Physicochemical properties of β-chlorovinylarsonous dichloroanhydride and anhydride and the low level of the maximum permissible conversion (MPC) preclude their direct determination by gas chromatography.

From the literature [1], it is known that lewisite is rather rapidly hydrolyzed with the abstraction of hydrogen chloride and the formation of β-chlorovinylarsine oxide:

\[
\text{Cl–CH=CH–AsCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cl–CH=CH–As}=\text{O}.
\]

Therefore, in the previously developed methods for the determination of lewisite [2–4] in samples of water, soil, construction materials, and air based on its conversion into acetylene, lewisite was determined together with the products of its oxidation and hydrolysis, which also react with a 30% aqueous solution of sodium hydroxide yielding acetylene.

Although lewisite and lewisite oxide belong to the compounds of the first hazard class, their MPCs in the air of work areas are substantially different, \(2.0 \times 10^{-4}\) and \(1.0 \times 10^{-2}\) mg/m\(^3\), respectively [2, 5, 6]. The above consideration indicates that the residual concentrations of lewisite and lewisite oxide in soil and construction materials must be known for their use in the national economy after detoxication.

Data on the separate determination of β-chlorovinylarsonous dichloroanhydride (lewisite) and anhydride (lewisite oxide) in different samples by gas–liquid chromatography are absent in the available literature.

Difficulties that emerge in separate determination in mixtures of anhydrides and haloanhydrides are due to the fact that nucleophilic reagents that are commonly used for converting mixture components into compounds suitable for chromatography yield identical derivatives [7–9].

In particular, the known reagent for the determination of lewisite, ethane-1,2-dithiol yields identical derivatives with β-chlorovinylarsonous anhydride and dichloroanhydride:

\[
\text{HC=CHAsX} + \text{HSCH}_2\text{CH}_2\text{SH} \rightarrow \text{HC=CHAs}+ \text{2HX} + \text{H}_2\text{O},
\]

where \(X = 2\text{Cl}\) and \(\text{O}\).

The aim of this work was to develop a method for the separate determination of lewisite and lewisite oxide in soil and construction materials at a trace level using gas–liquid chromatography.

**EXPERIMENTAL**

In this work, we used lewisite and lewisite oxide with the mass fraction of the major compound no lower than 85%.
Reagents and materials: a 30% aqueous solution of sodium hydroxide, hydrochloric acid, sodium chloride, a 0.1 N solution of hydrochloric acid, a 0.006% solution of sodium hydroxide in ethanol, and a saturated solution of sodium chloride.

Solvents: hexane and ethanol. All reagents were of chemically pure or analytical grade.

Apparatus: a Hewlett Packard model 6890 gas chromatograph with a flame-ionization detector (United States). A fused-silica open tubular column with a length of 30 m, an inner diameter of 0.53 mm, the HP-Plot/Al₂O₃ “s” stationary phase, and the thickness of the stationary phase layer of 0.15 µm.

Conditions of gas-chromatographic measurements were as follows:

Temperature, °C:
- injection port, 100;
- detector, 150;
- column thermostat, initial, 30;
- final, 170;
- temperature programming rate of the column thermostat, 25 K/min.

Flow rate of gas, mL/min:
- helium through the column, 7.1;
- purge gas, 45;
- hydrogen, 40;
- air, 450.

Procedure. Samples of soil or construction materials (1.0 ± 0.5 g) are weighed on an analytical balance in a bottle with a screw stopper. The samples are previously ground, and the fraction of 0.5–1.0 mm is taken. One milliliter of a hexane–ethanol (3 : 1) mixture is added to the sample. The bottle is kept in an ultrasonic bath for 30 min at a temperature of 50°C. The liquid upper layer is transferred from the bottle to a test tube and centrifuged for 3 min. Two aliquot portions of 0.1 cm³ are taken from the test tube and transferred to penicillin vials. A 0.005% solution of sodium hydroxide (10 µL) is added to the first vial, the contents are stirred, and the liquid is evaporated to dryness in a nitrogen flow. The vials are sealed in metal clamps. Next, 5 mL of air is taken from the vials with a medical syringe, and 5 mL of a 30% aqueous solution of sodium hydroxide is introduced with another syringe. The resulting mixtures are kept for 30 min at 50°C in an ultrasonic bath and allowed to settle for 5 min. One milliliter of the vapor–air mixture is taken from each vial with a gas-tight syringe and introduced into the injection port of a chromatograph. The time of the determination is no longer than 1.5 h. The detection limit is 0.01 mg/kg. The error in the determination is no larger than ±20 rel %.

RESULTS AND DISCUSSION

A necessary condition in the development of a method for the separate determination of lewisite and lewisite oxide is obtaining nonidentical compounds, which is rather problematic because lewisite oxide and lewisite are β-chlorovinylarsinous anhydride and dichloroanhydride, respectively. Another necessary condition is the possibility of the detection of the obtained derivatives using selective and highly sensitive detectors (thermionic, electron-capture, and flame-ionization detectors).

Form the data reported in the literature, it follows that nonidentical derivatives (complying with the above requirements) can be obtained by treating a mixture of lewisite and lewisite oxide (β-chlorovinylarsinous dichloroanhydride and anhydride, respectively) with diazoalkanes [10] or cyanides (see scheme):

\[
\begin{align*}
HC=CH-AsCl \quad + 2CHN_2 \\
\xrightarrow{I} \\
HC=CH-AsCHCl \quad + 2N_2, \\
HC=CHAs=O \quad + 2CHN_2 \quad \rightarrow \quad HC=CHAs-CH + 2N_2, \\
HC=CHAsCl + 2KCN \quad \rightarrow \quad HC=CHAsCN + 2KCl, \\
\end{align*}
\]

where \( R = H \) and \( CH_3 \).

Our studies demonstrated that the interaction of lewisite with diazomethane the following compounds are formed along with product II:

\[
\begin{align*}
HC=CHAsClCl + 2KCN \quad \rightarrow \quad HC=CHAsCHCl + 2KCl, \\
\end{align*}
\]

The chromatographic peaks were identified using chromatography–mass spectrometry. The ratio of the derivatives was not constant in different experiments. An analogous situation was observed with the use of diazoethane.

Cyanides (e.g., potassium cyanide) are insoluble or lowly soluble in solvents (aliphatic and aromatic hydrocarbons, acetone, ethyl acetate, etc.) suitable for use in gas–liquid chromatography. Therefore, we used metha-