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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Sokołowski, Mieczysław S. , Konopski, Leszek and Fröbe, Zlatko(2008) 'Detection of Lewisite-2 in the Presence of Alcohols and/or Thiodiglycol in Aqueous Matrices', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 183: 7, 1630 – 1640

To link to this Article: DOI: 10.1080/10426500701708137

URL: <http://dx.doi.org/10.1080/10426500701708137>

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Detection of Lewisite-2 in the Presence of Alcohols and/or Thiodiglycol in Aqueous Matrices

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Bis(2-chlorovinyl)chloroarsine (Lewisite-2) was detected in water in the presence of selected alcohols, thiols, hydroxy thiols and diols. The expected alkyl bis(2-chlorovinyl)arsinites or corresponding arsinodithiolites were obtained with alcohols and thiols, whereas reactions with bifunctional hydroxythiols and diols afforded S-thio monoesters or diesters, respectively. This reaction was found useful to smoothly transform at 40°C bis(2-hydroxyethyl) sulfide (thiodiglycol, a sulfur mustard decomposition product), into a stable diarsinite derivative, thiodiglycol bis[bis(2-chlorovinyl)]arsinite. After extraction with dichloromethane, the derivative may be detected easily and selectively using GS/MS, eliminating time-consuming evaporation and derivatization. The method may be applied to analyze Chemical Weapons Convention related environmental water samples.

Keywords Alcohols; derivatization; detection; diols; Lewisite; thiodiglycol; thiols

INTRODUCTION

Bis(2-chlorovinyl)chloroarsine (Lewisite-2 or L2, **1**) is a main impurity of 2-chlorovinylchloroarsine (Lewisite-1, **2**), which usually contains also minor amounts of tris(2-chlorovinyl)arsine (Lewisite-3, **3**). The mixture of these compounds used to be produced as the chemical warfare agent Lewisite. All three compounds are listed in Schedule 1 of toxic chemicals in the Annex on Chemicals of the Chemical Weapon Convention (CWC).¹ In a previous paper,² we have described a reaction of Lewisite-1 (**2**) with alcohols, thiols, hydroxy thiols and diols in water. Similarly to Lewisite-1, Lewisite-2 **1** also easily reacts with alcohols³ and thiols,^{4,5} in organic solvents affording appropriate

Received 12 September 2007; accepted 21 September 2007.

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esters or thioesters of bis(2-chlorovinyl)arsinous acid. Aliphatic dithiols $R(SH)_2$ were reported to produce only monothioesters with a general formula L2-S-R-SH.^{5,6} Also 3,4-dimercaptotoluene (DMT, **4**), a derivatizing agent for 2-chlorovinyl dichloroarsine **2**, produces with its impurity Lewisite-2 (**1**) in hexane the dithioester L2-DMT-L2, 4-methyl-1,2-phenylene bis[bis(2-chlorovinyl)]arsinodithiolite **5** as a side product, detectable using GC/MS.⁷

Reaction products of Lewisite-2 with some primary and secondary C_6 - C_{10} alcohols in water have been also reported recently.⁸ However, to the best of our knowledge, no reaction of Lewisite-2 with diols and hydroxy thiols in water has been described in the literature yet. Since the reaction of Lewisite-1 with bifunctional alcohols, especially with thiodiglycol **6**, afforded stable and easy to chromatograph derivatives,² we decided to investigate the analogous reaction of Lewisite-2 (**1**).

Bis(2-hydroxyethyl) sulfide (thiodiglycol, TDG, **6**), the most important sulfur mustard decomposition product and a starting material for its production as well, is a compound listed in Schedule 2 of toxic chemicals in the Annex on Chemicals of the CWC.¹ Due to its high polarity, TDG is difficult to extract and analyze in water matrices as well as to analyze on GC directly. A short review on TDG derivatization and determination methods was previously presented by us². In the same paper,² a novel method has been described. Derivatization with Lewisite-1 (**2**) in water at a 100 ng/g level afforded volatile cyclic 2-chlorovinyl-1,3,6,2-dioxathiarsothane **7**, easily detectable using GC/MS or GC/FPD.

