

## Short Original Communications

## Determination of Chemical Warfare Agents

## Gas Chromatographic Analysis of Chlorovinylarsines (Lewisite) and their Metabolites by Derivatization with Thiols

(2nd Communication)

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## Abstract

Chlorovinylarsines (Lewisites) were produced and handled during WW I and WW II as chemical warfare agents. Residues of these cwa and their metabolites are still present today and continue to contaminate soil and water.

A gas chromatographic method for the detection and determination of chlorovinylarsines (Lewisites) and their metabolites is shown. Lewisite II and Lewisite III, but not Lewisite I and the metabolites of Lewisite I and Lewisite II can be detected and determined using GC/ECD. After derivatization with thiols, the sum of Lewisite I or Lewisite II and their metabolites are detected. With the proper selection of the thiol, matrix interferences can be eliminated because of the different retention times of the derivatives.

**Keywords:** Analysis; arsenic compounds; chemical warfare agents; chlorovinylarsines; cwa; derivatization; detection; determination; gas chromatography; Lewisite

## 1 Introduction

2-Chlorovinylarsine dichloride (Lewisite I) was produced in WW I and WW II as a chemical warfare agent by Friedel Craft's alkylation of arsenic(III)chloride with ethine. During this production process, the by-products 2,2'-dichlorodivinyarsine chloride (Lewisite II) and 2,2',2''-Trichlorotrivinyarsine (Lewisite III) are built. A mixture of these chlorovinylarsine compounds was filled into cwa munition [1]. Old cwa munition continue to contaminate soil and water still today. Sometimes the original cwa are hydrolyzed or oxidized. These metabolites cannot be detected and determined with gas chromatographic analysis. After derivatization with thiols, the metabolites can be identified and determined with gas chromatography and an ECD detector.

## 2 Experimental

Lewisite II and Lewisite III, but not Lewisite I, can be detected with GC/ECD without derivatization. For the gas chromatographic detection of Lewisite I and the hydrolysis and oxidation products of Lewisite I and Lewisite II, a derivatization procedure is necessary. Lewisite I and its metabolites react with thiols by forming 2-chlorovinylarsine dithioether, Lewisite II and its metabolites react with thiols by forming 2,2'-dichlorodivinyarsine thioether.

For the derivatization, 20 µl of a thiol solution (c = 40 g/l) in acetone is added to 500 µl of an acetonic Lewisite solution (reaction time: 15 min; T = 20°C).

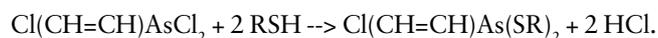
In analogy to the reactions of phenylarsenic compounds [2,3,4], oxidation products of Lewisite I and II should be reduced in the first reaction step to the corresponding As(III) compounds, while the thiols are oxidized to disulfides.

Derivatizations are performed with 1-ethane thiole [EtSH], 1-propane thiole [PrSH], thioglycolic acid methyl ether [TGM] and thioglycolic acid ethyl ether [TGE].

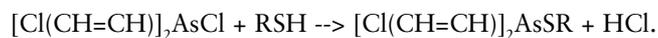
For the separation of the Lewisites and their derivatives, an HP 5890 gas chromatograph with HP 7673 autosampler and electron capture detector (ECD) was used. The temperatures of the injector block and the detector were 250°C and 300°C, respectively. The injection volume was 1 µl (split injection). A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

## 3 Results and Discussion

2-chlorovinylarsine dichloride (Lewisite I) reacts with thiols in a substitution reaction by forming 2-chlorovinylarsine dithioether:



2,2'-Dichlorodivinylarsine chloride (Lewisite II) reacts with thiols in a substitution reaction by forming 2,2'-dichlorodivinylarsine thioether:



The derivatives can be detected with GC/ECD and were identified with mass spectrometry. In Table 1, the retention times and the limits of detection of the Lewisites and their thiol derivatives are shown.

2,2',2''-Trichlorotrivinylarsine (Lewisite III) does not react with thiols. It can be determined very sensitively using GC/ECD without derivatization ( $\rightarrow$  Table 1).

The reaction of Lewisite II with the four tested thiols is quantitative. The derivatization is completed in 15 min at a temperature of 20°C. After derivatization, the sum of Lewisite I and its metabolites, or Lewisite II and its metabolites, is detected. These derivatives are more stable than other reaction products. e.g. hydrolysis products or ether [5,6].

The derivatives are stable. This derivatization reaction can be used for the gas chromatographic detection and determination of Lewisites and their metabolites in contaminated water and soil samples.

The derivatization procedure is quick and easy and the analysis is highly selective. By choosing an appropriate thiol, ma-

trix interferences can be eliminated because of the different retention times of the resulting thioether.

#### 4 References

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Received: October 24th, 1997

Accepted: February 23rd, 1998

**Table 1:** Retention times ( $t_r$ ) and limits of detection (LOD) of Lewisites and their thiol derivatives; GC conditions see experimental data; L1:  $\text{Cl}(\text{CH}=\text{CH})\text{As}$ ; L2:  $[\text{Cl}(\text{CH}=\text{CH})]_2\text{As}$

compound	thiol	derivative	$t_r$ min	LOD ng
LEWISITE I	EtSH	L1(SET) <sub>2</sub>	10.84	0.4
LEWISITE I	PrSH	L1(SPr) <sub>2</sub>	12.93	0.4
LEWISITE I	TGM	L1(SGM) <sub>2</sub>	18.34	0.2
LEWISITE I	TGE	L1(SGE) <sub>2</sub>	20.83	0.4
LEWISITE II	---	L2-Cl	7.04	0.35
LEWISITE II	EtSH	L2-SEt	10.13	0.3
LEWISITE II	PrSH	L2-SPr	11.22	0.3
LEWISITE II	TGM	L2-SGM	13.66	0.3
LEWISITE II	TGE	L2-SGE	14.40	0.3
LEWISITE III	---	$[\text{Cl}(\text{CH}=\text{CH})]_3\text{As}$	9.41	0.03