 192 and 194. Quantitation was performed against external standards with no allowance for recovery.

Quantitative trace analysis for thiodiglycol

Aliquots of soil samples 1, 4A and 4B (*ca.* 1g), and wool sample 2 (0.1 g), were extracted twice by tumbling for 10 min with ethyl acetate (2 ml) and sodium sulphate (0.3 g) in a 3-ml screw-cap vial. The extracts were concentrated just to dryness under a stream of nitrogen prior to derivatisation. Because of the relatively high concentrations of thiodiglycol present in soil sample 1, the combined extracts were diluted to 5 ml with ethyl acetate and aliquots (100 μl) then concentrated to dryness for derivatisation. Metal fragment 4A was extracted in a beaker with ethyl acetate (20 ml then 10 ml) (the dichloromethane extract used for mustard analysis was also analysed for thiodiglycol).

Thiodiglycol was converted to its bis(*tert.*-butyldimethylsilyl) derivative for GC–MS analysis. The dried residues were treated with pyridine (Regis derivatisation grade, 80 μl) and N-methyl-N-(*tert.*-butyldimethylsilyl)trifluoroacetamide–1% *tert.*-butyldimethylchlorosilane (Regis, 20 μl), and heated at 100°C for 90 min.

GC–MS analysis was performed using a Finnigan 4600 GC–MS system operated in the selected ion mode. The gas chromatograph was fitted with a BP5 25 m × 0.2 mm I.D. column, film thickness 0.25 μm. Helium at 103 kPa was used as carrier gas. The oven was held at 90°C for 0.5 min, programmed from 90 to 280°C at 15°C/min, and held at 280°C for 2 min. Splitless injection (1 μl) was employed (plus toluene needle flush), 0.5 min delay, injector temp. 265°C. The GC–MS interface was held at 260°C. Chemical ionisation was employed with methane as reagent gas, electron energy 100 eV, source pressure 107 Pa, source temperature 120°C. Ions monitored were *m/z* 219, 293, and 335, total scan time 1 s. Quantitation was performed against external standards.

RESULTS

Sample 1

The compounds identified in the headspace, dichloromethane extracts and thermal desorbate from soil sample 1, using full scanning GC–MS, are shown in Table I. Identification in most cases was by comparison with standards [5], with library spectra, or with spectra reported by others [6,7]; tentative identifications based on mass spectral interpretation are indicated in Table I. Partial mass spectra are compiled in Table II.

Headspace GC–MS analysis. Sulphur mustard was readily detected in the headspace above the soil in the plastic jar, along with several related

TABLE I

COMPOUNDS IDENTIFIED OR TENTATIVELY IDENTIFIED IN SOIL SAMPLE 1

Compounds listed in order of retention time.

Compound	Headspace	Extract	Thermal desorbate		
			50°C	100°C	250°C
Ethylene sulphide[a]					+
Divinyl sulphide[b]	+				
2,4-Dimethylthietane[a]	+				
2-Methyl-1,3-thioxalane[a]	+			+	+
1,4-Thioxane[b]	+				+
2-Chloroethyl vinyl sulphide[b]	+		+	+	
2-(Vinylthio)ethanol[b]	+	+	+	+	
1,4-Dithiane[b]	+		+		+
2-(Vinylsulphinyl)ethanol[b]		+	+		
1,4,5-Oxadithiapane[a]			+		+
1,2-Bis(vinylthio)ethane[c]	+				
Sulphur mustard[b]	+	+	+		+
Thiodiglycol[b]		+			
1,2,5-Trithiapane[a]					+
Bis(2-chloroethyl) disulphide[b]	+	+	+		
(2-Chloroethylthio)ethyl vinyl sulphide[c,d]	+				
2-(2-Hydroxyethylthio)ethyl vinyl sulphide[c]			+		
Bis(2-chloroethyl) sulphoxide[b]		+			
Bis[2-(vinylthio)ethyl] ether[c,d]	+	+	+		
Tri-isobutyl phosphate[b]		+			
2-(2-Hydroxyethylthio)ethyl vinyl sulphoxide[c]		+			
1,2-Bis(2-chloroethylthio)ethane[b]		+			
Trinitrotoluene[b]		+			
Tetryl[b]		+			
Bis[2-(2-chloroethylthio)ethyl] sulphide[c,d]		+			

[a] Library search.
[b] Standard.
[c] Tentative.
[d] Ref. 7.

compounds (see Table I). A GC–MS total ion current chromatogram from the headspace of sample 1, and a full spectral scan showing the presence of sulphur mustard, are shown in Fig. 1. Major components in the headspace were the elimination/hydrolysis product 2-(vinylthio)ethanol (2-hydroxyethyl vinyl sulphide) and the elimination product 2-chloroethyl vinyl sulphide, eluting between 10 and 12 min.

