

APPLICATION OF MIDDLE AND NEAR-IR FOURIER SPECTROSCOPY FOR STUDY OF SOME ISSUES CONNECTED WITH DESTRUCTION OF LEWISITE

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Introduction

An issue of lewisite destruction supposes solution of a great number of problems. Among them such as determination of composition of mixtures being detoxified, provision of continuous monitoring of neutralization extent of agent in different points of the technological scheme etc. At the last stage of the process, the detoxification of emptied reservoirs after discharge of lewisite mixtures is an actual issue.

Solution of such problems comes to identification of components of corresponding mixtures and determination of their qualitative and quantitative composition.

One of the methods successfully used for this purpose including concerning to toxicants relating to chemical weapons [1–5] is infrared (IR) spectroscopy. This method is characterized with high efficiency, selectivity and sensitivity. All these characteristics allow using it for monitoring of different chemical processes including real-time mode [6, 7].

The present report considers capabilities of the IR-Spectroscopy method in middle (MIR) and near (NIR) infrared spectrums applying

Experimental Procedure

IR spectra were registered with use of IR-Fourier spectrometers such as Nicolet Avatar-360 (4000-350 cm^{-1}) and Bruker Tensor 37 (10000-4000 cm^{-1}). Liquid samples were studied as solutions in cells with windows made of KBr or CaF_2 with a path length of 0.1 mm for MIR and 1-2 mm for NIR. IR spectra of solid samples were obtained with use of translucent pellet or as thin films applied onto a salt plate.

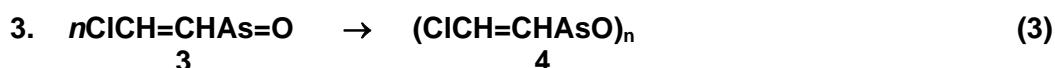
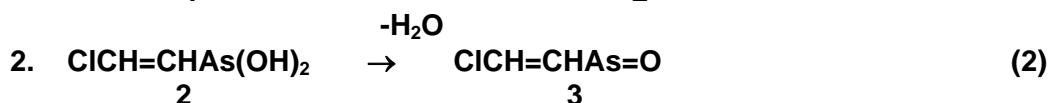
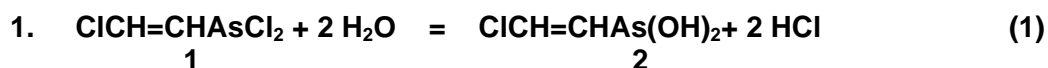
Results

Interaction of α - and β -modifications of lewisite and their mixtures with water

The approved technology for lewisite destruction includes reactions occurring in aqueous solutions [8]. One such reaction is supposed to be used for decontamination of empty reservoirs after discharge of lewisite mixtures by washing of these reservoirs with water.

It should be expected that this process might be accompanied with hydrolysis of the most components presented. 2-Chlorovinyl-dichloroarsine (α -lewisite) is a basis of these mixtures.

According to [9, 10] hydrolysis of this agent includes a few stages and occurs as depicted below:



In this case it is assumed that the first stage occurs very quickly [9, 10] while the others – much more slowly. Thus, acid **2** is present in the reaction mass for a long time.

According to other data [11, 12] the interaction of lewisite with water immediately results in formation of oxide **3**:



in this case, as it was reported in [12], this reaction occurs instantly. Somehow or other, the reaction mixtures may contain all four substances **1-4**.

At that the soluble in water acid **2** should be in liquid state, and practically insoluble in its oxide **3** should precipitate. At considerable surplus of lewisite and without intermixing it may deposit on the bottom immediately being covered with a layer of arsine oxide [12] that will hamper dilution and hydrolysis of lewisite.

Thus, according to the first variant aqueous phase after intermixing of lewisite with water should consist basically from **1** and **2** (reaction (1) is reversible), in accordance with the second variant aqueous phase should contain nothing beside hydrogen chloride dissolved (oxide **3** or its polymeric form **4** will be in sediment).

This report presents the study of interaction of α -lewisite, *bis*-(2-chlorovinyl) chloroarsine (β -lewisite), and lewisite mixtures containing these forms both.

Hydrolysis was conducted at different molar ratios of reagents in a closed flask at continuous intermixing and temperature about 22 °C. Contact duration of reagents was varied in the range from 5 to 60 min. After this period is over the reaction mass, which is usually heterogeneous mixture of liquid and solid phases, was left to settle for 10 to 15 min. After that the transparent aqueous layer was isolated. One portion of aqueous fraction was extracted with carbon tetrachloride or *n*-hexane. IR spectrum of the extract was recorded in the middle range (4000-350 cm⁻¹), and IR spectrum of the remained portion of aqueous fraction was recorded in the near range (10000-4000 cm⁻¹).

