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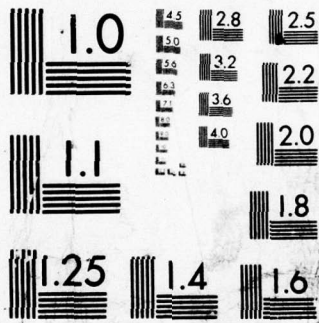
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TECHNICAL REPORT

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FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRIC
ANALYSIS FOR LEWISITE (L)

10 CPT BENJAMIN C. GARRETT

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CHEMICAL LABORATORY DIVISION

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FOREWORD

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I. INTRODUCTION

During the movement of chemical agents from Dugway Proving Ground to Tooele Army Depot-South Area, a need arose to monitor transport vehicles for the presence of Lewisite. This paper reports on a method that was developed for detection of Lewisite by analysis for arsenic, using flameless atomic absorption spectroscopy (FAAS). "Flameless atomic absorption spectroscopy" refers to work performed by means of a heated graphite furnace; that is, the volatilization of the species of interest takes place in a furnace, and the flame associated with conventional atomic absorption spectroscopy is not needed.

The procedure that was used is given along with a discussion of how this compares with other available methods for Lewisite analysis. In this regard, particular attention is paid to the requirement that the Lewisite analysis procedure used in support of the chemical agent move must certify the absence of Lewisite down to 3 ng of Lewisite per liter of air.

II. EXPERIMENTAL

A. Apparatus

All measurements were made on a Perkin-Elmer Model 503 atomic absorption spectrophotometer, equipped with a Perkin-Elmer Model 56 chart recorder and a Deuterium-arc background corrector. The light source was an arsenic electrodeless discharge lamp emitting light at 193.7 nm. A Perkin-Elmer Model HGA-2100 (heated graphite atomizer) controlled the time and temperature cycles for the furnace compartment. A Gilson adjustable micro-pipet and disposable pipet tips were used to dispense all samples into the graphite furnace.

B. Reagents

1. Arsenic Standard

All arsenic solutions were prepared fresh daily by serial dilutions from a 1000 ppm (mg/L) arsenic standard (As (III) as As_2O_3 in dilute (0.1 N) hydrochloric acid, obtained commercially from Ricca Chemical Company, Arlington, Texas, lot number D271).

2. Lewisite Standard

All Lewisite ($C_2H_2Cl_3As$; dichloro (2-chlorovinyl) arsine) solutions were prepared by serial dilutions from a 120 mg Lewisite/L standard that was prepared using a weighed amount of Lewisite from Ton Container #D49221. The solvent for all Lewisite solutions as well as the standard was 1 N NaOH. The use of sodium hydroxide as the Lewisite

solvent allowed the Lewisite-containing solutions to be handled routinely rather than as chemical agent solutions, because the strong hydroxide completely decontaminated the Lewisite by hydrolysis.

3. Nickel Solution

A solution containing approximately 1000 ppm Ni (II) was prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Mallinckrodt, AR grade, lot number 6384), using 1 percent (v/v) HNO_3 in glass-distilled water as the solvent.

C. Procedure

1. Selection of FAAS Operating Conditions.

The selection of optimum routine operating conditions for the heated graphite furnace involved determining the proper settings to be used for the temperature and duration of the drying, charring, and atomization cycles. In determining these for the routine assay of arsenic in Lewisite samples, the following steps were used:

a. Selection of the initial operating conditions, based upon those recommended for use in routine assay of aqueous arsenic solutions.¹

b. Determination of the atomization temperature giving the maximum absorbance, using the initial conditions.

c. Selection of the proper charring temperature, by measuring the effect of various charring temperatures on the absorbance. The selected charring temperature is the highest one giving high absorbance, that is, before there is a noticeable decrease in signal due to volatilization of arsenic during the charring sequence.

d. Determination of the shortest duration for the drying and charring cycles, giving no decrease in absorbance.

The drying cycle removes low boiling-point liquids, primarily the solvent, from the sample. The duration for this depends largely on the sample volume.

The charring or pyrolysis stage removes any components of the sample matrix which are more volatile than the element of interest prior to the atomization stage, and it is especially useful in decreasing broad-band absorption interferences. Charring must be sufficiently long and high enough temperature to remove as completely as possible interfering materials, yet short enough and at a low enough temperature to ensure minimum loss of the element being measured.

¹ Analytical Methods for Atomic Absorption Spectrophotometry Using the HGA Graphite Furnace, Perkin-Elmer, Norwalk, Connecticut, 1977, pp. 1-1 through 11-2.

