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DETERMINATION OF 2-CHLOROVINYLARSONIC ACID
IN ENVIRONMENTAL WATERS
BY ION CHROMATOGRAPHY

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RESEARCH DIRECTORATE

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13. ABSTRACT (Maximum 200 words) Lewisite, through its hydrolysate 2-chlorovinylarsonous acid, is thought to oxidize gradually in seawater, freshwater, and soil to form 2-chlorovinylarsonic acid (CVAOA). Like lewisite, CVAOA is also a potential vesicant. The high-performance liquid chromatography method is described here to directly detect and analyze CVAOA in seawater and surface water. Separating CVAOA from the aqueous matrix is carried out using both conventional (ion exchange) and ion-pair reverse phase ion chromatography. Using eluent suppression conductivity and ultraviolet as dual modes of detection, the detection limit is 10 ng.			
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PREFACE

The work described in this report was authorized under Project No. 1C162622A553A, CB Threat Agent Chemistry and Effects. This work was started in July 1989 and completed in November 1989. The experimental data are recorded in laboratory notebook 89-0038.

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This report has been approved for release to the public.

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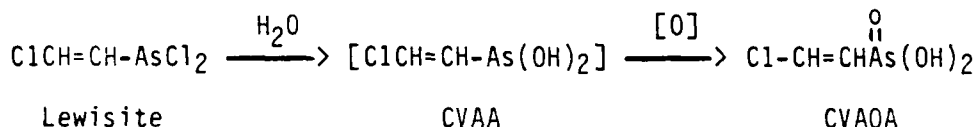
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DETERMINATION OF 2-CHLOROVINYLARSONIC ACID
IN ENVIRONMENTAL WATERS BY ION CHROMATOGRAPHY

1. INTRODUCTION

Through its hydrolysate 2-chlorovinylarsonous acid (CVAA), lewisite is thought to oxidize gradually in seawater, freshwater, and soil to form the stable and highly water soluble 2-chlorovinylarsonic acid (CVAOA).¹



Because CVAOA is also a potent blistering agent,² any detection protocol for lewisite should also apply to CVAOA.

The only method currently available for analyzing CVAOA in trace amounts in the environment involves measuring nonspecific arsenic using the atomic absorption spectroscopy technique. Although it is sensitive at the parts per billion (ppb) level, this method cannot differentiate an artificially imposed source of arsenic from real-world background levels.

Recently, this laboratory developed a methodology for analyzing CVAA in environmental waters by high-performance liquid chromatography (HPLC).^{3,4} The CVAA peak was identified by the oxidative derivatization (H₂O₂) of CVAA to CVAOA, followed by conventional ion-pair reverse phase (IPRP) liquid chromatography.³ Using this same liquid chromatographic technique, the presence of CVAOA was also detected in aged (>1 yr) laboratory standards of CVAA in deionized water.*

To determine the extent to which lewisite actually converts to CVAOA in the environment, the analytical methodology must be first available for detecting, separating, and quantitating CVAOA in environmental waters. This report describes the development of a new method for directly separating CVAOA from aqueous matrices by both conventional ion exchange (IE) and IPRP ion chromatography using eluent suppression conductivity and ultraviolet (UV) absorption as dual detection modes. The feasibility of this method for detecting and analyzing CVAOA in surface water and seawater is demonstrated.

*Bossle, P.C., Pleva, S.G., and Martin, J.J., U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, January 1990, unpublished data.,

2. MATERIALS AND METHODS

2.1 Chemicals.

Water used for standards in this study was distilled and deionized (10-14 meg/cm) using the Barnstead Nanopure II system (Barnstead/Sybron, Boston, MA). Acetonitrile, which was used as the organic modifier, was HPLC grade (Burdick and Jackson, Muskegon, MI). The ion-pair reagent, HPLC grade tetrapropylammonium hydroxide (TPAOH) (0.10 molar in water), was obtained from Dionex Corporation (Sunnyvale, CA). Analytical grade sodium bicarbonate and sodium carbonate were obtained from Mallinckrodt Chemical Works (St. Louis, MO). Simulated ocean water was prepared from "Instant Ocean" (Aquarium Systems, Incorporated, Mentor, OH) according to directions provided by the supplier. The CVAOA was synthesized using the procedures of Lewis and Stiegler⁵ and gave analytical data consistent with its chemical structure.