Solvent extraction with GC–MS analysis. Sulphur mustard was similarly detected in dichloromethane extracts of soil sample 1, although under the chromatographic conditions employed it was only partially resolved from much larger concentrations of its hydrolysis product thiodiglycol. Thiodiglycol and 2-(vinylthio)ethanol were identified as major components of the extract along with many minor components derived from sulphur mustard. A total ion current chromatogram obtained using the VG 7070EQ instrument is shown in Fig. 2. A similar total ion current chromatogram was obtained using the GC–MSD system. Improved resolution of mustard-related compounds containing an unhydrolysed CH_2CH_2Cl group could be obtained by constructing the mass chromatograms of m/z 63 and 65, ions which are usually relatively intense in compounds containing this

TABLE II

PARTIAL MASS SPECTRA[a] OF COMPOUNDS IDENTIFIED

Compound	m/z (%)
Ethylene sulphide	61 (MH^+, 7), 60 (M^+, 100), 59 (88), 58 (26), 57 (13), 45 (89)
Divinyl sulphide	86 (M^+, 64), 85 (100), 59 (55), 45 (51), 58 (49), 57 (21)
2,4-Dimethylthietane	102 (M^+, 56), 60 (100), 45 (54), 41 (36), 59 (35), 73 (29)
2-Methyl-1,3-thioxalane	104 (M^+, 58), 89 (17), 61 (43), 60 (100), 59 (62), 45 (55)
1,4-Thioxane	104 (M^+, 53), 74 (18), 61 (45), 60 (13), 47 (13), 46 (100)
2-Chloroethyl vinyl sulphide	122 (M^+, 43), 73 (93), 60 (68), 59 (58), 58 (50), 45 (100)
2-(Vinylthio)ethanol	104 (M^+, 36), 73 (51), 60 (52), 59 (33), 58 (27), 45 (100)
1,4-Dithiane	120 (M^+, 100), 61 (61), 60 (32), 59 (23), 46 (71), 45 (47)
2-(Vinylsulphinyl)ethanol	120 (M^+, 26), 74 (55), 61 (25), 47 (25), 46 (100), 45 (41)
1,4,5-Oxadithiapane	136 (M^+, 100), 64 (46), 60 (78), 59 (50), 45 (73), 43 (48)
1,2-Bis(vinylthio)ethane	146 (M^+, 0.2), 118 (33), 87 (64), 85 (47), 59 (67), 58 (49), 45 (100)
Sulphur mustard	158 (M^+, 25), 111 (38), 109 (100), 63 (40), 59 (21), 45 (27)
Thiodiglycol	122 (M^+, 2), 104 (38), 91 (25), 61 (100), 60 (20), 47 (26), 45 (68)
1,2,5-Trithiapane	152 (M^+, 100), 124 (24), 87 (40), 60 (50), 59 (46), 45 (36)
Bis(2-chloroethyl) disulphide	192 (M^+, 51), 190 (M^+,67), 128 (30), 65 (35), 64 (32), 63 (100)
(2-Chloroethylthio)ethyl vinyl sulphide	182 (M^+, 28), 123 (100), 73 (41), 63 (40), 61 (40), 59 (48), 45 (71)
2-(2-Hydroxyethylthio)ethyl vinyl sulphide	164 (M^+, 21), 105 (100), 104 (43), 61 (76), 59 (47), 45 (98), 44 (78)
Bis(2-chloroethyl) sulphoxide	174 (M^+, 15), 76 (26), 65 (28), 63 (100), 47 (21), 45 (32), 44 (55)
Bis[2-(vinylthio)ethyl] ether	190 (M^+, 0.1), 87 (100), 86 (39), 85 (29), 61 (40), 59 (59), 45 (71)
Tri-i-butyl phosphate	155 (20), 139 (9), 112 (10), 99 (100), 57 (18), 41 (17), [266, M^+ absent]
2-(2-Hydroxyethylthio)ethyl vinyl sulphoxide	180 (M^+, 18), 103 (100), 75 (19), 59 (18), 47 (21), 45 (32), 44 (55)
1,2-Bis(2-chloroethylthio)ethane	123 (100), 109 (66), 73 (52), 63 (78), 61 (87), 60 (55), [218, M^+ absent]
Trinitrotoluene	210 (M^+, 100), 89 (43), 76 (17), 63 (36), 62 (17), 51 (18)
Tetryl	242 (61), 194 (100), 77 (48), 76 (35), 75 (35), 51 (30), [287, M^+ absent]
Bis[2-(2-chloroethylthio)ethyl] sulphide	156 (27), 125 (37), 123 (100), 122 (54), 63 (34), 61 (33), 45 (26), [278, M^+ absent]