The atomization cycle volatilizes the element of interest and maintains a certain population of the element within the graphite tube throughout the cycle. It is during the atomization that the sample absorbance measurement takes place. The final selection of temperature and duration for atomization often is a compromise between absorbance signal obtained and graphite tube lifetime, because higher temperatures and longer times both increase absorbance and decrease lifetime of the tube.

2. Selection of Solvent.

The Lewisite samples were solubilized in 1 N NaOH to hydrolyze the Lewisite. However, alkaline media are frequently unsatisfactory for atomic absorption work, as they lead to formation of precipitates or favor absorption of the element on the solution container.² Initially, all Lewisite and inorganic arsenic samples in 1 N NaOH were acidified by adding one volume of 50 percent (v/v) HNO₃ to five volumes of sample. The inorganic arsenic standards prepared this way gave the same absorbance values as those prepared directly in 5 percent (v/v) HNO₃. Calibration curves were calculated for acidic- and alkaline-solution inorganic arsenic standards to determine whether the alkaline solvent affected the arsenic.

3. Sample Introduction Technique.

The desired volume of sample, usually 25 or 50 μ L, was introduced into the graphite tube using an adjustable micro-pipet. This technique is commonly used in graphite furnace work and is rapid and convenient; unfortunately, it is also the source of a great deal of sampling error due to both poor precision in pipetting such small volumes and contamination of pipet tips.³ Consequently, five replicate injections were made of every sample.

III. RESULTS AND DISCUSSION

A. FAAS Operating Conditions

Table 1 gives the initial conditions tried and the final conditions selected for use in the FAAS of arsenic in Lewisite samples. The effect of increasing atomization temperatures is shown in Figure 1. In the determination of arsenic, two techniques are frequently employed to

² K. S. Subramanian, C. L. Chakrabarti, J. E. Sueiras, and I. S. Maines, Anal. Chem., 50, 444 (1978).

³ H. L. Kahn, Martha Bancroft, and R. H. Emmel, Research/Development, 26(7), 30 (1976).

help meet the objectives of the charring cycle: (1) use of the Deuterium-arc background corrector and (2) treatment of the sample with a suitable reagent to convert the arsenic to a less volatile form. This second technique is known as matrix modification and commonly involves the use of nickel added to arsenic solutions, bringing about the formation of fairly stable nickel arsenides.^{4,5} The necessity of background correction for arsenic determinations has been investigated comprehensively^{6,7}; consequently, background correction was used throughout. The addition of 1000 ppm nickel to the Lewisite samples did not bring about any improvement in the maximum useable charring temperature, as shown by Figure 2. Quite possibly this is because the arsenic in Lewisite samples exists in a relatively refractory form, as is the case of many organoarsenic compounds⁸, and conversion to nickel arsenides does not occur or does not improve heat stability. In any event, matrix modification by the addition of nickel was unnecessary for the Lewisite samples.

Table 1. Flameless atomic absorption spectroscopy conditions used for determination of arsenic in Lewisite.

	Initial	Final
Drying Temperature (° C)	110	110
Drying Time (seconds)	40	30
Charring Temperature (° C)	300	1000
Charring Time (seconds)	30	25
Atomization Temperature (° C)	2000	2400
Atomization Time (seconds)	12	10
Purge Gas & Mode	Argon, interrupt	Argon, interrupt
Purge Gas Flow Rate	40 mL/min	40 mL/min

B. Effect of Solvent

Table 2 lists the calibration curve data obtained for the two sets of inorganic arsenic standards, one which was prepared in 1 N NaOH then acidified prior to injection and the other which was left alkaline.