2.2 Instrumentation.

Chromatography was performed using a Model 2120i Ion Chromatograph (Dionex Corporation) equipped with both a variable wavelength UV and a 5- μ L flow-through conductivity detector in series. Samples were introduced by an air-activated valve injector with a 50- μ L sample loop. This system was connected to a Model 4270 Recorder-Integrator (Dionex Corporation) that measured UV and conductivity detector response in terms of peak area. The UV spectrum of CVAOA was obtained in deionized water using a Varian 2300 Spectrophotometer (Varian Corporation, Sunnyvale, CA).

2.3 Chromatographic Procedure.

Ion exchange separations were performed under the following conditions: column, Dionex HPIC-AS4A; eluent, 0.75 mM sodium bicarbonate/2.2 mM sodium carbonate (Dionex type AFS fiber suppressor); and flow rate, 2 mL/min.

Ion-pairing reverse phase separations were performed under the following conditions: column, Dionex MPIC-NS1; column temperature, ambient; eluent, 2 mM TPAOH, 1 mM sodium carbonate, 1.2% acetonitrile (Dionex type AFS-2 fiber suppressor); and flow rate, 1 mL/min.

The UV detection of CVAOA was carried out at a 215-nm wavelength (0.01-0.05 AUFS). Conductivity detection was determined at a sensitivity of 0.3-3.0 μ SFS.

A stock solution of CVAOA at a concentration of 1,000 μ L/mL was prepared by adding 100 mg of CVAOA to a 100-mL volumetric flask and slowly dissolving the compound with shaking to volume with deionized distilled water. The stock solution of CVAOA was injected onto the column(s), and retention times of 9.26 min (IE) and 11.26 min (IPRP) were determined. The CVAOA peak fractions of the eluent were collected, evaporated down using a nitrogen stream at ambient temperature, and identified by mass spectrometry (MS). Calibration curves were obtained by injecting a known concentration (200, 400, 1,000, 4,000, and 10,000 ng/mL) of CVAOA in deionized water onto both an IE and an IPRP column in triplicate and measuring both the UV and conductivity detector responses obtained.

2.4 Sample Preparation.

Both a surface water and a simulated seawater sample were spiked with CVAOA at two concentration levels. For UV detection, the samples were spiked at 1,000 ng/mL. For conductivity detection, being both less selective and sensitive, the samples were spiked with CVAOA at 4,000 ng/mL. The samples were filtered, along with the unspiked surface water and simulated seawater samples, and injected into the liquid chromatograph.

3. RESULTS AND DISCUSSION

In environmental analysis, multiple analytical techniques are often required to cross confirm analyte identity and avoid serious misinterpretation of data. By using both IE and IPRP separations, two entirely different physical parameters of CVAO [i.e., acid dissociation (pK_a) and molecular lipophilicity, respectively] are employed as separation modes. The CVAOA, a strong divalent acid,⁶ is retained on an IE column while nonionic and cationic organic and inorganic species are swept through with the void. Analogously, the lipophilic character of the chlorovinyl moiety gives CVAOA in the IPRP separation mode a strong attraction to the polystyrene-divinyl benzene reverse-phase column and hence an increased retention time.

The use of both conductivity and UV detection makes possible the selective identification of CVAOA both as an anionic and UV absorbing species. However, a suppressor column must be used to decrease the high background conductance and UV absorbance of the eluent before conductivity and UV detection can take place. The result allows UV detection of CVAOA at 215 nm ($E = 4.67$) with moderate selectivity and sensitivity. Unlike lewisite and CVA4,⁴ the UV spectrum of CVAOA shows no absorption shoulder in the 225-230-nm spectral range. The CVAOA responded linearly (correlation coefficient >0.99) to both conductivity and UV detection over a range of 10-500 ng of injected CVAOA. Ultraviolet detection, in comparison to conductance, was significantly more sensitive with detection limits being approximately 10 ng (UV) and 50 ng (conductivity), respectively, with a signal-to-noise ratio of 3.