In this paper, the detection of Lewisite-2 (**1**) in presence of selected primary alcohols, a hydroxy thiol, and a diol (TDG) in water has been investigated, and the resulting derivatization products were analyzed using GC/MS and GC/FID/FPD.

EXPERIMENTAL

Materials

2-Bis(chlorovinyl)dichloroarsine **1**, 5 mg/mL solution in water (Lewisite-2), was obtained from Spiez Laboratories, Spiez, Switzerland. Bis(2-chloroethyl)sulfide **6** (for chromatography, International Enzymes Ltd.), propanol **8** (analytical grade, Baker 99+%), 2-(methylthio)ethanol **9** (Aldrich, 99%), 1-butanethiol **10** (Aldrich, 99%), 2-mercaptoethanol **11** (Aldrich, 98%), sodium cacodylate **24** (Aldrich, 98+%), dichloromethane (analytical grade, Baker, 99.9%), acetone (analytical grade, Baker, 99.5%), 0.1 M hydrochloric acid (analytical grade, Boom), and anhydrous sodium sulfate (Fluka, 99+%) were used.

Water matrix: demineralized or tap water.

Equipment

(a) GC/MS Conditions

HP 6890 Series gas chromatograph was coupled on-line with a HP 5792A Mass Selective Detector (MSD).

GC/MS analysis was performed on Hewlett-Packard HP 6890 GC/5792A MSD. The instrument conditions used were as follows:

GC Conditions. FSOT capillary column, 30 m \times 0.25 mm I.D., phase: 5-HP MS (95% dimethylsiloxane, 5% phenylsiloxane), film 0.25 μ m, carrier gas: helium, constant flow 0.9 mL/min; injection: split/splitless (splitless mode with 1 minute splitless period), injection volume 1–2 μ L (manually), injector temp.: 250°C. Column temperature: 40°C (2 min) then increased to 300°C (10°C/min) and at 300°C (2 min).

Mass Spectrometry Conditions. Electron ionization (EI) at 70 eV, ion source temperature 180°C, trap current 200 μ A, accelerating voltage 1870 V, analyzer: quadrupole. Resolution 0.7 u, mass range 40 to 600 u. The chromatograms were drawn in both Total Ion Current (TIC) and Selected Ions Monitoring (SIM) modes. Chemical Ionization (CI): reagent gas: methane, isobutane.

(b) GC/FID/FPD Conditions

HP 6890 Series gas chromatograph equipped with an autosampler and, in parallel, Flame Ionization Detector (FID) and Flame Photometric Detector (FPD); optical filter wavelength for sulfur: 394 nm. CG conditions: the same as for GC/MS.

Sample Preparation

(a) Derivatization and Sample Preparation—General Procedure

To 1 mL of the water solution of an appropriate alcohol, hydroxy thiol or diol **6** and **8–11** in a 4 mL vial with PTFE-lined screw-caps, the 5 mg/mL water solution of Lewisite-2 (**1**) was added in such amounts, so that the content of alcohol/hydroxy thiol/diol in the solution was in the range 10 ppb (ng/g)–1000 ppm (μ g/g), usually 10–500 ppm, and Lewisite-2 was in molar excess of 1 to 500 times (usually 1 to 5 times). Reaction was usually carried out at pH 6. When the reaction was performed at pH 2, the appropriate amount of 0.1 M aqueous hydrochloric acid was added. The cap was then screwed and derivatization was carried out at 40°C for 2–25 h, usually 17–22 h (overnight). After cooling, the water matrix was washed with dichloromethane (3 \times 1 mL), the combined organic layers were dried with anhydrous sodium sulfate for

30 min and filtered. Depending on the concentration of the alcohol, samples were concentrated (fivefold) in a mild nitrogen flow at room temperature (usually to 500 ppm).

