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Speciation of arsenic-containing chemical warfare agents by gas chromatographic analysis after derivatization with thioglycolic acid methyl ester

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ABSTRACT

Various organoarsenic halogenides, oxides and hydroxides were converted into the corresponding thioarsenites by reaction with thioglycolic acid methyl ester (TGM). The yields and the chemical structures of the TGM derivatives were evaluated by gas chromatography coupled with mass spectrometry and atomic emission spectrometry.

INTRODUCTION

During World Wars I and II, chemical warfare agents were produced in large amounts. After 1945, in Germany, the plants were destroyed and the stockpiles were sunk in the sea or deposited in dumping grounds, floated gravel pits and other places. These deposits still pose a serious risk today. For mapping out contaminated areas, monitoring the groundwater, etc., appropriate an alytical methods are required. One important group within these hazardous chemicals are the organoarsenic halogenides [1]. Representative substances, as far as available for this study, are listed in Table I, together with some presumable decomposition products. The objective of our work was to find a suitable method for detecting, identifying and quantifying such arsenic contaminants.

As it was thought to be the best choice, we decided to apply the gas chromatographic (GC) separation technique, coupled with mass spectrometry (MS) and atomic emission spectrometric detection (AED): by means of AED the elemental composition of the GC peak can be determined [2,3] which complements the MS identification in an ideal manner; furthermore, AED should enable us to quantify the analytes even in cases where authentic reference substances are not available.

However, thermally labile substances such as IV, V and VI (see Table I) cannot be gas chromatographed reliably as the precursor II and the hydrolysis products I and VIII–XI are totally inaccessible to GC [4]. Consequently, in the literature various methods are described for converting such substances into chromatographable derivatives: trimethylsilylation [5,6] (leading to rather unstable products [7]), reduction to hydrides [8,9] (not applicable for aryl arsenic compounds [10] and conversion into iodides [6] and thioarsenites [7,11–14]. In each case, however, the authors applied their procedures only to distinct groups of substances, mostly arsinic acids, or single compounds such as Lewisite (V).

As the most promising alternative with respect to general applicability, we opted for conversion into thioarsenites using thioglycolic acid methyl ester

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TABLE I

ARSENIC COMPOUNDS SUBJECTED TO DERIVATIZATION

	Compound	Formula	CA-RN	Source	Purity (%)	Stock solution (μmol/ml)
I	Sodium arsenite	$NaAsO_2$	7784-48-5	Merck	p.a.	0.05 *M*
II	Arsenic trichloride	$AsCl_3$	7784-34-1	Merck	Supra-pur	3.06
III	Methylarsin dibromide	H_3CAsBr_2	676-70-0	K&K Lab.	93	2.12
IV	Ethylarsin dichloride	$H_5C_2AsCl_2$	598-14-1	–[a]	?	3.40[b]
V	2-Chlorovinylarsin dichloride	$ClCH=CHAsCl_2$	541-25-3	–[a]	96	2.56
VI	Phenylarsin dichloride	$C_6H_5AsCl_2$	696-28-6	–[a]	–90[c]	3.69
VII	Diphenylarsin chloride	$(C_6H_5)_2AsCl$	712-48-1	–[a]	94[d]	3.53
VIII	Dimethylarsinic acid	$(CH_3)_2As(O)OH$	75-60-5	Aldrich	98	3.44
IX	Phenylarsinic acid	$C_6H_5AsO(OH)_2$	98-05-5	Aldrich	98	2.88
X	Phenylarsin oxide	C_6H_5AsO	637-03-6	Aldrich	97	2.76
XI	Diphenylarsinic acid	$(C_6H_5)_2As(O)OH$	4656-80-8	–[a]	?	1.25[b]
XII	Bis(diphenylarsin)oxide	$[(C_6H_5)_2As]_2O$	2215-16-9	–[a]	93	0.96

[a] Analytical samples were made available by the Bundesministerium Verteidigung, Bonn, Germany, via the Wehrwissenschaftliche Dienststelle der Bundeswehr, Munster, Germany.
[b] Assuming 100% purity.
[c] Contained 4% compound VI.
[d] Contained 5% compound V.