[a] Six most intense ions m/z 40 and above, plus molecular ion where appropriate; obtained using the GC–MSD system.

fragment; the mass chromatogram of m/z 65 is shown in Fig. 2. Traces of tri-isobutyl phosphate (see below) were also detected in the extract, observed more clearly by constructing a mass chromatogram of the ion m/z 99. This ion is useful for searching for the nerve agents isopropyl, cyclohexyl and pinacolyl methylphosphonofluoridate although none was detected in the extract. Two additional components of the total ion chromatogram, whose partial mass spectra are shown in Table II, were identified as the explosives 2,4,6-trinitrotoluene and tetryl (N-methyl-N,2,4,6-tetranitroaniline), confirmed by comparison with reference samples.

Thermal desorption analysis. Sulphur mustard was again detected as a minor component by thermal desorption of an aliquot of soil sample 1. A total ion current chromatogram obtained at a desorption temperature of 50°C is shown in Fig. 3. Bis(vinylthioethyl) ether was the major component observed using a desorption temperature of 50°C. At higher desorption temperatures cyclic products became more predominant, presumably formed as thermal decomposition products, *e.g.* by cyclisation of 2-(vinylthio)ethanol or via sulphonium intermediates. 2-Methyl-1,3-thioxalane and 2-(vinylthio)ethanol were the major compounds observed at a desorption temperature of 100°C, and 1,4-dithiane and 1,4-thioxane on further heating at 250°C. Other minor cyclic products desorbed at 250°C, identified by data system search, were ethylene sulphide, 1,4,5-oxadithiapane and 1,2,5-trithiapane.

Quantitative analyses for mustard, mustard sulphoxide and thiodiglycol. Quantitative analyses for mustard and its oxidation and hydrolysis products, using GC–MS-selected ion monitoring,

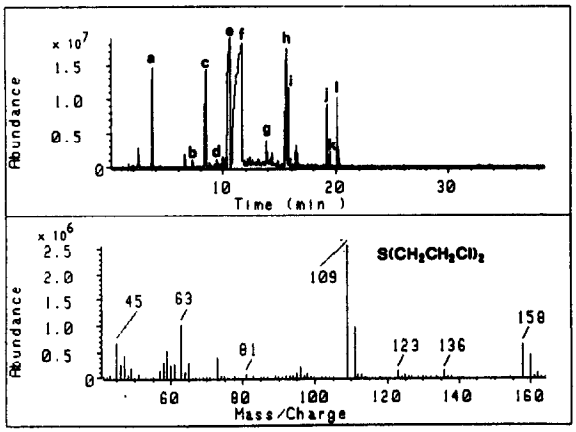

Fig. 1. Headspace of soil sample 1: GC–MSD total ion current chromatogram (upper) and a full spectral scan of peak i (lower) showing the presence of sulphur mustard. Peaks identified were: a = divinyl sulphide, b = 2,4-dimethylthietane, c = 2-methyl-1,3-thioxalane, d = 1,4-thioxane, e = 2-chloroethyl vinyl sulphide, f = 2-(vinylthio)ethanol, g = 1,4-dithiane, h = 1,2-bis(vinylthio)ethane, i = sulphur mustard, j = bis(2-chloroethyl) disulphide, k = (2-chloroethylthio)ethyl vinyl sulphide and l = bis[2-(vinylthio)-ethyl] ether.