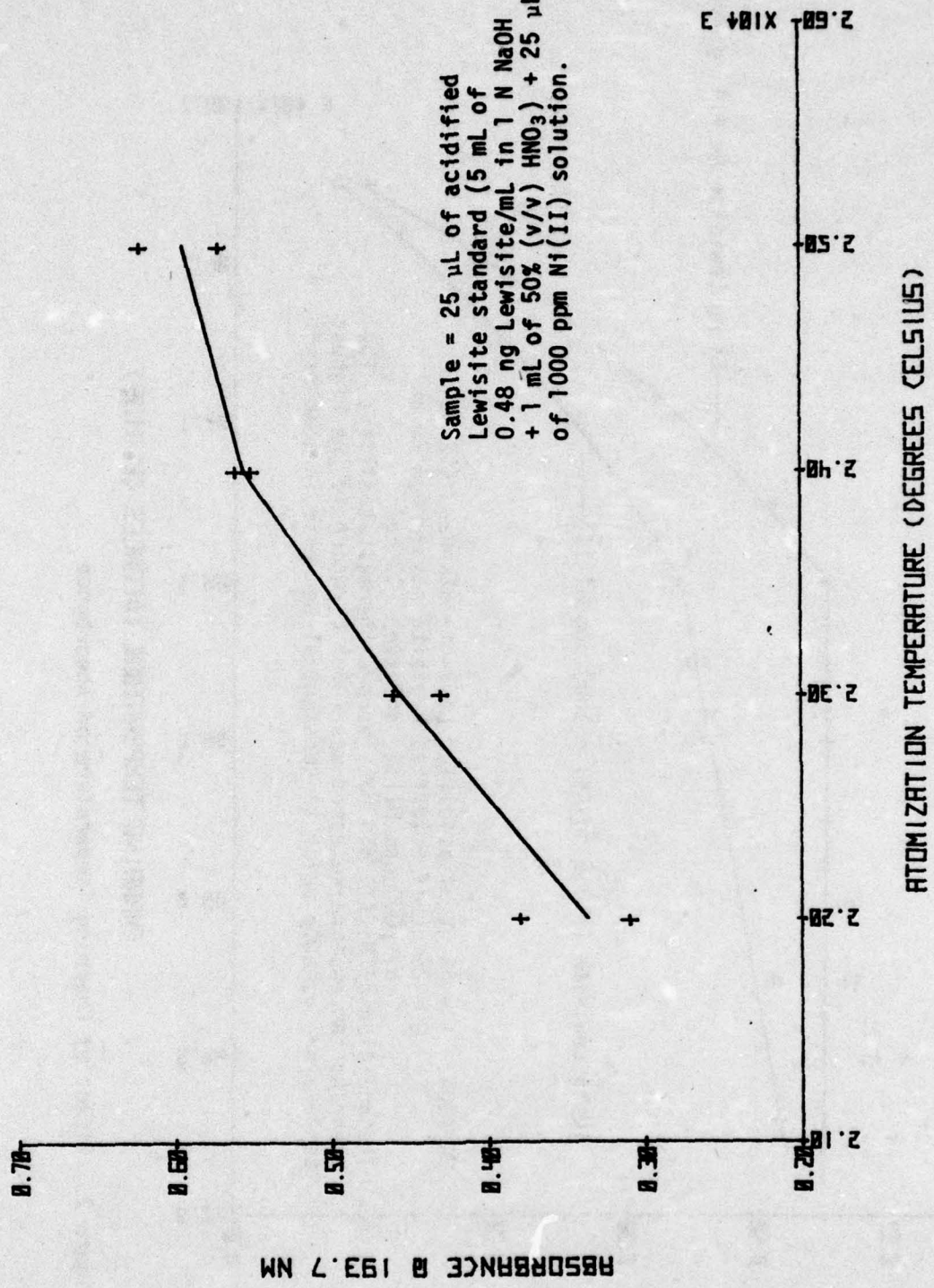
⁴ P. R. Walsh, J. L. Fasching, and R. A. Duce, Anal. Chem., 48, 1014 (1976).

⁵ R. Ediger, At. Absorp. Newsl., 14, 127 (1975).

⁶ J. W. Robinson, G. D. Hindman, and P. J. Slevin, Anal. Chim. Acta, 66, 1965 (1973).

⁷ A. W. Fitchett, E. H. Daughtrey, and P. Mushak, Anal. Chem. Acta, 79, 93 (1975).

⁸ G. C. Kunselman and E. A. Huff, At. Absorp. Newsl., 15, 29 (1976).



Sample = 25 μ L of acidified Lewisite standard (5 mL of 0.48 ng Lewisite/mL in 1 N NaOH + 1 mL of 50% (v/v) HNO₃) + 25 μ L of 1000 ppm Ni(II) solution.

Figure 1. Effect of Atomization on Absorbance.