(TGM). According to refs. 7, 12 and 13, TGM reacts in acidic aqueous solution with monomethylarsinic acid (MMA), dimethylarsinic acid (DMA), inorganic arsenite and arsenate in the following way to yield derivatives detectable by GC:

$$\underset{\text{DMA}}{(H_3C)_2As(O)OH} + 3\,\underset{\text{TGM}}{HSCH_2C(O)OCH_3} \rightarrow$$

$$\underset{\text{DMA-SGM}}{(H_3C)_2As\text{-}SCH_2C(O)OCH_3} +$$

$$\underset{(SGM)_2}{H_3CO(O)CCH_2S\text{–}SCH_2C(O)OCH_3} + 2\,H_2O$$

According, MMA yields $H_3CAs(SGM)_2$, and from inorganic arsenicals $As(SGM)_3$ is formed [12,13]. The derivatives contain the arsenic exclusively in the trivalent state; arsenic(V) compounds are reduced by the thiol, which in turn is oxidized to the disulphide.

After some procedural modifications, this derivatization reaction can now be applied to all the substances listed in Table I. Using GC–MS and GC–AED analysis, the chemical structures of the reaction products and their overall yields were evaluated.

EXPERIMENTAL

Chemicals

The following chemicals were used: dichloromethane, nanograde (Promochem), redistilled; *n*-hexane, nanograde (Promochem); thioglycolic acid methyl ester (TGM, CA-RN 2365-48-2), 98% (Aldrich), stored under argon to prevent oxidation; 0.005 *M* sulphuric acid, Titrisol (Merck); triphenylarsine, 97% (Aldrich); 1.4-dithiane, 97% (Aldrich); 1,2,4-trichlorobenzene, 99%+ (Aldrich); *n*-pentadecane, 99+% (Aldrich). The extraction solution contained 5 μg (23.54 nmol) of pentadecane per ml of *n*-hexane. The arsenic compounds used for the derivatization experiments are listed in Table I. The purities of V, VII and XII were determined by GC–AED analysis; the value given for VI is an estimate, because this compound was not reliably chromatographable; IV and IX could not be gas chromatographed at all.

Gas chromatographic equipment and conditions

Gas chromatography–mass spectrometry. An HP 5890 II gas chromatograph with an on-column injection port, an HP 7673 autosampler, and an HP 5970 B mass-selective detector (Hewlett Packard)

were used. The conditions were as follows: retention gap, WCOT FS deactivated, 2 m × 0.53 mm I.D. ("methyl", Chrompack 8009 3552); GC column HP 1, cross-linked methylsilicone, 25 m × 0.17 mm I.D. (Hewlett-Packard); helium, 55 kPa (0.6 ml/min); oven, 40°C (2 min), 10°C/min to 250°C (40 min); injection volume, 1 μl.

Gas chromatography–atomic emission spectrometry. The gas chromatograph, autosampler, retention gap and oven programme were as above. The conditions were as follows: atomic emission detector, HP 5921 A with ChemStation 5895 A (Hewlett Packard); the GC column was as described above but 25 m × 0.31 mm I.D.; helium 150 kPa; AED, ferrule purge 30.4, cavity vent 76.4 ml/min; nitrogen 2 l/min; oxygen 140, helium 350, helium 200, nitrogen/methane 450 kPa; injection volume, 1 μl.

Calibration of GC–AED

The GC–AED system was calibrated for the elements carbon, hydrogen, arsenic, chlorine and sulphur using four different concentrations of standard solutions in iso-octane, containing mixtures of the following compounds (concentration range in brackets): triphenylarsine (4–40 nmol/ml), 1,4-dithiane (15–150 nmol/ml), 1,2,4-trichlorobenzene (30–300 nmol/ml), pentadecane (6–60 nmol/ml); the concentrations of the first two solutions were corrected for the 97% purity indicated by the supplier.

Using oxygen as the reagent gas, carbon, hydrogen and chlorine were measured at 495.724, 486.133 and 480.192 nm, respectively; with oxygen and hydrogen as the reagent gas, carbon was determined at 193.031 and sulphur 181.379 nm; arsenic was measured at 189.042 nm applying hydrogen as the reagent gas and an increased make-up flow.

