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Capillary gas chromatography–atomic emission spectroscopy–mass spectrometry analysis of sulphur mustard and transformation products in a block recovered from the Baltic Sea

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Abstract

A block of yperite fished up from the Baltic Sea was analysed by gas chromatography coupled with atomic emission spectrometry and mass spectrometry. In the samples of the block about 50 compounds were detected, out of which 30 were identified. The identification of the compounds was performed by using the element chromatograms of the investigated compounds, and the data obtained by mass spectrometric detection. Thiodiglycol was not found among the compounds present in the investigated block. The calculations of the contents of sulphur mustard and some products in the block were performed by an external calibration method using bis(2-chloroethyl) sulphide as the standard. A satisfactory precision of elements determinations was obtained (RSD from 4.4 to 14.3%).

Keywords: Warfare agents; Sulphur mustard

1. Introduction

Analysis of chemical warfare agents (CWA) in complex environmental samples is a very important problem. It is connected, among other things, with the contamination of the marine environment by sulphur mustard (yperite) [1,2] and with the resolutions of the Convention on the Prohibition of Chemical Weapons [3].

The analytic techniques of high sensitivity, selectivity and speed of analysis are needed for the analyses of CWA. The most widely used technique for the analysis of yperite and its relatives has been capillary gas chromatography [4–8]. High-performance liquid chromatography has also been applied to successful identification of sulphonium ions formed during yperite storage and hydrolysis [9,10]. The chromatographic techniques permit for separating these agents and their degradation products in the environmental samples. One of the degradation products is thiodiglycol, the main product of hydrolysis of yperite [11–13].

The introduction of gas chromatography with an atomic emission detection (GC–AED) in the second half of the nineteen eighties [14] has contributed to the fact that gas chromatography becomes a more effective and universal analytical technique. GC–

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AED gives not only information about the number of sample components but also about their elemental composition [15]. This information, in combination with the information obtained by mass spectrometry (MS) [16], gives identification capability of compounds and the reliability of the analysis.

GC with AED was already used for the detection of CWA, their degradation products and CWA simulant in the environmental samples [15,17–22]. The possibilities of CWA analysis using gas chromatography with AED and MS were also described in a review [23].

In this work we report the analytical procedures employed to identify yperite residues in an yperite block, fished up by the crew of the cutter WŁA 206 in January 1997 from the Baltic Sea. The unidentified block was drawn from the net and placed on board the cutter. As an effect of contact, eight of the fishermen crew were poisoned by yperite and four were hospitalised. Initial chemical analysis made by military service showed that the block contained yperite. The identification of the compounds is performed using GC with AED and MS.

2. Experimental

2.1. Sample preparations

The yperite block was yellow–brown with a consistency resembling clammy grease and some part of it was solid. The mass of the block was about 5–6 kg. Ten small samples were taken randomly from different parts of the block and they were analysed separately. The samples were stored at ambient temperature in closed vials placed in a desiccator filled with anhydrous silica. The samples (ca. 2 g) were each extracted with 50 ml of dichloromethane and extracted by mechanical shaking for 20–30 min. After 5 min standing, the supernatants were decanted and filtered; extracts with a yellow to brown colour were obtained. The extracts were transferred to 10-ml vials fitted with PTFE-lined screw caps and concentrated, if required, to a small volume (ca. 200 μl) under nitrogen at 40°C.

2.2. Standards

Bis(2-chloroethyl) sulphide, the standard of yperite, was synthesised according to Meyer's method in our laboratory and its purity was confirmed by GC analysis. The purity of the standard was above 99%.

For quantitative determination of yperite, the main component of the yperite block, standard solutions of yperite in dichloromethane at concentrations from 0.01 to 2 mmol l^{-1} were used. The solutions were kept in closed glass test tubes for two weeks at ambient temperature.

2.3. Gas chromatography with atomic emission spectrometry

The dichloromethane extracts were analysed using a HP 6890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with AED type HP 2350A. The instrument was controlled and data were edited with an HP 35920A ChemStation program.

For separating the samples components a HP-5 fused-silica capillary column (30 m×0.32 mm I.D.) coated with 95% methyl- and 5% phenyl polysiloxane of 0.25 μm film thickness was used. The volume of the injected sample was 1 μl. Helium was used as carrier gas, at a flow-rate of 2 ml/min. The high purity (99.99%) reaction gases such as oxygen, hydrogen and mixture of methane with nitrogen (1:9, v/v) were used. The temperature of the injector was 260°C and the temperature of the transfer line between column and detector was 280°C. The temperature of the column was programmed: from 40°C (3 min) at the rate of increase 10°C/min to 280°C (30 min). The selected basic working characteristics of the AED are presented in Table 1.

2.4. Gas chromatography with mass spectrometry

The samples were also analysed using a Varian gas chromatograph type 3400/Magnum equipped with an ion trap mass spectrometric detector (Finnigan MAT, Hemel Hempstead, England).

