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DEVELOPMENT OF A FIELD-PORTABLE AIR MONITOR FOR LEWISITE

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J. H. Aldstadt,* A.F. Martin, and D. C. Olson†
Environmental Research Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439 and †FIA Solutions, Inc., P.O. Box 2297, Gig Harbor, WA 98335

The focus of this research is the development of a prototype field-portable ambient-air monitor for measuring trace levels of volatile organoarsenicals. Lewisite (dichloro[2-chlorovinyl]arsine) is a chemical warfare agent developed during World War I and stockpiled on a large scale by the former Soviet Union. A continuous air monitor for Lewisite at the eight-hour time-weighted-average concentration (3 μg/m^3) is necessary to protect the safety and health of arms control treaty inspectors. Flow injection is used to integrate an air sampling device based on liquid-phase extraction with a flow-through detector based on potentiometric stripping analysis. We describe a method for the sampling and preconcentration of organoarsenicals from ambient air by using a gas permeation membrane sampler. The sampler is designed to selectively preconcentrate analyte that permeates a silicone rubber membrane into a caustic carrier stream. Instrument design is described for the sampling and detection methodologies.

*Corresponding author.

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INTRODUCTION

The determination of traces of Lewisite and its decomposition products in the environment is critical to support efforts in environmental remediation at military installations and the verification of international arms control agreements. The measurement of Lewisite, however, has long been recognized to be difficult, especially at trace levels in environmental matrices. Several analytical methods for monitoring the presence of Lewisite and its adducts have been developed. Because Lewisite decomposes above 100°C,[1] alternatives to direct gas chromatography (GC) have been necessary. These methods are based on degradation of Lewisite to yield detectable products, including methods for atomic absorption spectroscopy (AAS),[2] liquid chromatography (LC),[3,4] colorimetry, and GC.[6-8] For example, Lewisite vapor is collected in a caustic-containing liquid impinger. The caustic solution in the impinger decomposes Lewisite as shown in the following reaction mechanism:[9]

$$\underset{\textbf{\textit{Lewisite}}}{C_2H_2AsCl_3} + 2H_20 \rightleftharpoons \underset{\textbf{\textit{CVAA}}}{C_2H_2AsCl(OH)_2} + 2HCl \qquad (1)$$

$$C_2H_2AsCl(OH)_2 + OH^- \rightleftharpoons C_2H_2 + HAsO_2 + H_20 + Cl^- \qquad (2)$$

In the first step, slightly water-soluble Lewisite (560 mg/L)[4] hydrolyzes to form its geminal diol, 2-chlorovinyl arsonous acid (CVAA). CVAA is the predominant form of Lewisite found in the environment.[10] In the second step, CVAA is rapidly base-hydrolyzed to products detectable by GC with flame ionization detection[6] (i.e., acetylene) or by AAS[6] (i.e., arsenite ion produced in solution as total arsenic). These methods generally have inadequate sensitivity and selectivity in environmental matrices. Moreover, they require large and fragile hardware and are thus more suitable for the laboratory than for field applications. A field-portable technique for determining Lewisite in the environment would provide advantages not only in information availability, cost savings, and analytical accuracy but also in the

elimination of the need to ship potentially hazardous samples internationally in support of arms control treaty verification inspections.

The concept for this monitor, the Flow Injection Trace Gas Analyzer (FITGA), is based on the selective preconcentration of low levels of Lewisite in air followed by indirect determination of Lewisite using electrochemical detection.[11] The design of a field-portable prototype for the determination of trace levels of Lewisite during treaty verification inspections is described in the following pages.