are shown in Table III, together with the results for samples 2, 4A and 4B. The values quoted are based on the amount of analyte detected in the extracts and make no allowance for recovery. All control samples (*i.e.* glassware blanks) were negative for the presence of the analytes. Concentrations of sulphur mustard in soil sample 1 were quantitated as *ca.* 10 ppm (10 μg/g). Mustard sulphoxide was quantitated in soil sample 1 at levels *ca.* one fifth those of mustard. As observed by full scanning GC–MS, thiodiglycol was present in very high concentrations, determined as *ca.* 450 ppm.

Sample 2

Headspace, extraction and thermal desorption with GC–MS analysis. No significant compounds were detected in the headspace in the container above sample 2, nor after extraction or thermal desorption of the wool or soil particles using full scanning GC–MS.

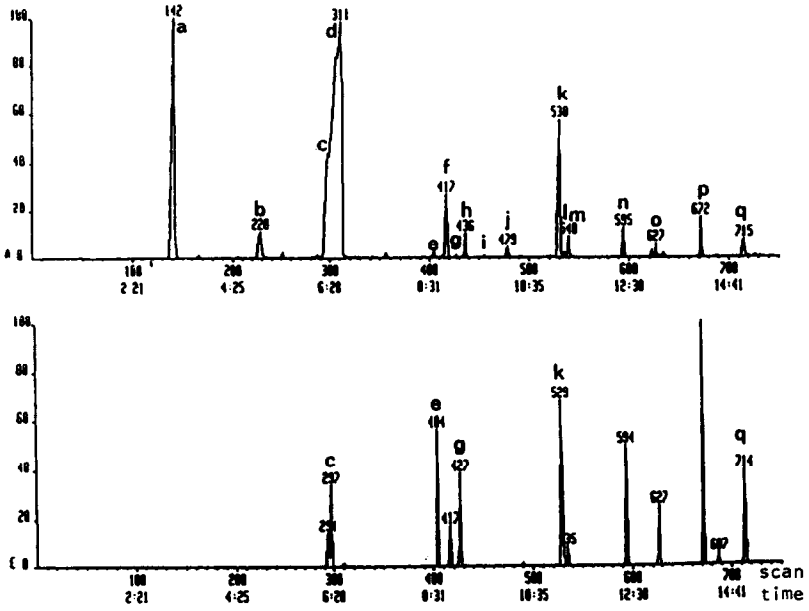

Fig. 2. Dichloromethane extract of soil sample 1: GC–MS (VG 7070EQ) total ion current chromatogram (upper) and mass chromatogram of *m/z* 65 (lower) showing improved resolution of compounds containing the CH_2CH_2Cl fragment. Peaks identified were: a = 2-(vinylthio)ethanol, b = 2-(vinylsulphinyl)ethanol, c = sulphur mustard, d = thiodiglycol, e = bis(2-chloroethyl) disulphide, f = unidentified, g = bis(2-chloroethyl) sulphoxide, h = bis[2-(vinylthio)ethyl] ether, i = tri-isobutyl phosphate, j = 2-(2-hydroxyethylthio)ethyl vinyl sulphoxide, k = 1,2-bis(2-chloroethylthio)ethane, l = trinitrotoluene, m = unidentified, n,o = dibutyl phthalates, p = tetryl and q = bis[2-(2-chloroethylthio)ethyl] sulphide. Time in min:s.

TABLE III

RESULTS OF QUANTITATIVE ANALYSIS FOR MUSTARD, MUSTARD SULPHOXIDE AND THIODIGLYCOL

Analysis	1 soil	2 wool	4A soil	4A fragment	4B soil
Mustard	10.8 ppm 8.2 ppm	7 ppb	4 ppb	18 ng	27 ppb
Mustard sulphoxide	2.1 ppm	[a]	nd[b]	nd	4 ppb
Thiodiglycol	470 ppm 436 ppm	nd	7 ppb	9 ng	26 ppb

[a] detected but not confirmable on ion ratios.
[b] not detected.