The feasibility of this method to detect CVAOA in environmental waters was demonstrated with spiked surface water and simulated seawater samples using IE and IPRP separations with conductivity and UV detection. Figures 1-4 show the experimental results using the four possible separation-detection combinations.

In all cases (Figures 1-4), the CVAOA peak in the chromatograms of spiked surface waters is free of matrix effect.

However, the CVAOA peak in the spiked seawater chromatograms of Figures 1 and 3 is totally obliterated by matrix effects. This phenomenon results because conductivity detection is nonselective in that it measures all ionic species present in the eluent stream. Therefore, conductance cannot be used to detect CVAOA in seawater at the tested concentrations. In Figures 2 and 4, only UV absorbing species are selectively measured with the consequence that the CVAOA peak in the chromatograms is relatively free of matrix effects.

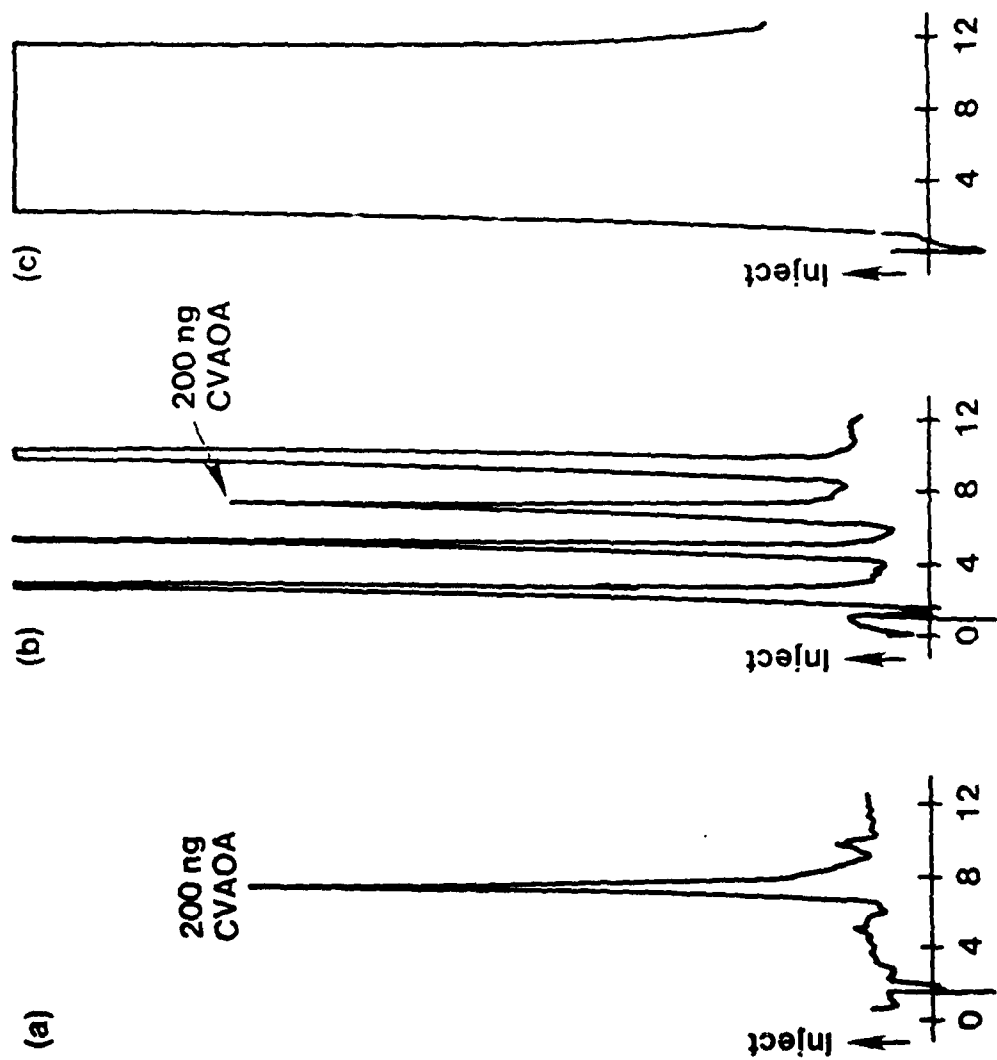


Figure 1. IE-Conductivity Chromatograms for (a) CVAOA Standard, (b) Spiked Surface Water, and (c) Spiked Simulated Seawater