The gas chromatograph was fitted with 30 m× 0.32 mm I.D. an HP-5 MS bonded phase column with film thickness of 0.25 μm. The chromatographic separations of yperite and its transformation products by GC–MS were performed under similar conditions as those used with the GC–AED system. The differences in chromatographic conditions were: the flow-rate of carrier gas was 2 ml/min at constant

Table 1
Basic working characteristics of the atomic emission detector

Group of elements[a]	Element	Wavelength [nm]	Limit of detection[b] [pg/s]	Relative standard deviation of determination [%] $N=5$	Reaction gases	Make-up flow [ml/min]
I	S	181	1	5.1	H_2/O_2	40
	C	193	0.5	4.4	H_2/O_2	40
II	Cl	479	15	6.8	O_2	–
	H	486	2	8.0	O_2	–
	C	496	20	5.7	O_2	–
III	O	171	50	14.3	$H_2/(CH_4:N_2$, 1:9 v/v)	–
IV	As	189	3	8.2	H_2	40

[a] In the first column the groups of elements simultaneously detected are indicated.
[b] Theoretical values, according to Hewlett-Packard data.

pressure of 103 kPa and the injected sample volume was 2 μl.

The mass spectrometer was operated in electron ionisation mode. The energy of electrons was 70 eV, the emission current 400 μA and temperature of the ions source was 215°C. The ions of the investigated compounds were detected in the range from 40 to 400 amu at a scanning rate of 0.7 s/scan.

2.5. Quantitative analysis

The quantitative analysis of the detected compounds was performed using an external calibration method with bis(2-chloroethyl) sulphide.

2.6. Stability study

To determine the stability of yperite and its transformation products, the samples of the yperite block were analysed by GC-AED during a period of 1.5 year.

3. Results and discussion

Ten samples of different consistency and colours were taken to the analysis. The extracts of these samples were preliminarily analysed using TLC and a few samples containing the greatest quantities of yperite and its transformation products were chosen for further GC analysis. The TLC procedure of the analysis is described elsewhere [24]. The composition of the samples was determined using GC with AED and MS.

About 50 compounds were detected in the samples of the yperite block during their gas chromatographic separations. Apart from the peak of yperite, other peaks were present in the chromatograms. The number of the compounds was different in particular samples of the yperite block.

The C, S, and Cl element chromatograms of one of the investigated samples are shown in Fig. 1A and 1B. Due to the different amount of particular compounds in the same sample the parts of chromatograms on Fig. 1A and 1B were registered at different attenuation. It is clear that the sulphur and chlorine traces are especially relevant to the identification of yperite and related compounds. The element chromatograms permit the evaluation of the total number of detected compounds in the samples (about 50) and the compounds containing in their molecules sulphur (30) and chlorine (31). The peaks of the compounds are well separated from each other and they are characterised by different retention times. All of the compounds contain different quantities of carbon, sulphur and chlorine in their molecules.

The peak identification of yperite was carried out by the comparison of the retention time of its