Quantitative analyses for mustard, mustard sulphoxide and thiodiglycol. A trace amount of mustard (7 ppb, *ca.* 1 ng) was detected in the dichloromethane extract of wool sample 2. Possible traces of mustard sulphoxide were not confirmable by ion ratios. No thiodiglycol was detected.

Samples 4A and 4B

Extraction with full scanning GC–MS. The total ion current chromatogram from soil sample 4A contained two major peaks of interest, identified as tetryl and a tri-butyl phosphate. Comparison with reference samples showed that the latter was not tri-*n*-butyl phosphate but the isobutyl isomer on the basis of retention time and minor differences in the mass spectra (*e.g.* very low abundance of *m/z* 125). The extract from soil sample 4B contained only one significant volatile component, identified as the explosive tetryl.

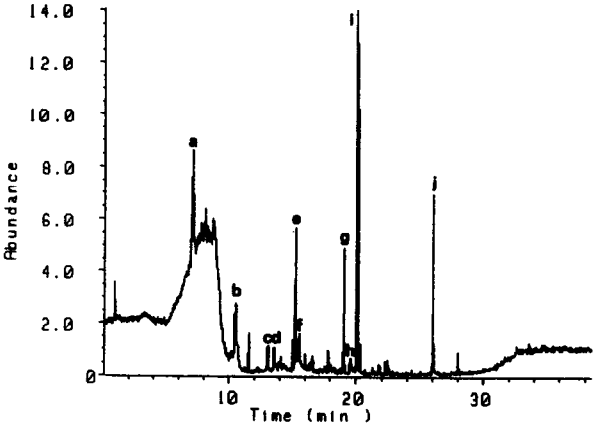

Fig. 3. Thermal desorption (50°C) of soil sample 1: GC–MSD total ion current chromatogram. Peaks identified were: a = 2-chloroethyl vinyl sulphide, b = 2-(vinylthio)ethanol, c = 1,4-dithiane, d = 2-(vinylsulphinyl)ethanol, e = 1,4,5-oxadithiapane, f = sulphur mustard, g = bis(2-chloroethyl) disulphide, h = (2-hydroxyethylthio)ethyl vinyl sulphide, i = bis[2-(vinylthio)ethyl] ether and j = dibutyl phthalate.

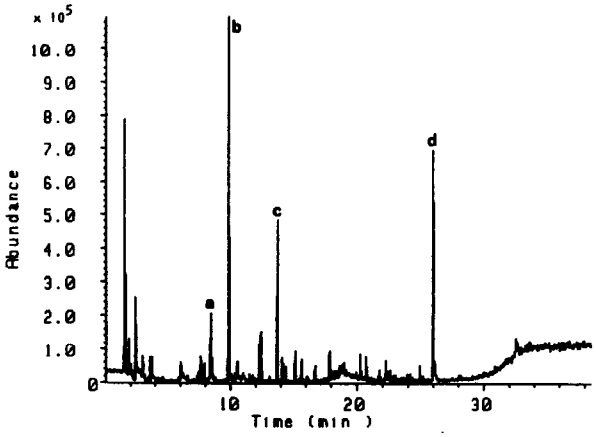

Fig. 4. Thermal desorption (250°C) of metal fragment 4B: GC–MSD total ion current chromatogram. Peaks identified were a = 2-methyl-1,3-thioxalane, b = 1,4-thioxane, c = 1,4-dithiane and d = dibutyl phthalate.

Thermal desorption. Thermal desorption of soil sample 4A at 250°C yielded traces of 1,4-dithiane; soil sample 4B yielded 1,4-dithiane and 1,4-thioxane. The metal fragment in sample 4B also yielded these cyclic products plus a smaller amount of 2-methyl-1,3-thioxalane. The total ion