After removal of water from the other part of aqueous fraction by natural evaporation on the air the solid residue formed was studied with use of IR spectroscopy in a wide range (10000-350 cm⁻¹). The remainder in the reactor after isolation of aqueous layer was extracted with solvents, and the IR spectrum of the extract was recorded.

Let discuss first the data relating to α -lewisite. These data are presented for mixtures containing reagents (lewisite and water) in molar ratio of 1 : 35 (such ratio is supposed to use for washing toxicant-reservoirs).

At their explanation there were used standard spectra of α -lewisite and 2-chlorovinylarsine oxide (the end product of destruction). We could not obtain 2-chlorovinylarsoinic acid (primary hydrolysis product) though there was mentioned in some sources such as [13] about a possibility of its existence.

As we can see from Table 1, IR spectra of standards differ, and their identification in the samples studied was not so difficult.

Table 1. Location of main absorption bands on IR spectra of α -lewisite, 2-chlorovinylarsine oxide, β -lewisite, and AsCl_3 ; ν , cm^{-1}

α -lewisite	2-chlorovinylarsine oxide	β -lewisite	AsCl_3
6014		6014	
5965	5986	5978	5985
		5943	5842
4324	4321	4319	4415
4218		4218	4256
4167	4160	4163	4172
3061		3061	
3047	3043	3047	
3031	3010	3031	
1685	1694		
1615	1585	1604	
1553	1537	1547	
1287	1287	1284	
1160		1161	
	1153		
1143		1148	
933	938	934	
806	781	799	
712	699	703	
680			
	629		
	525		
396			411
378		378	

The experiments performed according to the procedure mentioned above were resulted in the data presented in Table 2, Figures 1 and 2. The extracts from aqueous fraction of the reaction mixture are consisted basically, as we can see on Figure 1, from α -lewisite. The extract from the residue in the reactor after isolation of water is consisted basically from α -lewisite as well. IR spectrum of solid residue obtained after evaporation of water fraction most of all corresponds to IR spectrum of 2-chlorovinylarsine oxide. IR spectrum of reaction mass without water evaporated on the air is practically identical to IR spectra of oxide mentioned above (Figure 2).

Table 2. Study results of interaction of α -lewisite with water

Sample	Subject being studied	Method	Identified products
Aqueous fraction	Aqueous fraction before extraction	NIR	ClCH=CHAs(OH)_2
	Dry residue after water evaporated	MIR NIR	ClCH=CHAsO
	Extract (CCl_4 , <i>n</i> -hexane)	MIR NIR	ClCH=CHAsCl_2 (α -lewisite)
	Evaporated aqueous residue after extraction	NIR	ClCH=CHAsO
Residue in the reactor after water removal	Extract (CCl_4)	MIR NIR	ClCH=CHAsCl_2 (α -lewisite)
	Residue after evaporation	MIR NIR	ClCH=CHAsO