EXPERIMENTAL

All chemicals used were of analytical reagent grade quality or better and were prepared in high-purity (18 MΩ) water (Barnstead NanoPure system, Dubuque, IA). The $AsCl_3$ permeation tube (Kin-Tek Laboratories, La Marque, TX), vapor generator (VICI Metronics, Santa Clara, CA), potentiometric stripping analyzer (Radiometer America, Inc. West Lake, OH), and flow injection analysis system components (Global FIA, Inc. Gig Harbor, WA) were off-the-shelf commercial items. Details of the experimental procedures are found elsewhere.[12]

RESULTS AND DISCUSSION

Detector Design. The detection principle of the monitor is to convert Lewisite, which is electrochemically inactive, to arsenic (III) (as arsenite ion, AsO_2^-). Arsenic (III) species have been determined by using potentiometric stripping analysis (PSA) in aqueous environmental samples at trace levels.[13] Furthermore, PSA can be used to differentiate among various speciated forms of arsenic (e.g., As(III) in arsenious acid vs. As(V) in arsenic acid). This is accomplished by maintaining the potential during the deposition step at a more positive value than required to reduce the higher valence species. To minimize false positive identifications during treaty verification inspections, this speciation capability will be critical in that As(III) could be

distinguished from background As(V) that may be present as volatile organoarsenicals.

Flow injection (FI), implemented with PSA, is a powerful combination for trace metal determinations. For the FITGA, FI provides the framework for coupling the novel air sampler and the arsenite ion detector. Of the basic classes of flow cells for electrochemical detection in flowing streams, we chose the wall-jet design, which has been shown to have the fastest response and the least amount of carry-over between samples.[14,15] Several groups have published methods using PSA in acidic conditions to determine arsenic at <1 μg/L in acidified aqueous environmental samples, including a pending U.S. EPA method for determining arsenic at low μg/L levels in natural water samples.[13] These methods have been applied to environmental samples in which the extent of complexation of arsenic with organic material in the sample matrix is decreased upon acidification. However, because in our approach Lewisite will base hydrolyze after sampling, the sample would have to be strongly acidified (1 M) in order to have the proper conditions for detecting $HAsO_2$ by PSA. This would therefore require introducing a second (acidic) stream after the GPM but before the flow cell in order to obtain the optimal (low) pH for detection. Although this would be a routine addition to a bench-top analytical FI system, for a portable air monitor it increases the level of complexity significantly. Additionally, inspectors would have to transport concentrated (>1 M) HCl along with the FITGA, an undesirable situation logistically.

We therefore developed a new method for measuring AsO_2^- in alkaline solution, a method that compares favorably to the low pH method in terms of performance as well as being much easier to support logistically. This work was based on using a solid gold disc working electrode, which is much easier to implement than the gold film working electrode used with the low pH method. The prototype FITGA will be simpler, more compact, and lighter in weight as a result of this development.[20] In Figure 1,

typical instrument responses for the PSA measurement of arsenite ion at pH 12 are shown. The peak potential is approximately -480 mV under the conditions we used. Repetitive analysis of a sample containing arsenite ion at 10 ppb yielded a relative standard deviation for 30 consecutive measurements ppb of 9.0%.

Sampler Design. The challenge in monitoring hazardous volatile compounds such as Lewisite in air is the trace levels which must be selectively measured. A sampling technique for trace analysis will then optimally incorporate not only effective separation but also preconcentration of the target analyte(s). Our approach to monitoring Lewisite at the 8-hour Time Weighted Average (TWA) level (3 $\mu g/m^3$) is based on the use of a membrane-based gas sample module to selectively extract and preconcentrate Lewisite from the ambient air. Liquid-phase extraction based on a gas permeation membrane (GPM) technology is well-suited for a portable sampler, due to its simplicity, efficiency, and ruggedness.[16-18] The GPM exploits Lewisite's ability to quickly penetrate rubber materials. The key to the successful operation of the FITGA is the selectivity and enrichment that is possible with a GPM (Table I).

A "tube-in-shell" GPM design is used in the prototype FITGA. A thin-walled tubular GPM is inserted into a cylindrical shell made of Teflon, glass, or some other chemically inert material. The air sample passes into the outer shell while the acceptor stream flows through the inside of the tubing. The "tube-in-shell" design is superior to other designs because the sampling surface area may be adjusted by varying the length and orientation of the tubing, thereby increasing the collection efficiency that is essential for analyte enrichment.

