Short Original Communications

Determination of Chemical Warfare Agents

Gas Chromatographic Analysis of Ethylarsine Dichloride by Derivatization with Dithiols

(3rd Communication)

Rainer Haas

Corresponding address: Dr. Rainer Haas, Büro für Altlastenerkundung und Umweltforschung, Stadtwaldstr. 45a,
D-35037 Marburg, Germany

Abstract

Ethylarsine dichloride was used during WW I as a chemical warfare agent. Residues of this chemical warfare agent and its metabolites are still present today and continue to contaminate soil and water.

A gas chromatographic method for the detection and determination of ethylarsine dichloride is shown. Six dithiols were tested as possible derivatization reagents for ethylarsine dichloride. With selection of the dithiol, matrix interferences can be eliminated because of the different retention times of the derivatives.

Keywords: Analysis; arsenic compounds; chemical warfare agents; cwa; derivatization; detection; determination; ethylarsine dichloride; gas chromatography

1 Experimental

Ethylarsine dichloride [CAS-No.: 598-14-1] was produced in WW I as a chemical warfare agent. Ethylarsine dichloride can be detected with GC/ECD without derivatization. It reacts with dithiols by forming cyclic derivatives that can be detected with GC/ECD as well.

Derivatizations with dithiols are performed with 1,2-ethane dithiol [$Et(SH)_2$], 1,3-propane dithiol [$Pr(SH)_2$], 1,4-butane dithiol [$Bu(SH)_2$], 1,5-pentane dithiol [$Pe(SH)_2$], 1,6-hexane dithiol [$He(SH)_2$] and 1,8-octane dithiol [$Oc(SH)_2$].

For the derivatization, 20 µl of an acetonic dithiol solution [c = 100 g/l] and 20 µl of an acetonic ethylarsine dichloride solution [c = 6.8 g/l] is added to 500 µl acetone in 1.4 ml-vials (reaction time: 15 min; T = 20°C).

For the separation of ethylarsine dichloride and its dithiol derivatives, an HP 5890 gas chromatograph with HP 7673 autosampler and electon capture detector (ECD) was used. The temperatures of the injector block and the detector were 250°C and 300°C, respectively. The injection volume was 1 µl (split injection). A DB 5 column, 30 m, 0.25 mm i.d., 0.25 mm d_f was used. The carrier gas was nitrogen (head pressure 100 kPa). The column temperature was started at 100°C (1 min), was raised with 10°C/min to 230°C and then held for another 6 min.

2 Results and Discussion

Ethylarsine dichloride reacts with dithiols in a substitution reaction by forming cyclic compounds:

$EtAsCl_2 + R(SH)_2 \rightarrow EtAsS_2R + 2\ HCl$.

The derivatization is completed in 15 min at a temperature of 20°C. The cyclic derivatives are stable. The derivatives can be detected with GC/ECD. They were identified with mass spectrometry. In **Table 1**, the retention times and the limits of detection of ethylarsine dichloride and its dithiol derivatives is shown.

Table 1: Retention times (t_R) and limits of detection (LOD) of ethylarsine dichloride and its dithiol derivatives; for GC conditions see experimental data

thiol	derivative	t_R/min	LOD/ng
---	$EtAsCl_2$	2.84	3.5
$Et(SH)_2$	$EtAsS_2Et$	3.88	1.3
$Pr(SH)_2$	$EtAsS_2Pr$	5.48	3.5
$Bu(SH)_2$	$EtAsS_2Bu$	7.49	3.5
$Pe(SH)_2$	$EtAsS_2Pe$	12.26	3.5
$He(SH)_2$	$EtAsS_2He$	13.33	3.5
$Oc(SH)_2$	$EtAsS_2Oc$	15.77	1.7

The reaction of ethylarsine dichloride with the six tested dithiols is quantitative. After derivatization, no ethylarsine dichloride can be detected with GC/ECD.

Through the use of 1:1 molar mixtures of two dithiols, different rates of the possible derivatives are built. These rates present the thermodynamic stability of the cyclic ethylarsine dithiol derivatives. The most stable products are the derivatives of ethylarsine dichloride with 1,2-ethane dithiol and 1,3-propane dithiol. The same effect was shown for the derivatization of phenylarsine dichloride (PFIFFIKUS) and 2-chlorovinylarsine dichloride (LEWISITE I) with dithiols [1,2]. All of these arsenic containing chemical warfare agents are able to form cyclic derivatives. The results are shown in **Table 2**.