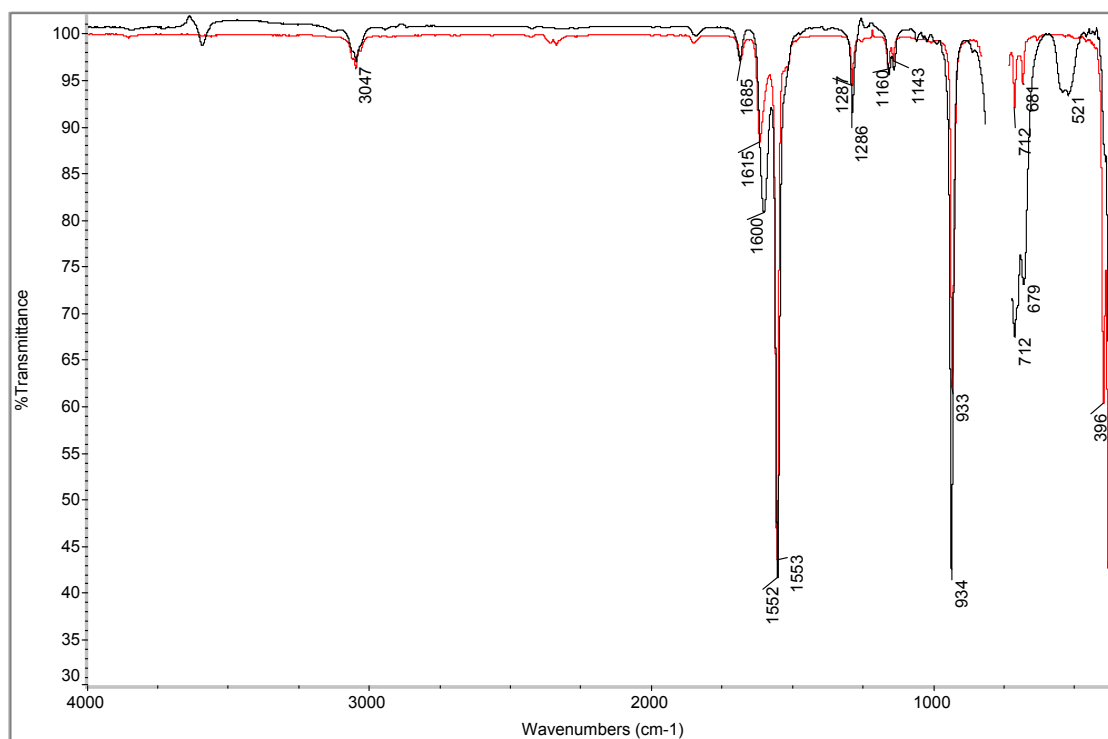


Figure 1. IR spectra in the range of $4000\text{-}350\text{ cm}^{-1}$ of lewisite (red) and of extract from aqueous layer (black). Solvent and extractant was CCl_4

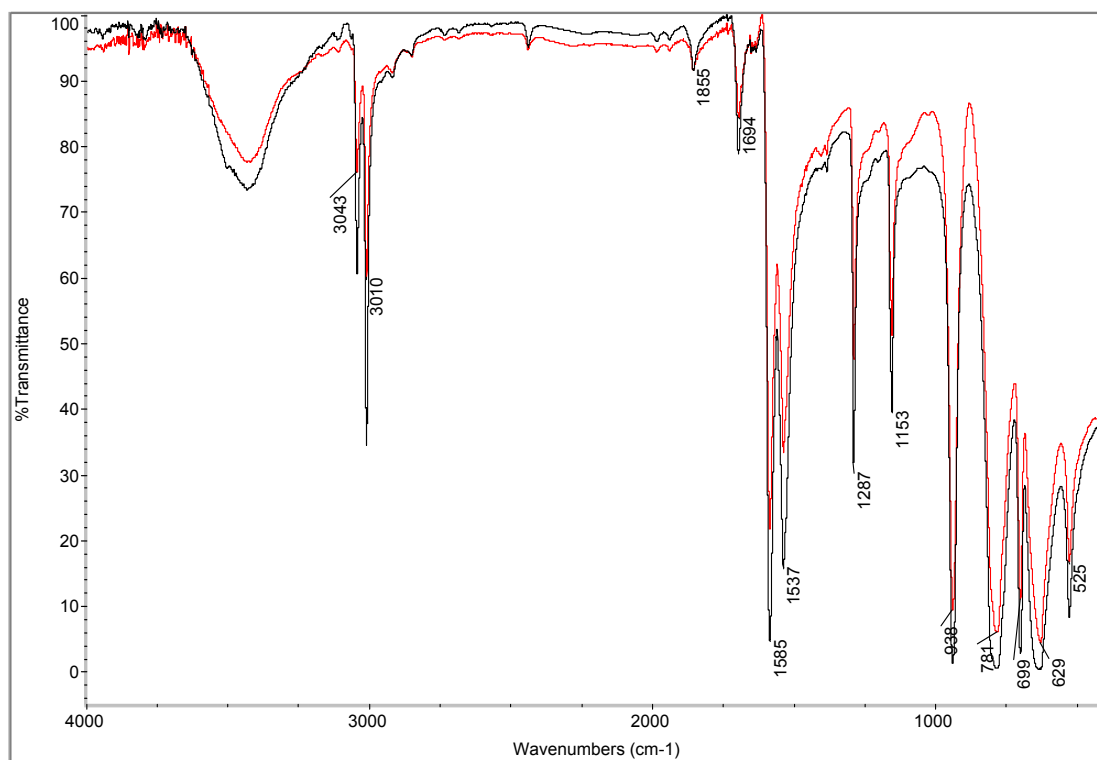


Figure 2. IR spectra in the range of 4000-350 cm^{-1} of 2-chlorovinylarsine oxide (red) and dry residue after water was evaporated (black)