Maximum preconcentration can be achieved in the GPM by stopping the flow of the acceptor stream during collection. The sampled air is kept at a continuous flow rate such that the analyte is continuously transported into the acceptor stream. As the analyte dissolves in the acceptor stream (or reacts to form a soluble product), a

concentration gradient forms that increases the membrane permeation rate as the product is swept off of the inner wall of the membrane into solution. For the prototype FITGA, this will occur as Lewisite in the (gas) donor stream is transported across the membrane into the acceptor stream, where it is hydrolyzed by base to arsenite ion in the (liquid) acceptor stream. After a preset time the acceptor stream now containing the sample plug of AsO_2^- is injected toward the detector. This sampling process is easily automated using FI and applied to continuous air monitoring using a variety of membrane materials, including nonporous (e.g., silicone or natural rubber), microporous (e.g., Teflon®, polyvinylidene difluoride, polyvinyl chloride, polypropylene, cellulose esters) and ion-exchange (e.g., Nafion®) semipermeable membranes.

Methods using gas permeation membrane (GPM) sampling were studied for a Lewisite simulant compound using an off-the-shelf tubular gas permeation unit for the FITGA prototype. The GPM was an inert glass cylinder (25 mm o.d., 17 mm i.d.) with stainless steel endcaps with a thin-walled silicone rubber tube wound around a Teflon rod along the central axis of the cylinder. We used $AsCl_3$ for simulating Lewisite, as like Lewisite it is volatile and hydrolyzes in base to arsenite ion. Furthermore, $AsCl_3$ is found as a byproduct (i.e., unreacted starting material) in weapons-grade Lewisite. Vapor-phase $AsCl_3$ was generated by using an $AsCl_3$ permeation tube, which allowed the precise introduction of low levels of simulant into the GPM. We found that the $AsCl_3$ permeates the silicone rubber membrane, but much slower than expected. Although a stable response was achieved within two cycles, the $AsCl_3$ was difficult to "clear" from the within the membrane (Figure 2). We suspect that $AsCl_3$ reacts with interstitial water in the silicone membrane to form an arsenic hydrolysis product of very low permeability. Although we found that the permeability rate of $AsCl_3$ across silicon rubber was low, we expect much permeation higher rates for the more hydrocarbon-like Lewisite molecule.

Based on the successful PSA method development work quantifying CVAA in alkaline solution, a portable method for measuring traces of Lewisite (i.e., CVAA) in environmental samples (e.g., surface water, soil, wipe samples, etc.) is available for possible use in a field environment. Our goal is a portable FITGA instrument that can, with slight modification, serve a dual purpose: first, as a TWA-level air monitoring system to protect inspector safety; and second, as a trace-level quantitative analytical instrument for suspect process or environmental liquid samples or extracts.

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Figure Legends:

Figure 1. PSA response to 10 μg/L arsenite ion under alkaline conditions (pH 12); the background response (i.e., blank injection) is shown also.

Figure 2. Response of the prototype FITGA to vapor-phase arsenic trichloride challenges. Time course plot following challenge of arsenic trichloride (two minutes at 2.6 μg/min emission rate) to gas permeation membrane sampler (5 cm silicone rubber) at 200 mL/min sampling rate.

TABLE I. System performance goals for monitoring ambient air at the TWA level (3 μg/m³)

• Detection Limit:	≤ 0.75 μg/m³ Lewisite
• Analysis Time:	≤ 15 min
• Relative Error:	< ±25% at TWA