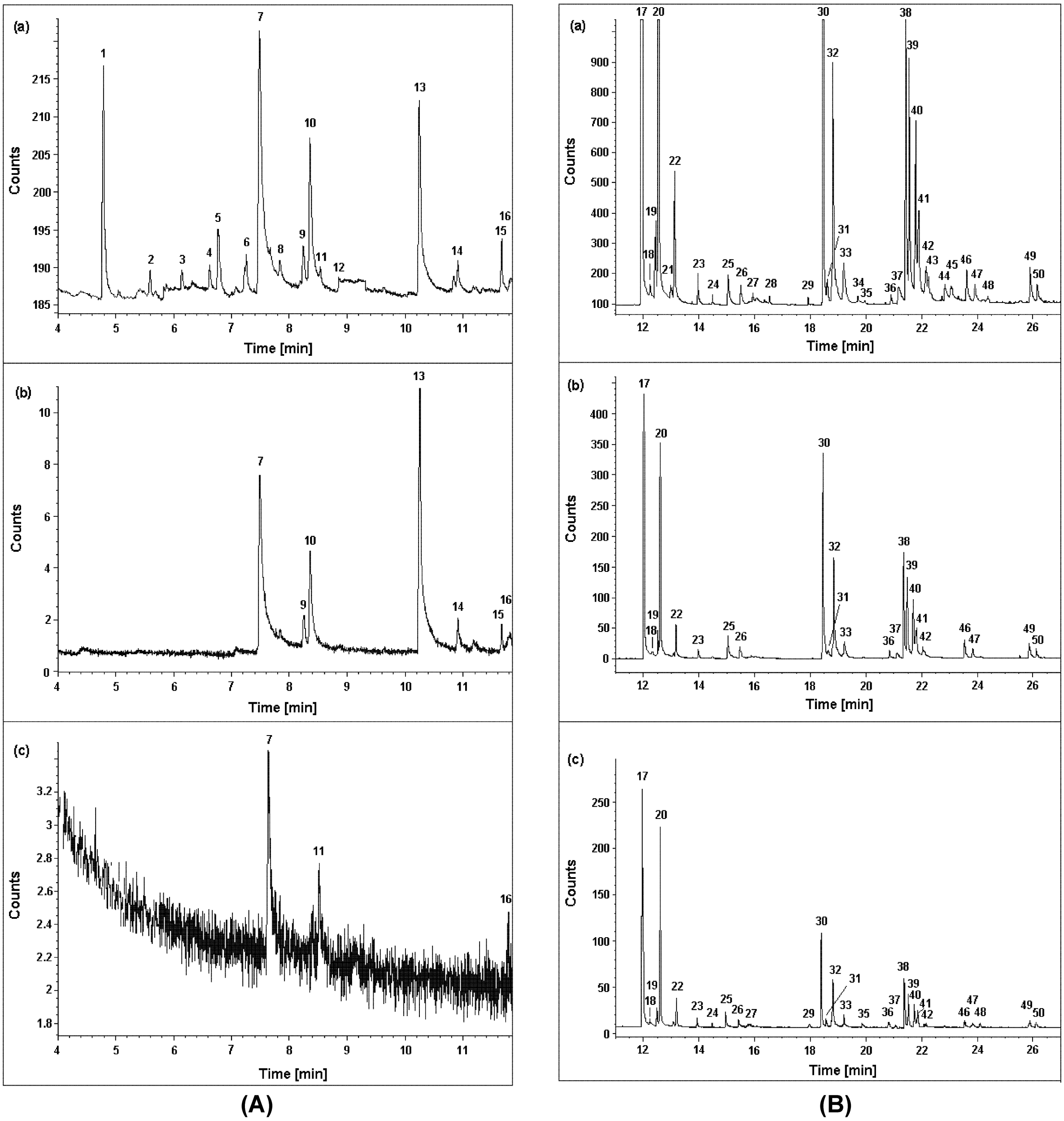


Fig. 1. (A) The first part of the element chromatograms of a sample of the yperite block obtained by GC–AED on channel: (a) carbon, C–193 nm, (b) sulphur, S–181 nm and (c) chlorine, Cl–479 nm; split ratio 20:1. (B) The second part of the element chromatograms of a sample of the yperite block obtained by GC–AED on channel: (a) carbon, C–193 nm, (b) sulphur, S–181 nm and (c) chlorine, Cl–479 nm; split ratio 60:1.

standard with the retention times of the proper compound of the samples. Bis(2-chloroethyl) sulphide standard in dichloromethane and the solutions of mixtures containing the investigated samples were used for the comparison. It was found that the largest peak, with a retention time of 12.03 min (peak 17 in Fig. 1B), corresponds to yperite.

Apart from compounds containing sulphur or chlorine, compounds containing oxygen in their molecules were also detected. These compounds containing oxygen are the potential products of oxidation and/or hydrolysis of yperite. Oxygen is the element with the weakest response (ca. 50 pg/s), but this element is generally detected by other detectors with even greater difficulty [25]. The chromatogram obtained on the oxygen channel (Fig. 2) displayed the presence of six compounds. In line with the low oxygen response, the oxygen shows a poor signal-to-noise ratio. The chromatographic analysis did not show the presence of thiodiglycol, the main hydrolysis product of yperite in any of the investigated samples.

Arsenic was also detected in the analysed samples. An arsenic chromatogram is shown in Fig. 3. The greatest peak ($t_R = 19.76$ min) corresponds to chlorodiphenylarsine (Clark I), whose identity was confirmed by GC–MS.

The presence of arsenic compound in the analysed block may be caused by its addition to sulphur mustard, to bring down the melting point of yperite for its military use in cold regions. It cannot also be excluded, that the yperite block had had contact with an arsenic substance, which sunk in the same region of the Baltic Sea [26].

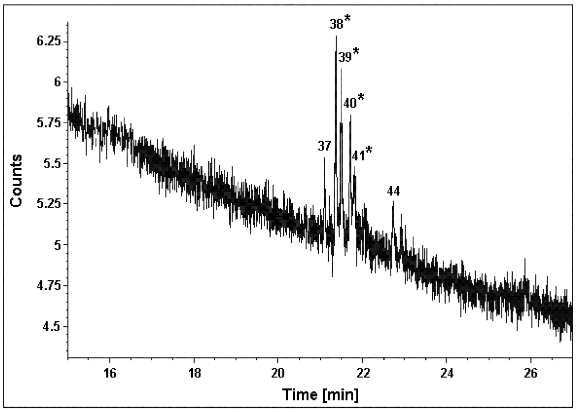


Fig. 2. Oxygen chromatogram (O–171 nm) of a sample of the yperite block obtained by GC–AED. Starlets mark oxygen mustards. The peaks of 37 and 44 represent aliphatic ethers.