Using three GC injections per standard solution at each of the three reagent gas settings, linear calibration functions were obtained in each case. From these, the individual response factors were derived. With the lowest concentrations of solutions, the highest standard deviations were found as follows: 5% (carbon, 193 nm); 2% (carbon, 496 nm); 17% (hydrogen); 2% (arsenic); 4% (chlorine); 3% (sulphur). Under the conditions applied, the detection limits (pg/s) were for carbon 193, 3; carbon 496, 65; hydrogen, 5; arsenic, 56; chlorine, 181; sulphur, 17.

Derivatization and analysis

From one of the individual stock solutions, 10 μl were pipetted into a 1.8-ml crimp-top vial containing 500 μl of 0.05 *M* sulphuric acid. After flushing the headspace with argon, 10 μl (106 μmol) of TGM were added and the vial closed with a septum (PTFE/butyl rubber) and kept for 30 min in an ultrasonic bath at 60–70°C. After cooling to room temperature, the vial was opened, 400 μl of extraction solution (see above) were added and the vial was closed and shaken for 2 min. From the organic phase, 250 μl were transferred into an autosampler vial with a 250-μl insert and analysed by GC–MS and GC–AED (injection volume 1 μl). The experiments were carried out in duplicate.

Evaluation of results

The peak areas, obtained from the AED signals (Fig. 1), were converted into pg atoms (1 pg atom = $1 \cdot 10^{-12}$ g atoms) of the respective element. Taking the lowest number of pg atoms (here generally that of arsenic) as unity, an approximate empirical formula and presumable molecular weight were calculated. This was compared with the information given by the mass spectrum, to confirm the structure of the reaction product. The empirical formula was then recalculated on the basis of the number of carbon atoms (theoretically) present in the molecule (with respect to the calibration procedure, the carbon data should be most reliable).

Knowing the empirical formula and the pg atoms of carbon and of any other element) present in the GC peak, the picomoles which had reached the detector could be calculated. A similar calculation for the internal standard gave the procedural recovery ratio (pentadecane introduced/found). After correcting the picomoles of analyte in the same way, the overall yield was calculated by relating the picomoles of analyte found to the amount of starting compound which had been introduced into the assay.

RESULTS AND DISCUSSION

From each of the compounds listed in Table I, a thioarsenite derivative could be obtained. In addition, several attempts were made to derivatize 5,10-dihydrophenarsazin chloride (adamsite, CA-RN 578-94-9) in this way but were unsuccessful. It is

TABLE II

TGM DERIVATIVES OF ARSENIC COMPOUNDS

Key fragments[a] in the mass spectra ("SGM" = $-SCH_2COOCH_3$).

Starting compound[a]	Derivative (mol. mass)	M^+ (%)	M^+-15 (%)	M^+-73 (%)	M^+-105 (%)	285 (%)	180 (%)	107 (%)
I, II	$As(SGM)_3$ (390)	–	–	3	100	(100)	8	18
III	$H_3CA_s(SGM)_2$ (300)	–	96	3	100	(96)	1	30
IV	$H_5C_2As(SGM)_2$ (314)	–	20	5	18	100	4	32
V	$ClC_2H_2As(SGM)_2$ (346)	–	–	1	22	1	100	20
VI, IX, X	$C_6H_5As(SGM)_2$ (362)	5	–	6	100	1	22	18
VII, XI, XII	$(C_6H_5)_2AsSGM$ (334)	30	–	100	28	–	12	10
VIII	$(H_3C)_2AsSGM$ (210)	38	100	35	25	–	–	23

[a] Tentative interpretation: M^+-15 = M^+-CH_3; M^+-73 = M^+-$CH_3C(O)OCH_2$; M^+-105 = M^+-$SCH_2C(O)OCH_3$; 285 = $As(SGM)_2$; 180 = AsSGM; 107 = AsS.

not clear whether the product formed could not be gas chromatographed or whether adamsite did not react at all.

The results obtained from the GC–MS runs are given in Table II. As expected, the products obtained from phenylarsin dichloride, phenylarsin oxide and phenylarsinic acid exhibited identical mass spectra, as did those from the corresponding diphenylarsinic compounds VII, XI and XII. Molecular ions appeared only in the spectra of thioarsenites containing either one SGM group or a phenyl moiety attached to the arsenic atom. The formation of $M^+ - 15$ fragments was confined to methyl- and ethylarsenic compounds. $M^+ - 105$ represents the structure-related key fragment, in each case accompanied by the mass 107 (arsenic sulphide [11]).