One to two μL of the resulting dichloromethane solution was injected in GC/MS or GC/FID/FPD. Linear (van den Dool) retention indices (RI) were calculated by a linear polygon method⁹ with retention times (R_T) of hydrocarbons from C_8 (octane) to C_{30} (tricosane), 10 $\mu\text{g/mL}$ each, injected under the same conditions in the GC/MS.

All discussed mass spectra fragmentation pathways were confirmed by calculating the intensity of the isotope peaks of the fragmentation ions.

(b) Derivatization of Thiodiglycol 6 with Lewisite-2 (1) in Water

To 1 mL of water containing 500 μg of thiodiglycol **6** (500 ppm) in a 4 mL vial with PTFE-lined screw caps, 380 μL of a water solution of Lewisite-2 (**1**) (5 mg/mL, 2 molar equivalents) was added. The cap was then screwed and derivatization was carried out at 40°C for 17 h (overnight). After cooling the reaction mixture was washed with dichloromethane ($3 \times 1 \text{ mL}$), the combined organic layers were dried with anhydrous sodium sulfate for 30 min and filtered. 1 μL of the resulting dichloromethane solution was injected in GC/MS. Under the above described conditions, the R_T of thiodiglycol *O,O*-bis[bis(2-chlorovinyl)]arsinite (L2-TDG-L2, **23**), was 27.96 min.

(c) Derivatization of 2-Chlorovinylarsinous acid 14 with 1-Butanethiol 10 in Water

One mL of Lewisite-2 in water (1 mg/mL) was washed carefully with dichloromethane ($6 \times 1 \text{ mL}$). To the water phase, containing mainly bis(2-chlorovinyl)arsinous acid **14**, a solution of 1-butanethiol **10** in acetone (5 mg/mL, 100 μL) was added. After 10 min at room temperature, the reaction mixture was worked up as described in general procedure. 1 μL of the organic solution was directly injected in GC/MS and GC/FID/FPD. Under the above-described conditions, R_T of *S*-butyl bis(2-chlorovinyl)arsinothiolite **21** was 17.70 min.

(d) Attempts of Derivatization with Sodium Cacodylate 24

Experiments were performed in the same manner as described in the general procedure, using a 5 mg/mL water solution of sodium cacodylate **24**, and the alcohols **8**, **9** or thiodiglycol **6**, at both pH 6 and pH 2. No derivatization product was detected on GC/MS.

RESULTS AND DISCUSSION

In a water solution, Lewisite-2 undergoes complex transformations, depending on pH. Only if pH is lower than 2 and in presence of hydrochloric acid, Lewisite-2 is expected to exist in water solution mainly in its form **1**.

In weakly acidic and neutral water solutions, Lewisite-2 has the tendency to hydrolyze affording bis(2-chlorovinyl)arsinous acid L2-OH **14**. This acid is in equilibrium with its anhydride, called Lewisite-2 oxide. In contrast to Lewisite-1 (**2**) oxides,² Lewisite-2 oxide exists only in one form as bis(2-chlorovinyl)arsinous acid anhydride or L2-O-L2 **15**. This form is unpolar and moderately soluble in water (may precipitate as an oil phase from the water solution of Lewisite-2), easy to extract from water solutions with dichloromethane, volatile and easy to detect by gas chromatography within an affordable retention time under standard conditions (RIs = 2066, 2080, 2094).