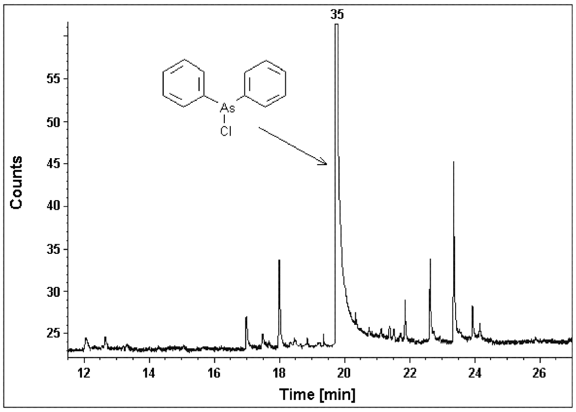


Fig. 3. Element chromatogram of chlorodiphenylarsine (Clark I) detected in the sample of the yperite block obtained by GC–AED on arsenic channel (As–189 nm). The remaining peaks originate from environmental residues.

The investigations aimed at the detection of nitrogen or phosphorus did not give any chromatograms with peaks corresponding to these elements. The obtained signals were very weak and comparable to the level of noise.

The elements of the components of samples can be quantitatively determined from the following Eq. [27]:

$$(C/E)_{\mathrm{i}} = \frac{A_{\mathrm{C_i}}}{A_{\mathrm{E_i}}} \cdot RRF_{\mathrm{C/E}} \qquad (1)$$

where: C/E is relation of number of carbon atoms (C) to an other element (E) present in a molecule of unknown component of the sample (i); A_{Ci} is the peak area of unknown component on the chromatogram registered on carbon channel; $A_{\mathrm{E_i}}$ is the peak area of an unknown component on the chromatogram registered on the channel of the other element, e.g.: Cl, O, S; and $RRF_{\mathrm{C/E}}$ is the ratio response factor. The $RRF_{\mathrm{C/E}}$ is determined from the relation:

$$RRF_{\mathrm{C/E}} = \frac{A_{\mathrm{E_o}}}{A_{\mathrm{C_o}}} \cdot (C/E)_{\mathrm{o}} \qquad (2)$$

where the bottom index (o) marks the known compound (yperite standard).

The calculations of element relations (C/E) were performed after four chromatographic separations for every analysed sample, for which the chromatograms of all present elements were received. The element ratios C/E were determined for the same chromatographic separation. The calculated values of C/E for 30 detected components present in the samples of yperite block are set in Table 2. The C/O element fractions were not determined because of lack of proper standard.

Table 2
The calculation results of the element relations of the compounds detected in the samples of the yperite block on the ground of the analysis of the element chromatograms

Peak	Retention time [min]	Element relations[a]			
		C/H	C/Cl	C/S	C/O
7	7.49	0.55	4.24	3.63	
10	8.36	0.47	4.34	–[b]	
13	10.25	0.47	–	1.86	
14	10.91	0.43	–	8.98[c]	+
16	11.77	0.53	10.42[c]	10.07[c]	+
17	12.03	0.50	2.00	3.99	
18	12.33	0.41	4.24	2.82	
19	12.55	0.50	2.63	4.55	
20	12.62	0.51	2.60	4.64	
22	13.17	0.53	3.20	5.47	
23	13.98	0.49	3.17	5.97	
25	15.04	0.50	2.56	2.14	
30	18.60	0.51	2.94	3.05	
31	18.65	0.49	4.03	3.34	
32	18.85	0.54	4.15	3.37	
33	19.23	0.56	7.98	3.89	
35	19.76	1.25	11.45	–	
37	21.12	0.43	–	–	+
38	21.36	0.51	3.98	4.12	+
39	21.48	0.50	4.68	4.31	+
40	21.70	0.53	4.52	4.56	+
41	21.81	0.54	6.49	5.35	+
42	22.04	0.59	6.50	7.14	
43	22.10	0.71	16.99	16.16	
44	22.72	0.71	–	–	+
45	22.98	0.66	–	–	
46	23.53	0.57	4.08	2.45	
47	23.82	0.52	11.81	2.47	
49	25.86	0.58	6.46	3.38	
50	26.12	0.59	9.91	4.14	

[a] C is the reference element.

[b] The sign of minus marks the lack of definite element in the analysed compound and the sign of plus marks the element detected but not determined.

[c] The data obtained for peaks differing less than two times from the noise level.

The quantities of identified components in the analysed samples were evaluated by using an external calibration method. For that purpose, 1 μl of solution containing the standard of yperite in a concentration near to the concentration in the investigated sample was introduced onto the chromatographic column. This procedure was repeated five times introducing solutions with increasing concentrations Calibration curves for carbon, hydrogen, chlorine and sulphur were prepared in this way. The courses of all graphs were linear and the coefficients of correlation were situated in the range from 0.9898 to 0.9970. The agreement between the peak area and the mass for each element was good.

Preserving the same chromatographic conditions 1 μl volumes of the investigated samples were injected onto column and the chromatograms were registered. Putting the obtained values of area of peaks to the equations describing the calibration curves and taking into account the size of the injected sample, the contents of the detected components in the investigated samples were determined.

Using the results of qualitative and quantitative analysis the summary formulae of the components detected in the yperite block were determined. The results are shown in Table 3. The summary formulae were determined by using the ChemStation programme accepting the definite number of carbon atoms, which should be present in the molecules of the analysed components. Carbon was chosen as the reference element, because the sensitivity at its detection wavelength ($\lambda = 193$ nm) makes its determination reliable. Then the number of atoms of the remaining elements were calculated.