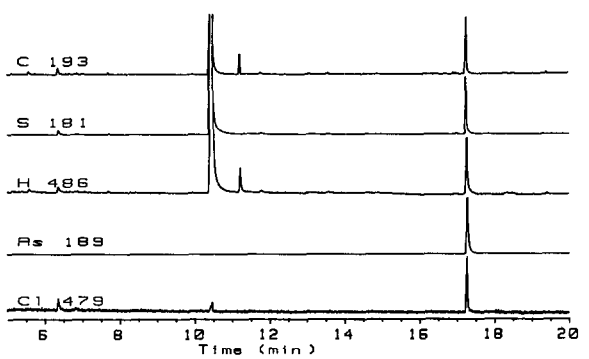

Fig. 1. GC–AED chromatogram of a sample (diluted 1:5 with hexane) containing the TGM derivative of compound V (Lewisite): 6.8 min, unknown; 10.9 min, disulphide $(SGM)_2$ (impurity from the reagent); 11.2 min, pentadecane, 4.7 pmol; 17.3 min, $ClC_2H_2As(SGM)_2$, 44 pmol.

The empirical formulae resulting from the GC–AED analysis are given in Table III, together with the overall yields and the relative retention times (RRT = retention time of analyte/retention time of pentadecane). The elemental compositions found are consistent with the formulae derived from the mass spectra. In the empirical formulae, the deviations from the theoretical values amount to 20%. The source of these errors is not yet clear; with growing experience in handling this analytical system, which is relatively new in our laboratory, a somewhat better performance will probably be achievable.

Regarding the reactivity towards TGM, the twelve test substances behaved differently. For example, DMA could be derivatized completely even at room temperature within a few minutes,

TABLE III

TGM DERIVATIVES OF ARSENIC COMPOUNDS

Relative retention times (RRT), empirical formulae and overall yields ("SGM" = $-SCH_2COOCH_3$).

Starting compound	Derivative, empirical formula	RRT[a]	Empirical formula found[b]					Overall yield	
			C	H	As	Cl	S	Pmol found[c]	%
I	$As(SGM)_3$	1.82							
	$C_9H_{15}AsO_6S_3$		9	12.4	0.9	–	3.1	10	40
II	$As(SGM)_3$	1.82							
	$C_9H_{15}AsO_6S_3$		9	13.9	1.1	–	3.0	29	37
III	$H_3CAs(SGM)_2$	1.31							
	$C_7H_{13}AsO_4S_2$		7	11.1	0.8	–	1.9	40	81
IV	$H_5C_2As(SGM)_2$	1.38							
	$C_8H_{15}AsO_4S_2$		8	12.8	0.9	–	2.1	45	53[d]
V	$ClC_2H_2As(SGM)_2$	1.55							
	$C_8H_{12}AsClO_4S_2$		8	11.2	1.1	0.9	2.1	44	66
VI	$C_6H_5As(SGM)_2$	1.77							
	$C_{12}H_{15}AsO_4S_2$		12	16.1	1.0	–	2.2	68	~80
VII	$(C_6H_5)_2AsSGM$	1.69							
	$C_{15}H_{15}AsO_2S$		15	14.5	0.9	–	1.1	85	103
VIII	$(H_3C)_2AsSGM$	0.61							
	$C_5H_{11}AsO_2S$		5	12.7	1.0	–	0.9	87	102
IX	$C_6H_5As(SGM)_2$	1.77							
	$C_{12}H_{15}AsO_4S_2$		12	12.5	0.9	–	2.0	56	80
X	$C_6H_5As(SGM)_2$	1.77							
	$C_{12}H_{15}AsO_4S_2$		12	15.6	0.8	–	2.2	55	81
XI	$(C_6H_5)_2AsSGM$	1.69							
	$C_{15}H_{15}AsO_2S$		15	16.9	1.1	–	1.1	15	47[d]
XII	$(C_6H_5)_2AsSGM$	1.69							
	$C_{15}H_{15}AsO_2S$		15	14.3	1.0	–	1.2	32	82

[a] Relative retention time: RRT = retention time of analyte/retention time of pentadecane, retention time of pentadecane: GC–MS, 16.8 min; GC–AED, 11.2 min.