All Lewisite derivatives discussed in the paper showed in TIC usually three or more peaks (for Lewisite-2 oxide **15** at least three). This is due to geometrical isomerism of the Lewisite molecules. In Lewisite-2 (**1**), the more intense peak with the lowest RI corresponded to the (*E,E*)-isomer, [(*E*)-Cl-CH=CH-]₂AsCl **1a**, whereas the lower peaks corresponded mainly to the (*Z*)-isomers: (*E,Z*), [(*E*)-Cl-CH=CH-][(Z)-Cl-CH=CH-]AsCl **1b** and (*Z,Z*), [(*Z*)-Cl-CH=CH-]₂AsCl **1c**. According to the literature and supported by NMR spectra, the (*E*) and (*Z*) isomers are mainly expected in the Lewisite molecules, whereas the geminal, *i.e.*, 1-chlorovinyl, isomers [(*E*)-Cl-CH=CH-][CH₂=CCl-]AsCl **1d**, [(*Z*)-Cl-CH=CH-][CH₂=CHCl-]AsCl **1e** and [CH₂=CCl-]₂AsCl **1f** are practically absent. The *gem*-isomers were however reported to have been identified in place of the (*Z*) isomers based on NMR spectra.¹² The various methods of synthesis may be the reason of these ambiguities. In more complex molecules, more isomers may be expected; thus, Lewisite-2 oxide **15** has 16 theoretically possible different (*E*), (*Z*), *gem*-isomers. Nonetheless, in the Lewisite-2 sample examined in our studies, the all-(*E*)-isomer **15a** (RI = 2177) is the dominant one and the next smallest peaks seem to correspond to the (*E,E*)-(*E'*,*Z'*) isomer **15b** (RI = 2080) and the (*E,Z*)-(*E'*,*Z'*) isomer **15c** (RI = 2094), respectively (Figure 1). The mass spectra of the isomers of all compounds discussed in this paper did not show any significant differences, however.

Furthermore, acetylene elimination by a *retro*-Michael reaction may also be observed. The resulting dichloroarsenous acid derivative undergoes hydrolysis, HCl elimination followed by elimination of water thus affording inorganic arsenic(III) compounds. At higher pH, this *retro*-Michael reaction occurs quantitatively: bis(2-chlorovinyl)arsinous acid

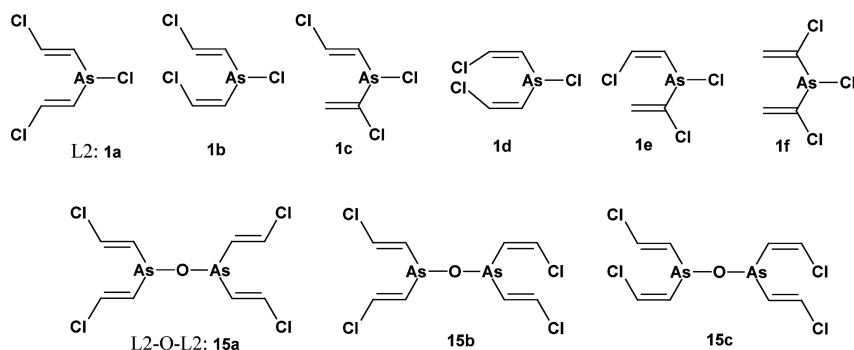


FIGURE 1 Geometrical isomers of Lewisite-2 **1a–f** and main geometrical isomers of Lewisite-2 oxide **15a–c**.

loses two $\text{HC}\equiv\text{CH}$ **16** molecules, and due to the alkaline conditions, the dichloroarsenic acid obtained is in the same time transformed into its disodium salt affording sodium dichloroarsenite **17**. Under stronger alkaline conditions also the remaining chlorine atoms hydrolyze and finally only inorganic compounds, mainly trisodium arsenite Na_3AsO_3 **18** are present in the water solution (Figure 2). However, since the *gem* isomers—if they exist at all—are not typical Michael addition products, they are expected to be much more resistant to acetylene elimination compared to the (*E*) and (*Z*) 2-chlorovinyl isomers.¹⁰

Reactions of Lewisite-2 **1** with propanol **8**, 2-methylthioethanol **9** and 1-butanethiol **10** were first investigated (Figure 3). Reactions with