Among the detected components 25 were probably the transformation products of yperite and the identity of most of them (16) were confirmed by MS. The identification of the unknown components of the GC–AED analysed samples was performed by GC–MS, with comparison of mass spectra to a standard mass spectrum library of mass spectrometer enriched with additional spectra of sulphur containing compounds. The data characterising the mass fragments of yperite and its transformation products with relative intensities of ions greater than 15% are collected in Table 4. In the investigated block apart

Table 3
The molecular formulae obtained by GC–AED analysis of 30 compounds present in the yperite block fished up from the Baltic Sea

Peak	Empiric formula	Summary formula	Contents[b] [%]
7[a]	$C_4H_{7.27}$	$C_4H_7Cl_1S_1$	0.4–0.8
10	$C_4H_{8.51}Cl_{1.84}$	$C_4H_8Cl_2$	0.1–0.5
13[a]	$C_4H_{8.51}S_{2.15}$	$C_4H_8S_2$	0.1–0.6
14[a]	$C_8H_{18.60}S_{0.89}O_2$	$C_8H_{18}S_1O_2$	0.1–0.3
16[a]	$C_4H_{7.55}Cl_{0.38}S_{0.40}O_1$	$C_4H_7Cl_1S_1O_1$	0.03–0.3
17[a]	$C_4H_{8.00}Cl_{2.00}S_{1.00}$	$C_4H_8Cl_2S_1$	14–20
18	$C_4H_{9.76}Cl_{0.94}S_{1.42}$	$C_4H_9Cl_1S_1$	1–1.6
19	$C_5H_{10.00}Cl_{2.19}S_{1.09}$	$C_5H_{10}Cl_2S_1$	1.4–2.6
20[a]	$C_5H_{9.80}Cl_{1.92}S_{1.08}$	$C_5H_{10}Cl_2S_1$	7–16
22[a]	$C_6H_{11.32}Cl_{1.88}S_{1.09}$	$C_6H_{12}Cl_2S_1$	0.4–3
23[a]	$C_7H_{14.29}Cl_{2.21}S_{1.17}$	$C_7H_{14}Cl_2S_1$	0.8–1.7
25[a]	$C_5H_{10.00}Cl_{1.95}S_{2.33}$	$C_5H_{10}Cl_2S_2$	1.4–1.5
30[a]	$C_6H_{11.76}Cl_{2.04}S_{1.97}$	$C_6H_{12}Cl_2S_2$	12–14.3
31	$C_7H_{14.29}Cl_{1.83}S_{2.09}$	$C_7H_{14}Cl_2S_2$	0.8–1.3
32[a]	$C_7H_{12.96}Cl_{1.48}S_{2.08}$	$C_7H_{13}Cl_1S_2$	8.5–11
33[a]	$C_8H_{14.29}Cl_{1.00}S_{2.06}$	$C_8H_{14}Cl_1S_2$	2–2.6
35[a]	$C_{12}H_{9.60}Cl_{1.05}As_1$	$C_{12}H_{10}Cl_1As_1$	0.5–1.3
37	$C_{10}H_{23.39}O_2$	$C_{10}H_{23}O_2$	0.1–0.3
38[a]	$C_8H_{15.68}Cl_{2.01}S_{1.94}O_1$	$C_8H_{16}Cl_2S_2O_1$	6.5–9.3
39[a]	$C_9H_{18.00}Cl_{1.92}S_{2.09}O_1$	$C_9H_{18}Cl_2S_2O_1$	6–9.7
40	$C_9H_{16.98}Cl_{1.99}S_{1.97}O_1$	$C_9H_{17}Cl_2S_2O_1$	4.3–13.9
41[a]	$C_{10}H_{18.52}Cl_{1.54}S_{1.87}O_1$	$C_{10}H_{19}Cl_1S_2O_1$	2.9–4
42	$C_{14}H_{23.72}Cl_{2.16}S_{1.96}$	$C_{14}H_{24}Cl_2S_2$	0.4–1
43	$C_{17}H_{23.94}Cl_{1.00}S_{1.05}$	$C_{17}H_{24}Cl_1S_1$	1–1.6
44	$C_{10}H_{14.08}O_2$	$C_{10}H_{14}O_2$	0.4–1
45	$C_{12}H_{18.18}$	$C_{12}H_{18}$	0.2–0.3
46	$C_{12}H_{21.05}Cl_{2.94}S_{4.90}$	$C_{12}H_{21}Cl_3S_5$	1.5–4
47	$C_{12}H_{23.08}Cl_{1.02}S_{4.86}$	$C_{12}H_{23}Cl_1S_5$	0.8–2.2
49	$C_{14}H_{24.14}Cl_{2.16}S_{4.14}$	$C_{14}H_{24}Cl_2S_4$	0.4–1.4
50	$C_{13}H_{22.03}Cl_{1.13}S_{3.14}$	$C_{13}H_{22}Cl_1S_3$	0.4–0.7

[a] The identity of the substance confirmed by mass spectrometry.