[b] The reference element carbon, is underlined; oxygen was not determined.

[c] Upon GC injection of 1 μl.

[d] Assuming the starting compound to be of 100% purity.

whereas under these conditions the halogenated compounds gave only poor yields, or none at all. Hence, the procedure described is the result of an optimization with regard to the slow-reacting compounds. By lowering the temperature, it may be possible to increase the yield of the most thermolabile derivatives, $As(SGM)_3$ and $ClC_2H_2As(SGM)_2$; however, the main losses, probably occur on the GC column [11]. Upon split–splitless injection into the hot injector (250°C), all TGM derivatives underwent thermal decomposition; hence, exclusively on-column injection was applied.

The reaction mixture should be acidic [12,13]; in fact, no chromatographable products could be extracted from slightly alkaline solutions. The content of dichloromethane, a common extracting solvent, in the reaction mixture should not exceed 10%; addition of 20% dichloromethane resulted in lower yields and several non-identified byproducts.

As mentioned above, the derivatives contain arsenic in the trivalent state; arsenic(V) compounds are reduced by the reagent, from which an equivalent amount of disulphide (RRT 0.94) is formed. This offers an opportunity for differentiating between arsenic(III) and arsenic(V) compounds.

From the test substances VI, IX and X, the same

product, $C_6H_5As(SGM)_2$, is formed, and VII, XI, XII all lead to $(C_6H_5)_2AsSGM$. In a water analysis, for example, a certain discrimination between the different starting compounds is still possible; upon extraction with dichloromethane, VI, VII and XII will be transferred into the organic phase, whereas the two acids IX and XI remain in the aqueous phase (the partitioning behaviour of phenylarsin oxide may be ambivalent). Direct GC of the organic phase will yield phenylarsin dichloride, VI (RRT 1.14, but not reliably chromatographable), diphenylarsin-chloride, VII (RRT 1.37) and bis(diphenylarsin) oxide, XII (RRT 2.82); derivatization leads to $C_6H_5As(SGM)_2$ in an amount corresponding to VI and X, and to $(C_6H_5)_2AsSGM$ from VII and XII. Finally, derivatization in the (preconcentrated) aqueous phase yields the derivatives of IX + X and XI; the portion of IX in IX + X can be estimated from the amount of disulphide formed. In this context it should be noted, however, that repeated injections of arsenic tri- and dichlorides cause irreversible damage to the GC column.

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REFERENCES

1 K. E. Jackson, *Chem. Rev.*, 17 (1935) 251.
2 B. D. Quimby and J. J. Sullivan, *Anal. Chem.*, 62 (1990) 1027.
3 J. J. Sullivan and B. D. Quimby, *Anal. Chem.*, 62 (1990) 1034.
4 Z. Witkiewicz, M. Mazurek and J. Szulc, *J. Chromatogr.*, 503 (1990) 293.
5 C. J. Soderquist, D. G. Bowers and D. G. Crosby, *Anal. Chem.*, 46 (1974) 155.
6 F. T. Henry and T. M. Thorpe, *J. Chromatogr.*, 166 (1978) 577.
7 B. Beckermann, *Anal. Chim. Acta*, 135 (1982) 77.
8 Y. Taimi and D. T. Bostic, *Anal. Chem.*, 47 (1975) 2145.
9 H. Mukai and Y. Ambe, *Anal. Chim. Acta*, 193 (1987) 219.
10 S. Franke, *Militärchemie*, Vol. 2, Deutscher Militärverlag, Berlin, 2nd ed., 1976, p. 340.
11 U. Hannestad and B. Sörbo, *J. Chromatogr.*, 200 (1980) 171.
12 K. Dix, C. J. Cappon and T. Y. Torbara, *J. Chromatogr. Sci.*, 25 (1987) 235.
13 H. Haraguchi and A. Takatsu, *Spectrochim. Acta*, 42B (1987) 235.
14 J. K. Fowler, D. S. Stewart and D. S. Weinberg, *J. Chromatogr.*, 558 (1991) 235.