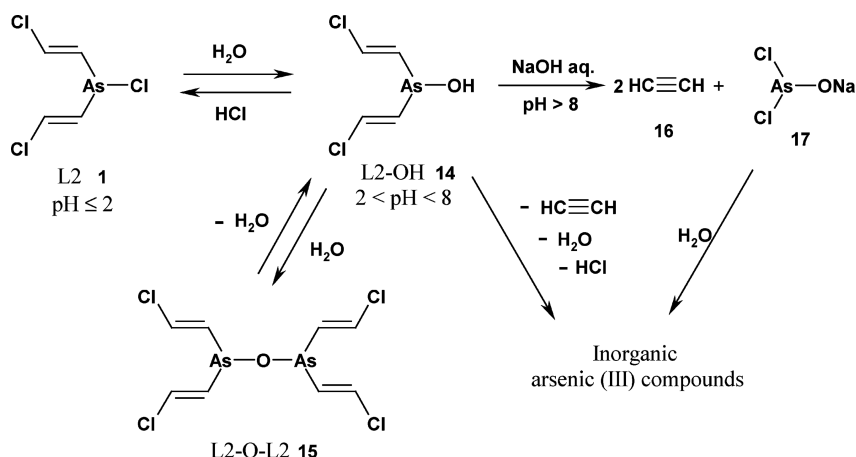


FIGURE 2 Transformations of Lewisite-2 (**1**) in water.

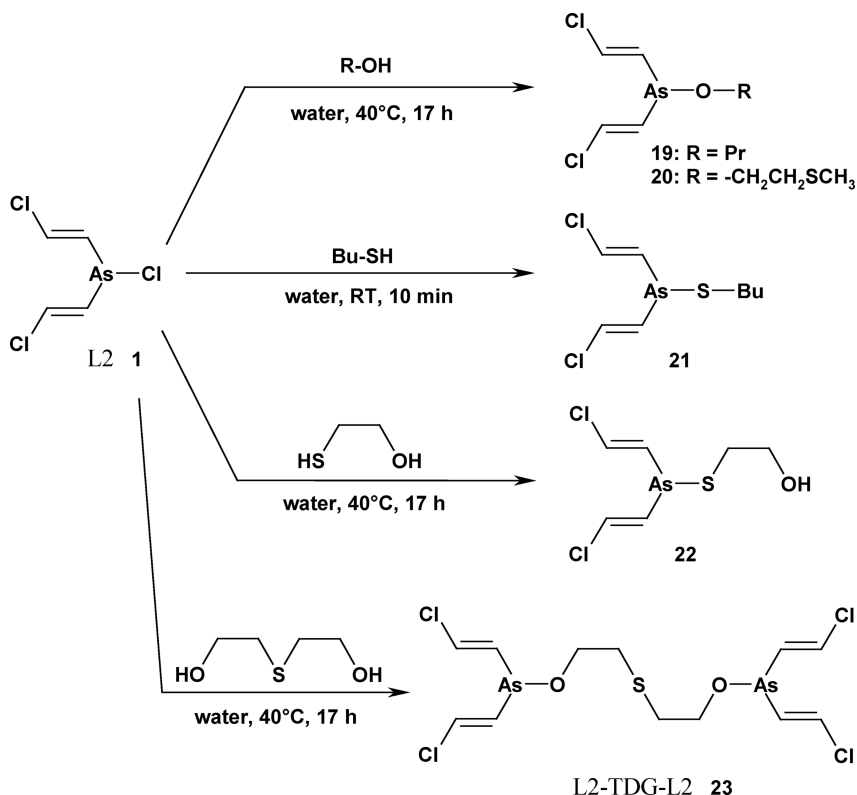


FIGURE 3 Reactions of Lewisite-2 (**1**) with alcohols, thiols and thiodiglycol.

the alcohols **8** and **9** were carried out at 40°C overnight (17 h) with a solution of the appropriate alcohol (10 μ L) and a large excess of the Lewisite-2 solution (1 mg/mL water). The investigated alcohols afforded the appropriate alkyl bis(2-chlorovinyl)arsinites L2-OR **19-20**, detected on GC/MS (Figure 3). The reaction with alcohol may be also carried out successfully with both Lewisite-2 oxide **15** in dichloromethane (obtained by extraction L2-O-L2 from the L2 water solution using a previously described method²), and non-extractable arsinous acid L2-OH **14**, which remains in the water phase. However, attempts to decrease the reaction time (up to 6 h) and the alcohol concentration (up to 10–50 ppm) failed, since no significant amount of the L2-OR derivative could be obtained in those cases.