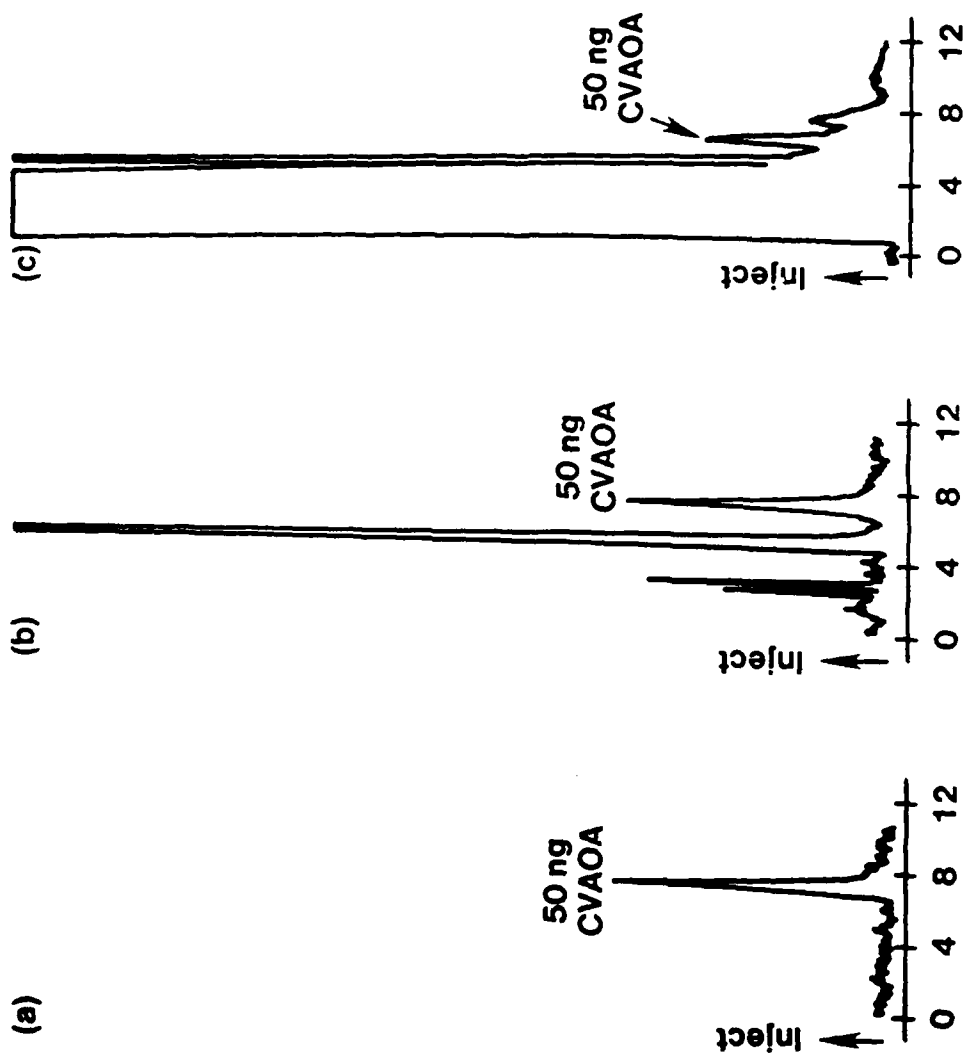


Figure 2. IE-UV Chromatograms for (a) CVAOA Standard, (b) Spiked Surface Water, and (c) Spiked Simulated Seawater