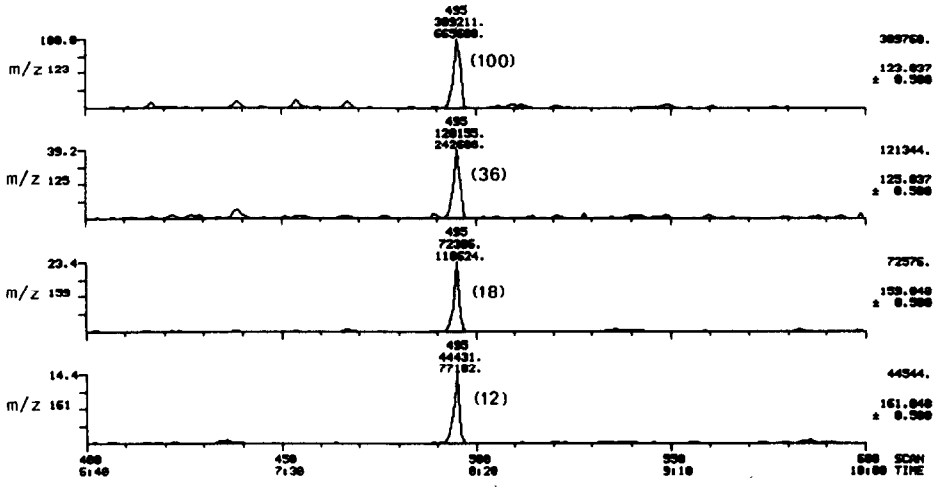

Fig. 5. Dichloromethane extract of metal fragment 4A: selected ion current chromatograms for m/z 123, 125, 159 and 161, showing the detection of sulphur mustard. Ion ratios are shown in parentheses.

current chromatogram obtained from the metal fragment 4B is shown in Fig. 4.

Quantitative analysis for mustard, mustard sulphoxide and thiodiglycol. Low concentrations (up to 27 ppb) of mustard and thiodiglycol were detected in extracts of soil samples 4A and 4B, as shown in Table III, plus a trace of mustard sulphoxide (4 ppb) in sample 4B. Trace levels of mustard and thiodiglycol were also detected in extracts of metal fragment 4A. Selected ion current chromatograms showing the detection of mustard on fragment 4A, and thiodiglycol in soil sample 4B, are shown in Figs. 5 and 6.

DISCUSSION

The results provided unambiguous evidence that the samples were contaminated with sulphur mustard, plus related compounds resulting from hydrolysis, oxidation, elimination reactions, thermal decomposition, or the manufacturing process. Several of these related compounds were detected by D'Agostino and Provost [7] in

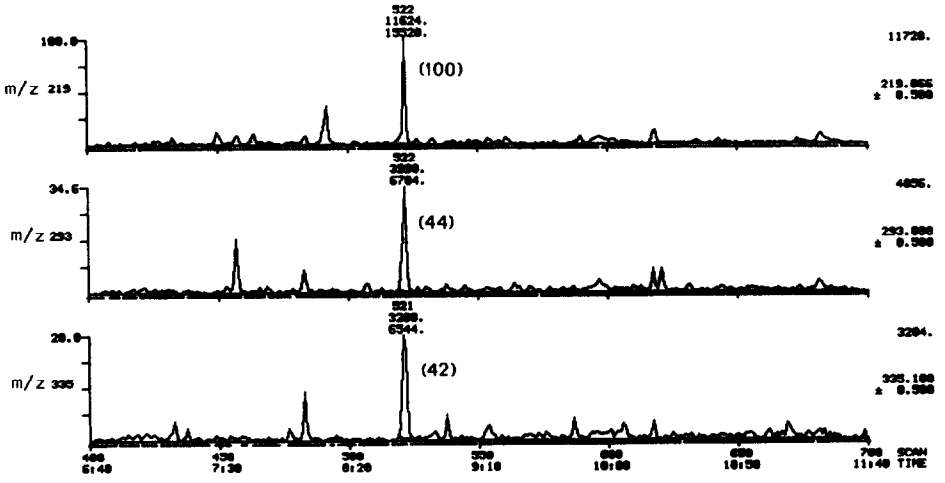

Fig. 6. Ethyl acetate extract of soil sample 4B: selected ion current chromatograms for m/z 219, 293 and 335, showing the detection of thiodiglycol as its bis-TBDMS derivative. Ion ratios are shown in parentheses.

munition residues and hydrolysates of sulphur mustard or in a different soil sample [7,8] obtained from the Iraq–Iran region. The additional detection of two explosives, tetryl and trinitrotoluene, supported the conclusion that the samples originated from a chemical weapon. The samples were also analysed for traces of nerve agents, Lewisite and their hydrolysis products but with negative results.