[b] The total quantity of unidentified components of the yperite block did not exceed 3.75%.

from compounds of sulphur, the arsenic compound chlorodiphenylarsine was also detected. The mass spectra of the some identified compounds are presented in Fig. 4.

For most of the transformation products of yperite in their mass spectra $M^{+\cdot}$ ions were well visible. Only for oxygenic mustards the $M^{+\cdot}$ ions were weak or absent.

The comparison of the obtained spectra with the spectra published in literature shows their good agreement. Slight differences existing in the mass spectra, e.g. in the spectrum of bis(2-chloroethylthioethyl)ether, refer to the fragmentation ions, the intensities of which differ only a little [28]. The incomplete separation of chromatographed components of the sample can be the reason of the contamination of the given component with another compound present in the sample.

On the basis of the analysis of the obtained spectra suitable constitutional formulae of the detected compounds were determined and they are placed in Table 5. For the majority of components their constitutional formulae agreed with summary formulae (Table 3).

The analysis of the most identified transformation products of yperite evidences proceeding of nucleophilic substitution of yperite and its partial polymerisation. Among the identified compounds,

Table 4
The list of mass spectra of yperite and related compounds plus chlorodiphenyl-arsine

Chemical compound	Mol. mass	Data of mass spectrum[a] [%]	
		$\mathrm{M}^{+\cdot}$[b]	*m*/*z*
2-Chloroethylovinyl sulphide	122	+ (13)	47(21), 49(15), 57(24), 58(78), 59(100), 60(68), 73(81), 121(48), 123(15)
1,4-Dithiane	120	+ (61)	46 (100), 47(17), 58(21), 59(30), 60(22), 61(56), 64(21), 120(61)
2-Chloroethylpropenyl sulphide	137	+ (100)	47(16), 49(17), 56(24), 57(32), 59(37), 61(28), 63(33), 75(20), 137(100), 139(38)
Bis(diethylether) sulphide	178	–	59(72), 73(30), 86(83), 101(53), 131(17), 132(100), 133(36)
2-Chlorovinyl-2-hydroxyethyl sulphide	138	+ (15)	57(18), 58(59), 59(79), 60(50), 63(100), 65(26), 73(52), 76(71), 122(21)
Bis(2-chloroethyl) sulphide (Mustard gas)	158	+ (29)	47(79), 49(26), 58(35), 59(57), 60(37), 61(81), 63(81), 65(25), 73(44), 75(32), 109(100), 111(37), 158(29)
2-Chloroethyl-3-chloropropyl sulphide	172	+ (34)	47(55), 49(22), 59(42), 61(37), 63(51), 73(42), 109(100), 111(38), 123(29), 137(28), 172(34), 174(22)
2-Chloroethyl-4-chlorobutyl sulphide	186	+ (41)	46(61), 47(78), 59(37) 74(29), 75(32), 77(32), 85(32), 87(91), 123(100), 125(38), 151(35), 186(41), 188(26)
2-Chloroethyl-5-chloropentyl sulphide	200	+ (4)	53(18), 55(20), 59(35), 61(53), 63(35), 67(22), 69(100), 123(84), 125(30)
Bis(2-chloroethyl) sulphone	190	+ (47)	46(24), 58(31), 59(100), 63(89), 64(47), 73(22), 92(30), 128(26), 190(47), 192(36)
Bis(2-chloroethyl) disulphide	190	+ (47)	58(24), 59(33), 63(100), 64(39), 65(35), 79(16), 92(23), 128(21), 190(47), 192(35)
2-Chloroethyl-3-chloropropyl disulphide	204	+ (66)	47(42), 49(40), 57(33), 58(42), 59(66), 61(30), 63(100), 64(59), 65(36), 73(85), 77(74), 79(54), 92(33), 128(75), 130(31), 204(66), 206(51)
Bis(2-chloroethyl) sulphoxide	174	+ (6)	49(12), 59(16), 63(100), 65(27), 76(23), 83(13), 109(28), 111(14)
1,2-Bis(2-chloroethylthio)ethane	218	+ (4)	46(33), 47(35), 58(42), 59(69), 60(53), 61(69), 63(89), 73(53), 109(40), 122(30), 123 (100), 125(38)
1-(2-Chloroethylthio)-3-vinylthio-*n*-propane	196	+ (40)	46(29), 47(26), 59(47), 60(31), 61(66), 63(39), 87(26), 123(100), 125(37), 137(39), 196(40)
1-(2-Chloroethylthio)-3-propenylthio-*n*-propane	210	+ (24)	46(24), 47(24), 59(40), 60(26), 61(65), 73(22), 87(33), 137(100), 139(39), 210(24)
Chlorodiphenylarsine	264	+ (11)	50(16), 51(31), 77(15), 151(19), 152(19), 154(100), 227(14)
Bis(2-chloroethylthioethyl) ether	262	–	46(24), 47(18), 59(49), 60(67), 61(100), 63(68), 65(20), 122(47), 123(91), 124(19), 125(34)
(2-Chloroethylthioethyl)- -(2-chloroethylthiopropyl) ether	276	–	46(18), 59(31), 61(70), 63(44), 123(100), 125(37), 137(16)
(2-Chloroethylthiopropyl)-(allylthioethyl) ether	254	+ (3)	46(21), 47(19), 59(34), 60(24), 61(95), 63(31), 73(19), 123(20), 136(23), 137(100), 139(38)

[a] In parentheses the values of intensity of fragmentation ions expressed in percentages are given.