In the EI mass spectrum of *O*-propyl bis(2-chlorovinyl)arsinite **19** a weak peak corresponding to the molecular ion M^{+} at m/z 256 (1 %) is observed. The structure is confirmed by the fragmentation ions

$[M - \text{Pr}]^+$ at m/z 227, $[M \cdot \text{OPr}]^+$ at m/z 197, $\text{ClCH}=\text{CH}-\text{As}=\text{Cl}^+$ at m/z 171, $\text{HC}\equiv\text{C}-\text{As}^+-\text{CH}=\text{CHCl}$ at m/z 161, AsCl_2^+ at m/z 145 (100 %), $\text{ClCH}=\text{CHAs}^{++}$ at m/z 136, $\text{Cl}-\text{As}=\text{O}^+\text{H}$ at m/z 127, C_2HASO^+ at m/z 116, AsCl^+ at m/z 110, AsC_2H_2^+ at m/z 101, AsC_2H^+ at m/z 100, $\text{As}\equiv\text{O}^+$ at m/z 91, As^+ at m/z 75, $\text{C}_4\text{H}_5\text{O}^+$ at m/z 69, oxetanium ion $\text{C}_3\text{H}_5\text{O}^+$ at m/z 57 and Pr^+ at m/z 43.

The EI MS of *O*-(2-methylthio)ethyl bis(2-chlorovinyl)arsinite **20** displays a more intense peak for the molecular ion M^+ at m/z 288 (10%), as well as peaks for the following major fragmentation ions: $[M - \text{Me}]^+$ at m/z 273, $(\text{ClCH}=\text{CH})_2\text{As}-\text{O}^+=\text{CH}_2$ at m/z 227, $\text{CH}_3-\text{S}^+=\text{CH}_2$ at m/z 61 (100%), CH_3S^+ at m/z 47 and $\text{C}_2\text{H}_5\text{O}^+$ at m/z 45, as well as peaks for the ions with m/z 197, 171, 161, 145, 136, 110, 100, 91 and 75, identical to those discussed above for compound **19**.

Due to the high affinity of Lewisites to sulfur,² the reaction of Lewisite **2** with thiols is expected to be much faster, even with the acid form L2-OH **14**. Thus, the derivative of **14** with 1-butanethiol **10**, *S*-butyl bis(2-chlorovinyl)arsinite **21**, was easily obtained after 10 min at room temperature (Figure 3). In the EI MS of compound **21**, a relatively intense peak for the molecular ion M^+ at m/z 286 (16%) was observed, and the structure was further confirmed by the following fragmentation ions: $[M - \text{Bu}]^+$ at m/z 229, $[M - \text{Bu} - \text{HC}\equiv\text{CH}]^+$ at m/z 203, $[M - \text{SBu}]^+$ at m/z 197, $\text{As}\equiv\text{S}^+$ at m/z 107, Bu^+ at m/z 57, $[\text{Bu} - \text{CH}_4]^+$ at m/z 41 (100%, diagnostic for *n*-butyl group), as well as the above mentioned ions at m/z 171, 145, 136, 110, 101, 100, and 75.

To show that the affinity of sulfur towards arsenic is higher than that of oxygen, a derivatization reaction of Lewisite-2 (**1**) and 2-mercaptoethanol **11** in water was carried out. Only the *S*-thioester **22** was formed even after overnight derivatization at 40°C, and neither the *O*-ester nor the *O*, *S*-thiodiester was found (Figure 3).

In the EI MS spectrum of *S*-2-hydroxyethyl bis(2-chlorovinyl) arsinthiolite **22**, a moderately intense peak for the molecular ion M^+

TABLE I The Bis(2-chlorovinyl)arsinous Acid Esters and Thioesters Obtained

	Chemical name	M.w. (m/z)	RI
19	<i>O</i> -propyl bis(2-chlorovinyl)arsinite	256	1378*
20	<i>O</i> -(2-methylthio)ethyl bis(2-chlorovinyl)arsinite	288	1717*
21	<i>S</i> -butyl bis(2-chlorovinyl)arsinthiolite	286	1699*
22	<i>S</i> -2-hydroxyethyl bis(2-chlorovinyl)arsinthiolite	274	1789*
23	thiodiglycol <i>O</i> , <i>O</i> -bis[bis(2-chlorovinyl)]arsinite	514	2878, 2901, 2923**

*The most volatile isomer; and **RIs of 3 isomers.