From the data presented we may conclude that the reaction of interaction of α -lewisite with water at selected conditions was not resulted in destruction of the most part of the toxicant introduced into reaction. Its significant quantity was revealed on the bottom of the reactor in insoluble in water residue after water was removed. Moreover, high concentration of α -lewisite (~ 15 -50%) was found in extracts from aqueous phase as well. But if the fact of lewisite presence in the reactor is undoubted, its high concentration in extracts may be explained otherwise. The fact is that, as we discussed earlier, the first stage of the hydrolysis (reaction 1) supposing formation of 2-chlorovinylarsoinic acid **2** is reversible. And in accordance with Le Chatelier's principle during extraction equilibrium (1) may be shifted as one components of the system removing (in this case lewisite) to the left. In this case quantity of α -lewisite in the extract may not correspond to its actual concentration in the aqueous solution.

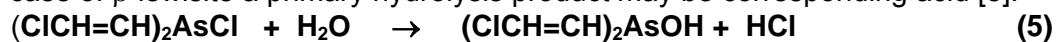
More objective and correct data may be obtained just at study of exactly aqueous phase. However, application of IR spectroscopy both in the middle and near IR ranges, where characteristic bands of α -lewisite are located, is impossible due to water has strong absorption band in this range. These difficulties may be overcome partially if deuterated water will be used instead of regular one that in analytical ranges of spectrum has lower absorption. Study of the system α -lewisite — D_2O resulted in practically the same conclusions. However, in this case we succeeded in recording very small absorption characteristic for α -lewisite (bands ~ 4330 and ~ 4170 cm^{-1}). Therefore, we may conclude that the basis of aqueous fraction is most likely acid **2**, and α -lewisite is in a small quantity if presents. This fact is in agreement with NMR data according to which the only substance presented in the reaction mixture on the basis of D_2O identified with high probability is the acid **2** possibly as a complex with water [14].

When the system β -lewisite — H_2O (D_2O) was studied there were obtained the data not differing qualitatively from the study results of the mixture α -lewisite — water. Extracts from aqueous layer and from residue in the reactor contained significant quantities of

β -lewisite. There were found no any principle difference in behavior of the mixture of α -and β -lewisite in water in a comparison with behavior in it of individual substances.

Thus, based on the study conducted we may conclude that α -lewisite, β -lewisite, and their mixture at conditions selected were not destructed completely at interaction with water (H_2O and D_2O). In this case a primary hydrolysis product of α -lewisite is obviously acid **2** (reaction 1) that is transformed into corresponding oxide at water removal (dehydration reaction 2).

In case of β -lewisite a primary hydrolysis product may be corresponding acid [8]:



High acidity of water mixtures (pH=2) may serve as indirect confirmation of the fact that reactions (1) and (5) in the processes studied are dominating ones.

Identification of components of lewisite mixtures

Availability of selective absorption of lewisite in the near IR region (Table 1) makes it possible to solve a problem of identification lewisite mixture components being detoxified (input check). These mixtures beside lewisite contain significant quantity (till 25%) of arsenic trichloride, and both these components should be determined quantitatively. As we demonstrated earlier [15], it may be done by the MIR method. However, this method is not suitable for use in real-time mode because it requires preliminary sample preparation (dilution of samples with solvents). Moreover, for analysis in this case, cells with very short pathlength (0.1 mm) is used what may hamper flowing the liquid through them.

These difficulties may be overcome if a NIR method is applied because in the near IR region substances have much lower absorbance (sometimes in orders of magnitude). Therefore, for analysis in real-time mode cells with long pathlength (a few millimeters) may be used what makes liquid flowing easier and reduces a possibility of cell plugging.

We have used this approach for development of the procedure for determination of lewisite and arsenic trichloride in their mixtures. Identification and analysis of these substances assumes the presence on their spectra in near IR region of characteristic so called analytical absorption bands. As we can see from the Table 1, IR spectra of lewisite and $AsCl_3$ are different. The most suitable for joint quantitative determination of these components in the mixture are the following bands: $5842cm^{-1}$ for $AsCl_3$ and doublet $5965/6014 cm^{-1}$ for lewisite.

The experiments conducted with use of laboratory mixtures containing lewisite and $AsCl_3$ at different ratios have shown that there are taken place an exact dependence of absorption intensity of doublet $5965/6014 cm^{-1}$ and band $5842 cm^{-1}$ against concentration of corresponding components in a wide range of concentrations both for lewisite (2-83%) and $AsCl_3$ (98-17%).