[b] Plus sign marks presence of $\mathrm{M}^{+\cdot}$ ion in the spectrum.

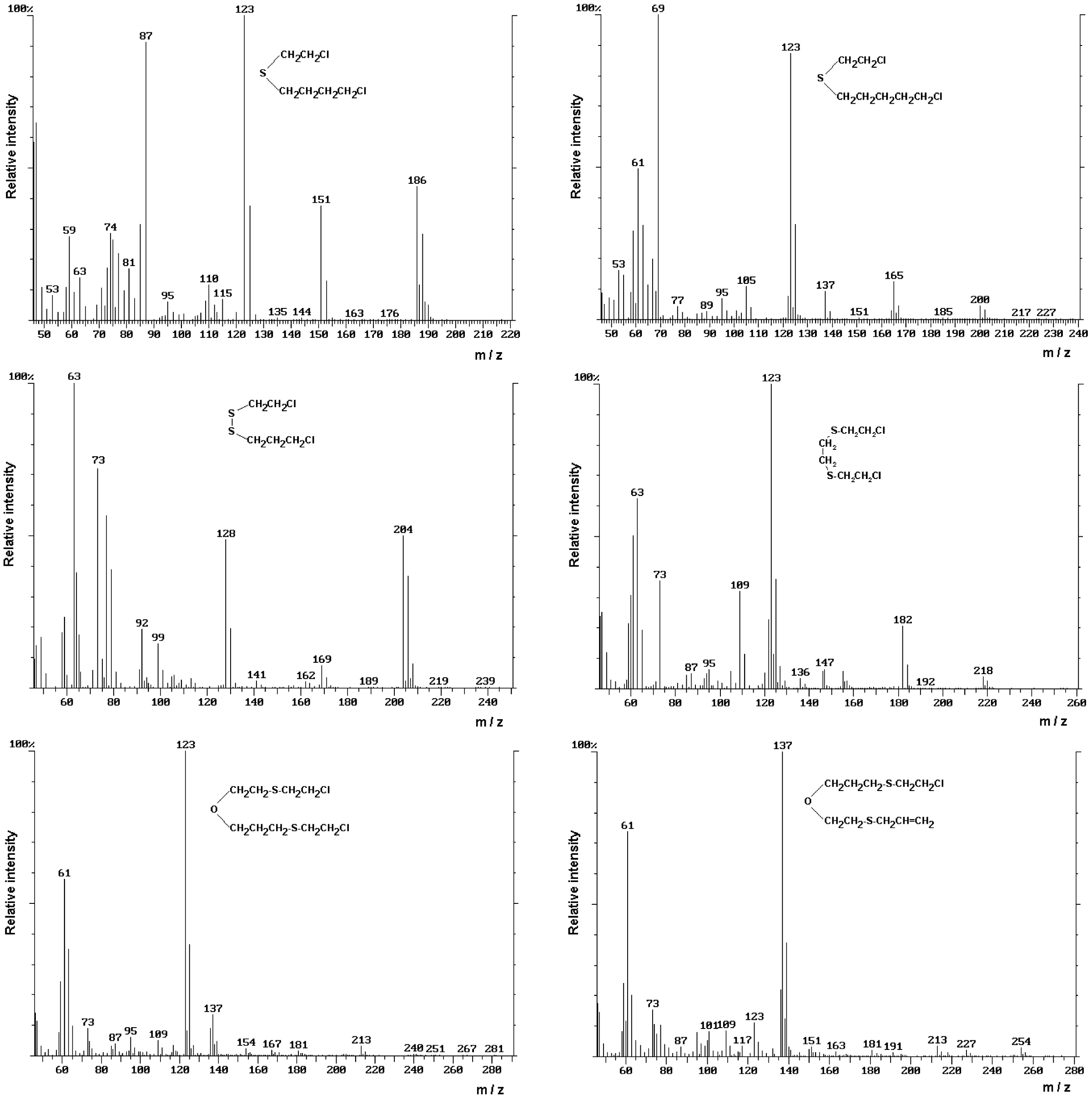


Fig. 4. The selected mass spectra of some compounds detected in the dichloromethane extract of the yperite block.

two of them, the retention times of which were 21.48 min (peak 39) and 21.81 min (peak 41), have probably not been known till now. These are compounds belonging to the group of oxygenic mustards – (2 - chloroethylthioethyl) - (2 - chloroethyl - thiopropyl)ether and (2-chloroethylthiopropyl)-(allylthioethyl)ether.