Table 2: Rate of ethylarsine dithiol derivatives by using equimolar mixtures of two dithiols

thiol 1	thiol 2	derivative 1 %	derivative 2 %
Et(SH)$_2$	Pr(SH)$_2$	97	3
Et(SH)$_2$	Bu(SH)$_2$	99	1
Et(SH)$_2$	Pe(SH)$_2$	97	3
Et(SH)$_2$	He(SH)$_2$	97	3
Et(SH)$_2$	Oc(SH)$_2$	99.5	0.5
Pr(SH)$_2$	Bu(SH)$_2$	87	13
Pr(SH)$_2$	Pe(SH)$_2$	100	0
Pr(SH)$_2$	He(SH)$_2$	67	33
Pr(SH)$_2$	Oc(SH)$_2$	81	19
Bu(SH)$_2$	Pe(SH)$_2$	25	75
Bu(SH)$_2$	He(SH)$_2$	29	71
Bu(SH)$_2$	Oc(SH)$_2$	36	64
Pe(SH)$_2$	He(SH)$_2$	56	44
Pe(SH)$_2$	Oc(SH)$_2$	51	49
He(SH)$_2$	Oc(SH)$_2$	39	61

The derivatization procedure is quick and easy and the analysis is highly selective. The limits of detection differ between 1.3 ng and 3.5 ng. By choosing an appropriate dithiol, matrix interferences can be eliminated because of the different retention times of the resulting ethylarsine derivatives.

This derivatization reaction can be used for the gas chromatographic detection and determination of ethylarsine dichloride in contaminated water and soil samples together with other arsenic containing chemical warfare agents, e.g. diphenylarsine chloride (CLARK I), phenylarsine dichloride (PFIFFIKUS), 2-chlorovinylarsine dichloride (LEWISITE I) and 2,2'-dichlorodivinylarsine chloride (LEWISITE II) [1,2,3,4].

Figure 1 shows the overlayed gas chromatograms of five cyclic ethylarsine dithiole derivates.

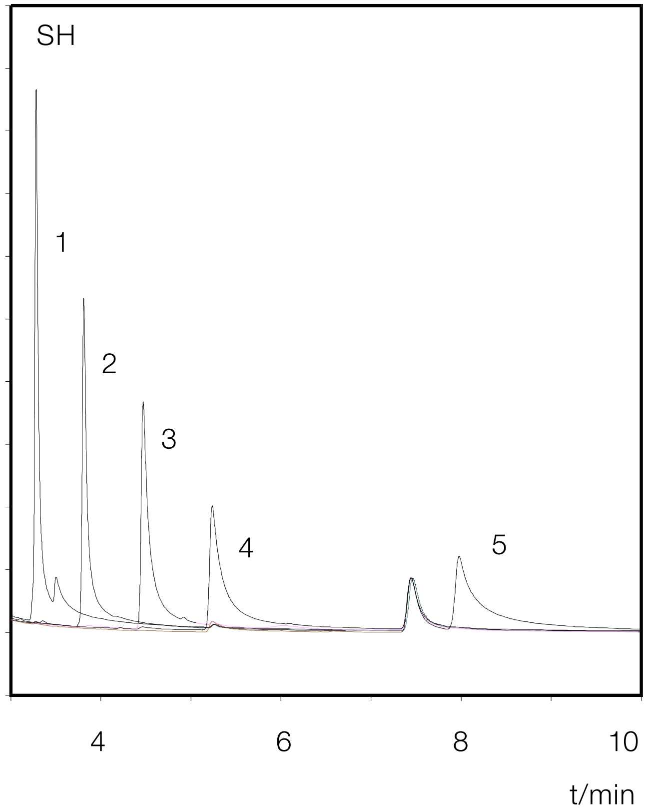

Fig. 1: Overlayed gas chromatograms of ethylarsine dichloride derivatives (68 ng) with Pr(SH)$_2$ [1]; Bu(SH)$_2$ [2], Pe(SH)$_2$ [3], He(SH)$_2$ and Oc(SH)$_2$; GC conditions see experimental data; column temperature: 210°C isotherm

3 References

[1] Haas, R.; Schmidt, T.C. (1997): Chemische Reaktionen von Phenylarsinverbindungen. 3. Reaktion von Phenyl-Arsen-Verbindungen mit Dithiolen. UWSF – Z. Umweltchem. Ökotox. 9 (1997), 183-184

[2] Haas, R. (1998): Chemische Reaktionen von Chlorvinylarsinverbindungen (Lewisite). 3. Reaktion von Lewisit I und Lewisit II mit Dithiolen. UWSF-Z. Umweltchem. Ökotox. in print

[3] Haas, R. (1997): Chemische Reaktionen von Phenylarsinverbindungen. 2. Reaktion von Diphenylarsinverbindungen mit Dithiolen. UWSF – Z. Umweltchem. Ökotox. 9 (1997), 123-124

[4] Haas, R.; Schmidt, T.C.; Steinbach, K.; v. Löw, E. (1997): Gaschromatographische Bestimmung von Arsenkampfstoffen und Umwandlungsprodukten. Fachtagung Rüstungsaltlasten (Grundwassersanierung), Munster 7./8.10.97

Received: October 24th, 1997
Accepted: February 23rd, 1998