The same studies have been conducted with use of a system included NIR MatrixF Spectrometer (Bruker), specific sensor serving as a cell (O.K.Tec Company), and fiber-optic cable connecting them (these experiments were conducted with participation of specialists from GfE and O.K.Tec Companies). As a result, there was found that linear equations connecting concentrations of components with corresponding integral absorbance exist (Figure 3).

$$C_L = 1,37A_{5965} - 5,93 \quad R^2 = 0,990 \quad (6)$$

$$C_{As} = 4,04A_{5842} - 16,09 \quad R^2 = 0,998 \quad (7)$$

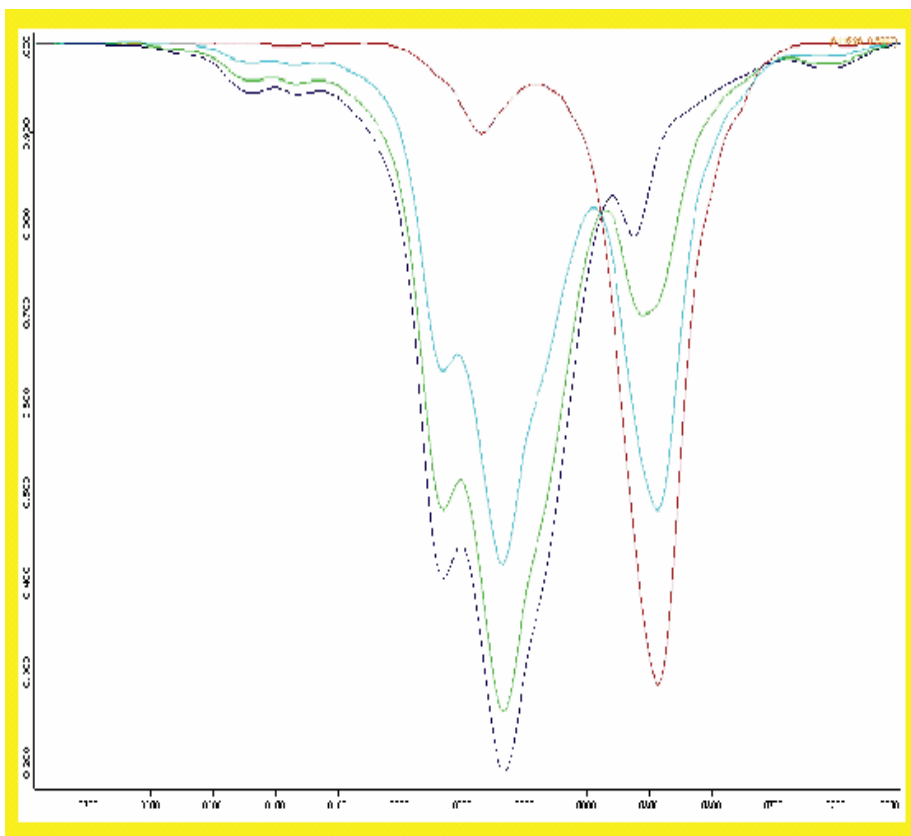


Figure 3. IR spectra in the range of 6300-5850 cm^{-1} of mixtures of lewisite with arsenic trichloride (2.1% lewisite and 97.9% AsCl_3 -red, 34.4% lewisite and 65.6% AsCl_3 - blue, 67.3% lewisite and 32.7% AsCl_3 - green, 82.6% lewisite and 17.4% AsCl_3 - black)

Thus, laboratory experiments have shown that quantitative analysis of the mixture of lewisite and AsCl_3 may be realized remotely with use of the above described system.

Conclusions

The method of IR-Fourier spectroscopy was used for study of issues connected with lewisite destruction.

The process of interaction of α - and β -modifications of lewisite and their mixtures with water has been studied. There was shown that complete destruction of these substances at the experiment conditions (molar ratio lewisite: water was 1:35, $t=22^{\circ}\text{C}$, contact duration was 5–60 min) was not occurred. On portion of substances at the end of the process remained in the reactor as insoluble in water mass, and another one interacting with water formed corresponding acids, primary hydrolysis products. These products were transformed to secondary hydrolysis products (corresponding oxides) when water was removed from the system by evaporation on the air.

There has been shown that a principle possibility of quantitative determination of the main components of lewisite mixtures to be destructed (lewisite and arsenic trichloride) exists. With use of corresponding instruments (Matrix F Spectrometer, specific sensor, and fiber-optic cable connecting them) this operation may be realized in real-time mode.

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