The results obtained during the chromatographic investigations show, in soluble parts of the yperite block, the maximum presence of some toxic substances, such as: yperite–to 20%; sesquiyperite and its analogues–to 29%; oxygenic yperites–to 33%; oligomeric yperite–to 7%; and chlorodiphenyloarsine–to 1.3%. Their percent shares in the whole

Table 5
The list of chemical compounds identified by GC–MS in the yperite block

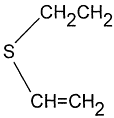
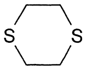
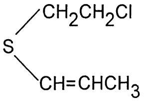
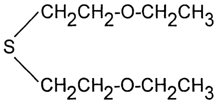
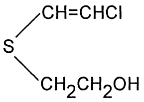
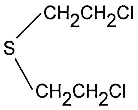
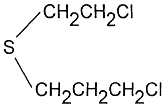
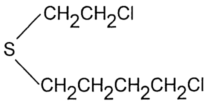
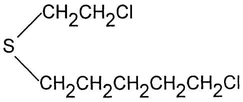
Relative retention time[a]	Name of compound	Constitutional formulae
0.62	2-Chloroethylovinyl sulphide	
0.85	1,4-Dithiane	
0.91	2-Chloroethylpropenyl sulphide	
0.91	Bis(diethylether) sulphide	
0.98	2-Chlorovinyl-2-hydroxyethyl sulphide	
1.00	Bis(2-chloroethyl) sulphide (Yperite)	
1.05	2-Chloroethyl-3-chloropropyl sulphide	
1.09	2-Chloroethyl-4-chlorobutyl sulphide	
1.16	2-Chloroethyl-5-chloropentyl sulphide	

Table 5. Continued

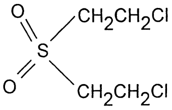
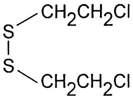
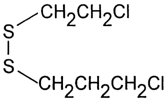
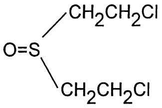
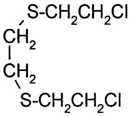
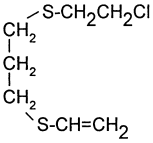
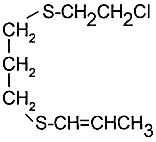
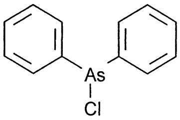
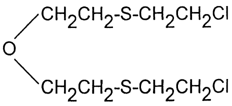
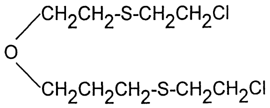
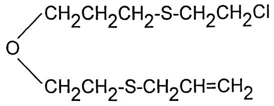
Relative retention time[a]	Name of compound	Constitutional formulae
1.21	Bis(2-chloroethyl) sulphone	
1.23	Bis(2-chloroethyl) disulphide	
1.25	2-Chloroethyl-3-chloropropyl disulphide	
1.26	Bis(2-chloroethyl) sulphoxide	
1.55	1,2-Bis(2-chloroethylthio) ethane	
1.57	1-(2-Chloroethylthio)-3-vinylthio-*n*-propane	
1.60	1-(2-Chloroethylthio)-3-propenylthio-*n*-propane	
1.64	Chlorodiphenylarsine	
1.78	Bis(2-chloroethylthioethyl) ether	

Table 5. Continued

Relative retention time[a]	Name of compound	Constitutional formulae
1.79	(2-Chloroethylthioethyl)- -(2-chloroethylthiopropyl) ether	
1.81	(2-Chloroethylthiopropyl)- (allylthioethyl) ether	

[a] According to yperite.

mass of the block are however much lower and depend on the kind of the investigated samples. The error of quantitative determination for the same components (maximum to 14.3%) did not have importance in meaning because the yperite block was non-homogeneous and the composition of its fragments was accidental.

The comparatively small amount of yperite in the investigated yperite block can be caused by the fact, that it was probably only a part of yperite preparation, in which a thickening agent was the major part of the block. That kind of condensed preparations was used in some types of chemical ammunition. The investigated block could have been formed after the complete corrosion of metal walls of ammunition or container as a result of physico–chemical processes of yperite preparation with components of sediments and other materials present on the sea bottom.

The comparative analysis of samples of the yperite block was carried out after about 1.5 years and the chromatograms received were very similar to one another.

4. Conclusions

The obtained results indicate that some part of sulphur mustard sunken in the Baltic Sea may exist in a not changed form after 50 years. The other compounds present in the block (sesquiyperite and its analogues as well as oxygenic compounds) may originate from the transformation of another part of sulphur mustard or may be the components of technical sulphur mustard which was used in chemical munitions. It cannot be excluded, that apart from chemical compounds detected in the yperite block using gas chromatography other compounds (ionic and with bigger molecule masses) not amenable to gas chromatography were present in it [9].

An interesting observation was made that the final product of hydrolysis of yperite, thiodiglycol, was not present in the yperite block. Presumably thiodiglycol, as a water-soluble substance, passes to water and therefore was not detected in the investigated samples [29].

The knowledge of the existence in the Baltic Sea, CWA and products of their transformation determines the base of all activities connected with the dumped chemical munition. It includes the qualification of the real threats originating from the sunken chemical ammunition and the possibilities of counteraction.

Acknowledgements

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