The bulk soil sample 1 was relatively heavily contaminated with sulphur mustard and related compounds at concentrations in the ppm range. The wool, metal fragments and their associated soil contained trace (nanogram) levels of mustard and thiodiglycol. The different levels of contamination found in the samples allowed a useful comparison of the different methods of analysis employed. With the high levels present in sample 1, all methods of analysis gave positive results for sulphur mustard and related compounds. As would be expected, the more volatile compounds predominated in the headspace and thermal desorption analyses, and these methods provide a very useful means of concentrating these volatiles from high levels of background materials. Cyclic products predominated when soil was thermally desorbed at the higher temperature of 250°C. Headspace and thermal desorption methods did not however detect the major contaminant of the soil which was the hydrolysis product thiodiglycol, although the cyclic products observed at high thermal desorption temperatures may be partly derived from thiodiglycol. Extraction was clearly superior for detecting the less volatile compounds such as thiodiglycol, and these are likely to be particularly important under environmental conditions where hydrolysis is favoured. The method of analysis employed was more crucial for samples where contamination was at low ppb levels. Mustard and thiodiglycol were detected in extracts of all of the samples which were analysed using extraction with GC–MS-selected ion monitoring, where the analysis was directed specifically at these compounds. Thermal desorption, with full scanning GC–MS, also provided a very sensitive method, cyclic decomposition products 1,4-thioxane and/or 1,4-dithiane being detected in all samples analysed with the exception of wool sample 2. Fig. 3 shows the excellent signal-to-noise ratios obtained with this method. Combined with selected ion monitoring thermal desorption would be even more sensitive. The methods employed are therefore complementary, each providing different information, and each with certain advantages depending on the state and amount of the sample, the concentrations of the analytes and the level of background present.

The hydrolysis product thiodiglycol and hydrolysis/elimination product 2-(vinylthio)ethanol appear to be useful indicators of mustard contamination in soil samples when employing extraction methods. The soil in these samples was collected some 10–12 weeks after the incident from an area in cool conditions (0–6°C daytime temperatures) with some rain. Thiodiglycol was present in sample 1 at concentrations approximately 50 times those of sulphur mustard. Cyclic decomposition products, 1,4-thioxane and 1,4-dithiane, appear to be useful indicators of mustard contamination when using thermal desorption analysis. In these particular samples the oxidation product mustard sulphoxide, which reacts with water considerably slower than does sulphur mustard, was present at lower concentrations than mustard.

CONCLUSIONS

Headspace analysis, solvent extraction and thermal desorption methods, in combination with GC–MS, have been successfully applied to the confirmation of sulphur mustard in the residues from a chemical weapon. In addition to the intact agent, 21 compounds related to sulphur mustard were detected plus traces of the explosives TNT and tetryl.

REFERENCES

1 S.J. Lundin, in *SIPRI Yearbook (1989). World Armaments and Disarmament*, Oxford University Press, New York, 1989, Ch. 4.
2 A. Hay and G. Roberts, *JAMA, J. Am. Med. Assoc.*, 263 (1990) 1065.
3 E. Mattila, K. Siivinen, H. Kenttamaa and P. Savolahti, *Int. J. Mass Spectrom. Ion Phys.*, 47 (1983) 371.
4 *Systematic Identification of Chemical Warfare Agents B.3.*

Identification of Non-Phosphorus Warfare Agents, Ministry of Foreign Affairs of Finland, Helsinki (1982).
5 R.M. Black, K. Brewster, J.M. Harrison and N. Stansfield, *Phosphorus, Sulfur Silicon Relat. Elem.*, 71 (1992) 31.
6 E.R.J. Wils and A.G. Hulst, *Fresenius' Z. Anal. Chem.*, 321 (1985) 471.
7 P.A. D'Agostino and L.R. Provost, *Biomed. Environ. Mass Spectrom.*, 15 (1988) 553.
8 P.A. D'Agostino and L.R. Provost, *J. Chromatogr.*, 436 (1988) 399.