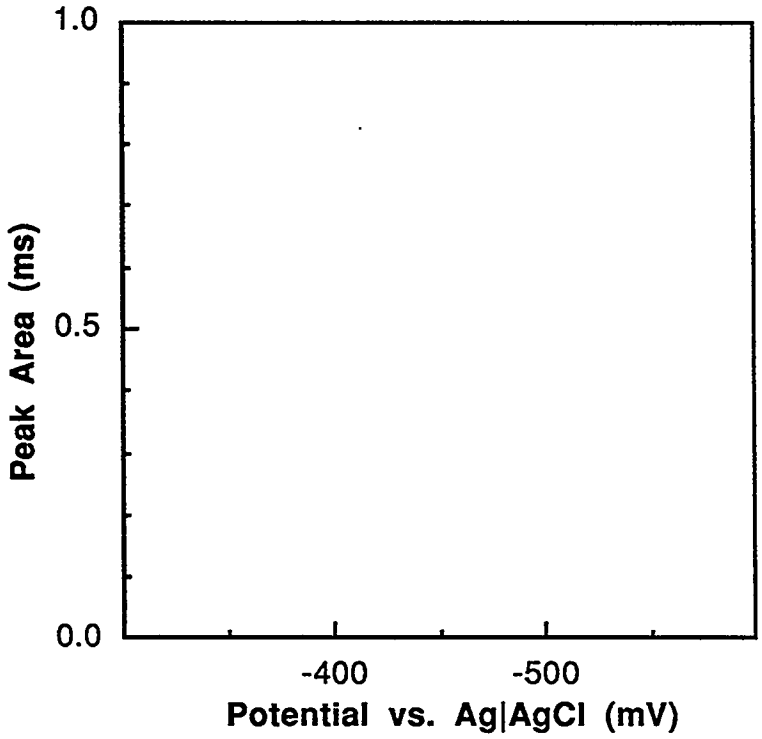

Figure 1

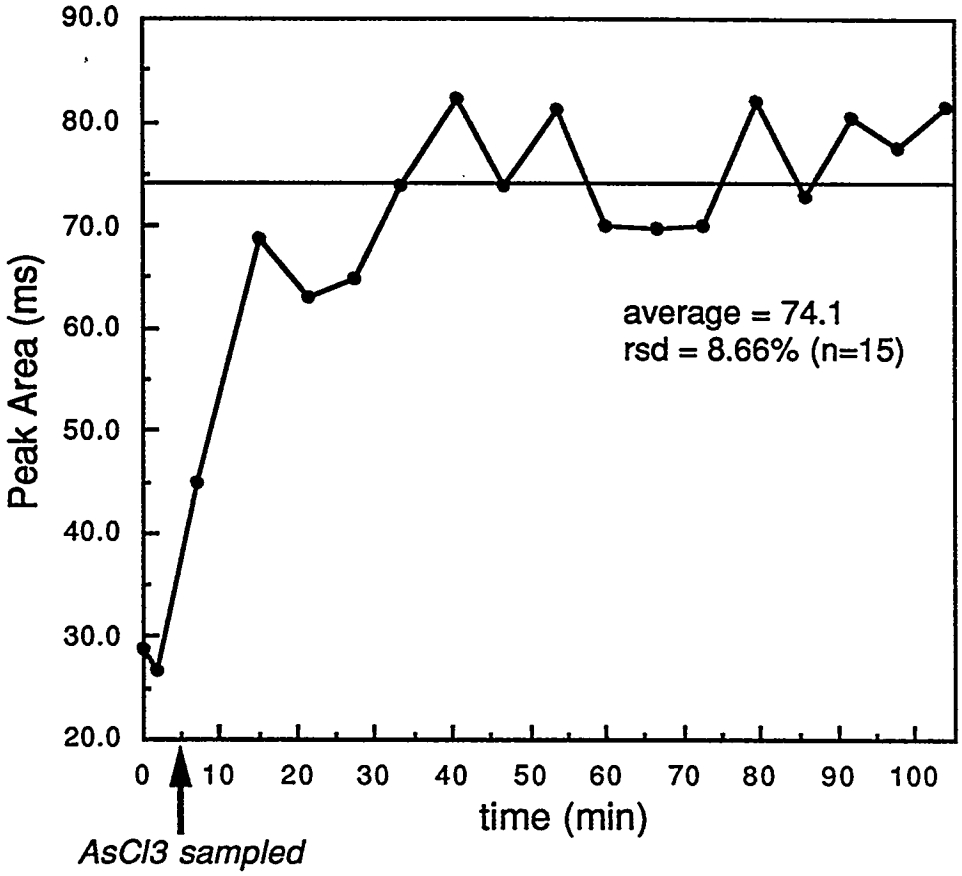
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
Peak Area (ms)
average = 74.1
rsd = 8.66% (n=15)
0
10
20
30
40
50
60
70
80
90
100
time (min)
AsCl3 sampled

Figure 2

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