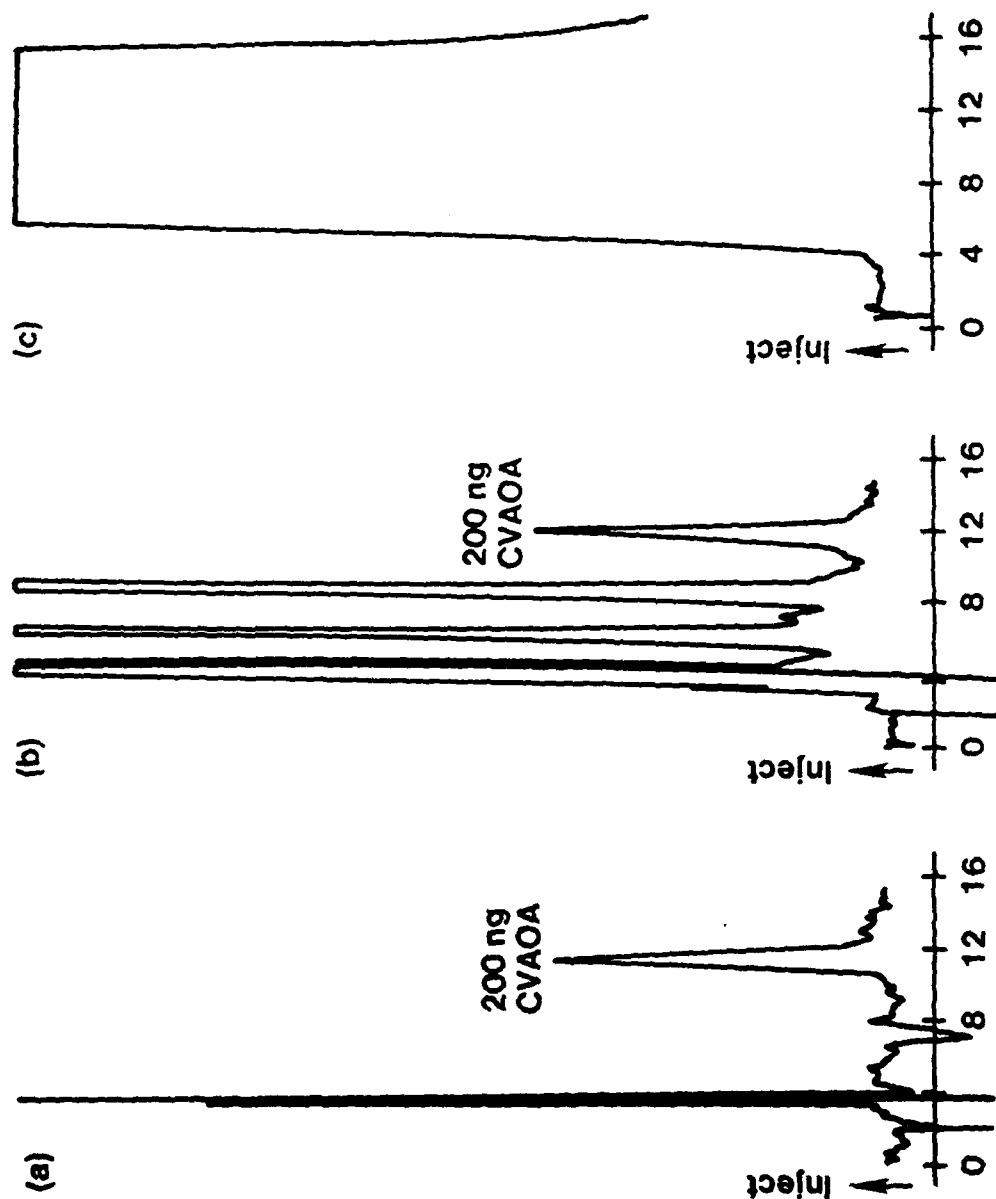


Figure 3. IPRP-Conductivity Chromatograms for (a) CVAOA Standard, (b) Spiked Surface Water, and (c) Spiked Simulated Seawater