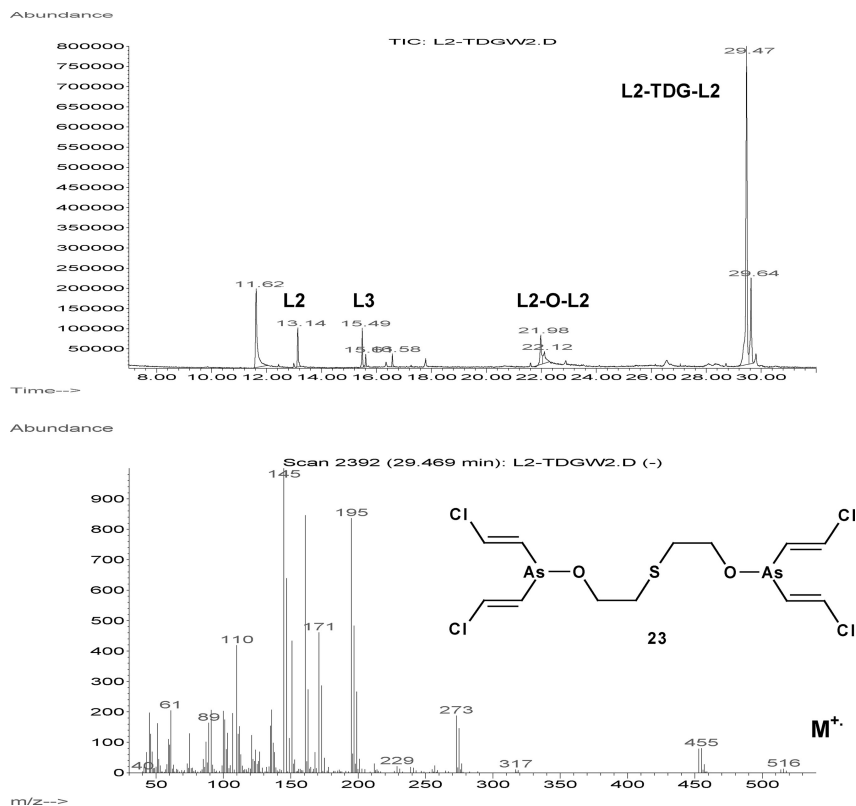


FIGURE 4 TIC and EI MS of L2-TDG-L2 (**23**).

at m/z 274 (10%), as well as prominent peaks of the ion CH_2AsS^+ at m/z 121 (100%) and of the oxiranium ion $\text{C}_2\text{H}_4\text{OH}^+$ at m/z 45 were observed. The previously mentioned ions at m/z 229, 213, 203, 197, 171, 145, 136, 127, 110, 107, 101, 100, and 75 additionally confirm the structure of compounds **22**.

Nevertheless, in a derivatization reaction with thiodiglycol **6** the expected diester, the thiodiglycol *O, O*-bis[bis(2-chlorovinyl)]arsinite (L2-TDG-L2, **23**), was obtained with 500 ppm TDG content in water and a twofold excess of Lewisite-2 (**1**) after 17 h at 40 °C (Figure 3). The derivatization failed when the concentration of the thiodiglycol was lower than 100 ppm, however. Although L2-TDG-L2 (**23**) was less volatile, the GC was still easy to perform under standard conditions (for the main isomer $R_T = 27.96$ min, Figure 4). The fragmentation pathways in EI MS of compound **23** are shown in the Figure 5.

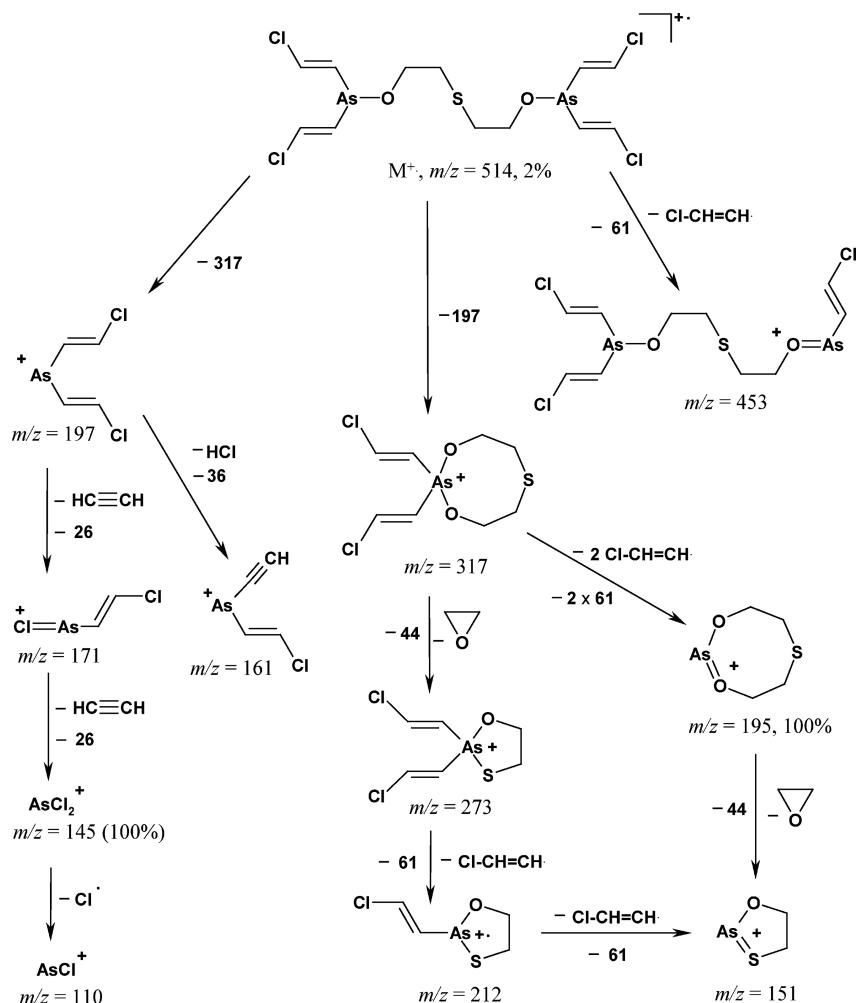


FIGURE 5 EI MS fragmentation pathways of thiodiglycol *O, O*-bis[bis(2-chlorovinyl)]arsinite **23**.

The identification of the L2-TDG-L2 (**23**) was also confirmed by chemical ionization using isobutane as a reagent gas (CI MS). The quasi-molecular peak MH^+ (3%) was visible at $m/z = 515$.

The retention indices of the Lewisite-2 derivatives obtained with alcohols and thiols are presented in Table I.

The attempts to replace Lewisite-2 (**1**) by a more commercially available arsenic compound, as cacodylic acid $Me_2As(O)OH$ (**24**), an arsenic(V) organic compound, failed. No esters with alcohols and TDG

in water were formed under the above conditions, probably due to a different molecule geometry and the lower reactivity of As(V) compounds.

CONCLUSIONS

The method for the derivatization of alcohols and thiols with Lewisite-2 (**1**) described above seems to be less sensitive and to give less volatile products than the previously described² method with Lewisite-1 (**2**). It may, however, be used as an option for direct derivatization of diols, especially of such as thiodiglycol **6**, in water matrices at the 100-ppm level or higher, providing an alternative to the tedious evaporation and silylation. Thiodiglycol *O,O*-bis[bis(2-chlorovinyl)]arsinite, the mutual derivatization product, may always be expected when both thiodiglycol and Lewisite 2 are present, even in water solution. This simple novel method has been applied to analyze Chemical Weapons Convention related environmental water samples.

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