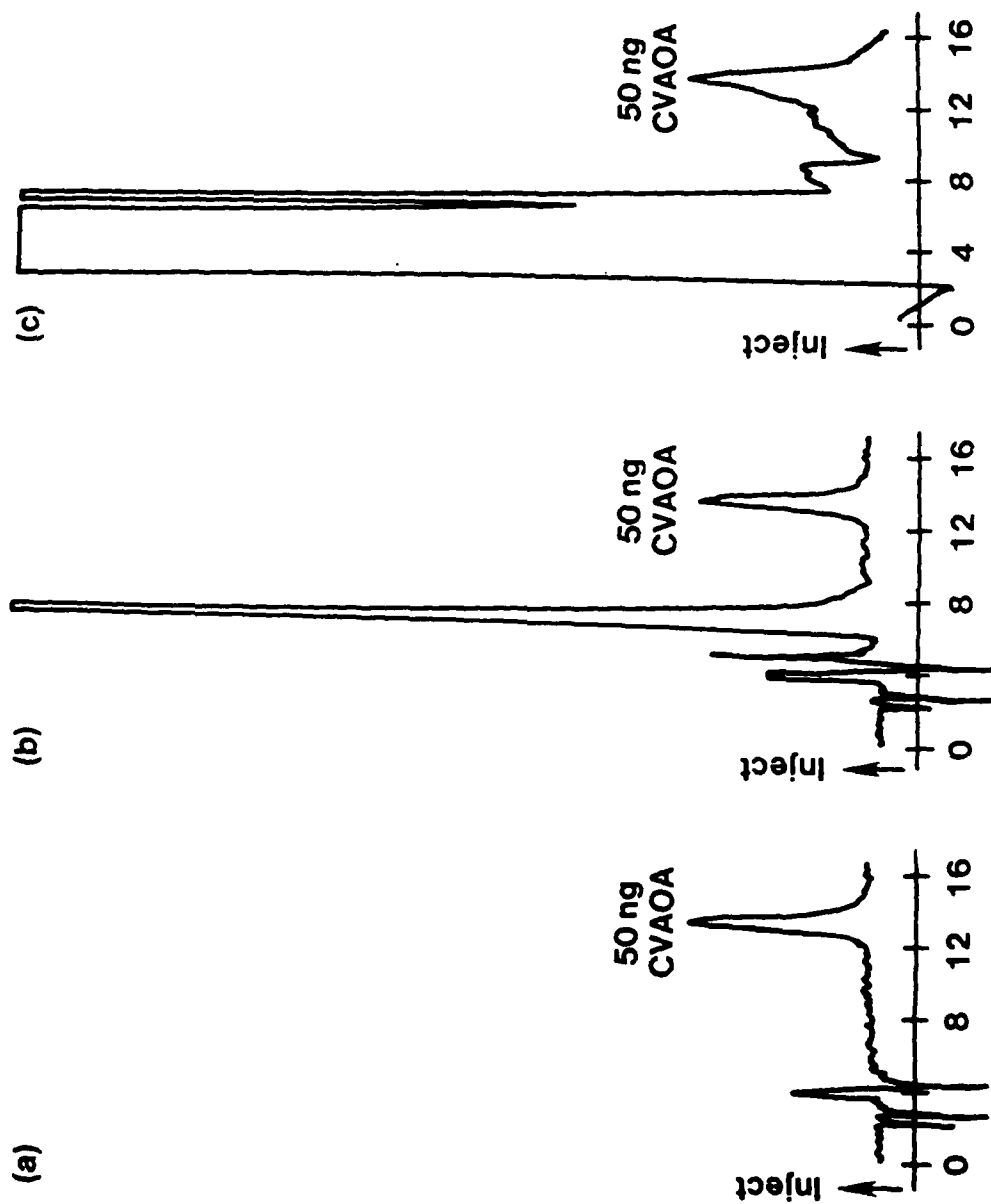


Figure 4. IPRP-UV Chromatograms for (a) CVAOA Standard, (b) Spiked Surface Water, and (c) Spiked Simulated Seawater

4. CONCLUSION

Ion exchange and IPRP ion chromatography with conductivity and UV detection is a rapid and direct method for analyzing 2-chlorovinylarsonic acid (CVAOA) in aqueous matrices in quantities as low as 10 ng. The feasibility of this method for detecting and analyzing CVAOA in surface water and seawater is demonstrated.

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