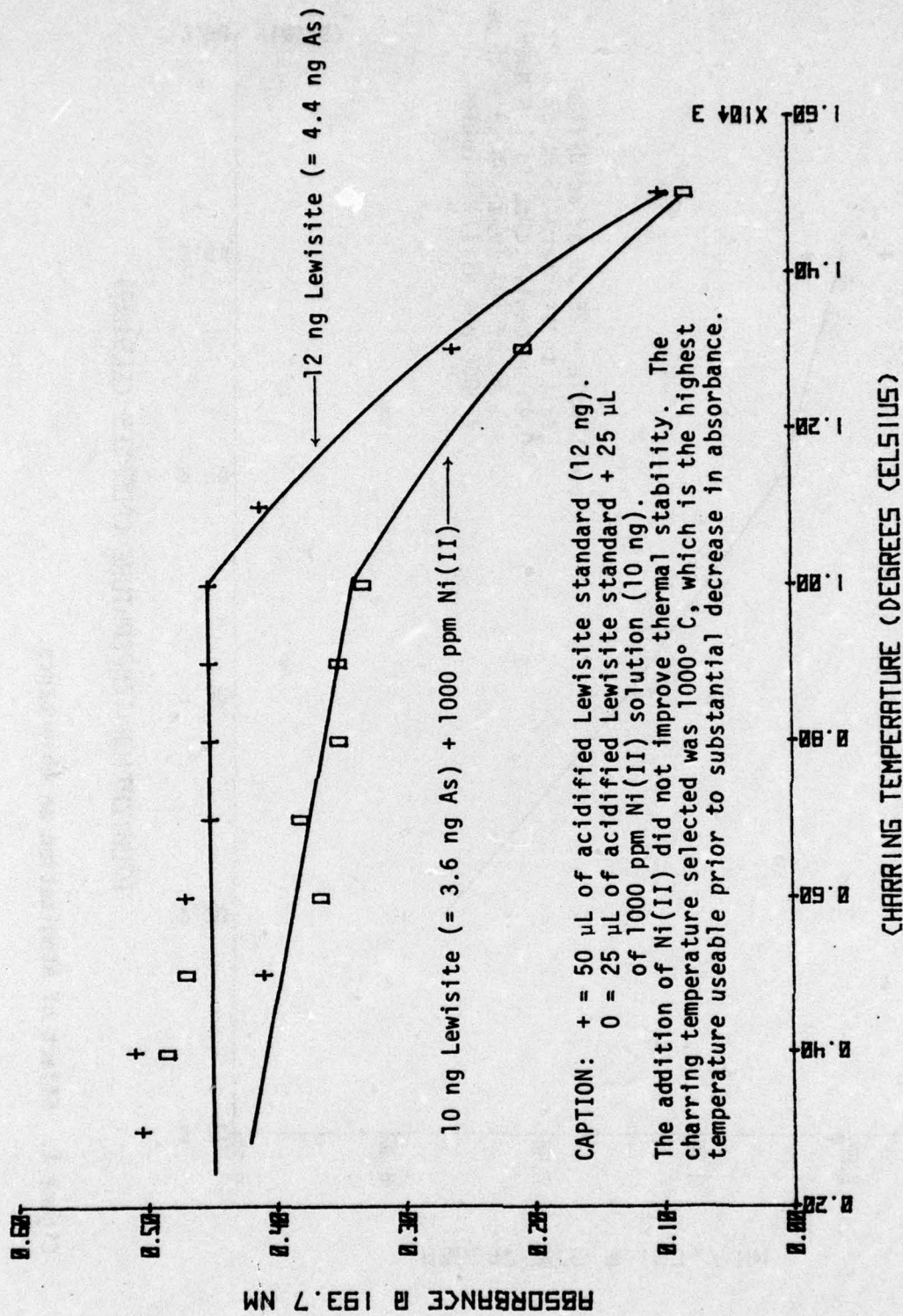


Figure 2. Effect of Charring Temperature on Absorbance

The analytical calibration curves calculated by regression analysis of the two sets of data show close agreement; the values for the slope, which reflect the sensitivity of the method, are identical at 0.118 a.u./ng As. The values of the y-intercept differ by 0.005 ng, probably reflecting errors in standard preparation. Therefore, the response for acidified and alkaline samples is equivalent. The need for acidification of the Lewisite samples was eliminated, making it possible to inject the sample directly in the sampling solvent.

Table 2. Calibration curve data

Samples	Arsenic (ng)	Absorbance (193.7 nm)	Regression Line (Y=abs., X=[As])
Acidified	Blank	0.012	$Y = 0.118X + 0.016$
	0.208	0.038	
	0.417	0.066	
	0.833	0.118	
	1.67	0.215	
	2.08	0.262	
	4.17	0.505	
Alkaline	Blank	0.015	$Y = 0.118X + 0.021$
	0.313	0.053	
	0.625	0.102	
	1.25	0.168	
	1.88	0.246	
	3.13	0.400	
	6.25	0.756	

C. Analysis of Lewisite Samples

Six different dilutions of the same Lewisite standard were prepared and analyzed, using the acidification procedure. Table 3 lists the experimental results, which give an average value of 35.6 percent As in the Lewisite. This compares with a value of 36.7 percent As obtained when it was analyzed in accordance with military specifications.^{8,9}

D. Comparison.

In addition to the FAAS method introduced here, the other commonly available methods for Lewisite analysis are iodometric titration of arsenious acid, colorimetric determination of ferric thiocyanate,

⁹ Military Specification MIL-L-10658A, 5 August 1964.

Table 3. Analysis of Lewisite samples

Lewisite (ng)	Absorbance (@ 193.7 nm)	Arsenic ^a (ng)	Percent Arsenic ^c in Lewisite
0.60	0.035	0.163 ^b	32.60 ^b
1.20	0.058	0.358	35.80
2.40	0.101	0.723	36.15
4.80	0.182	1.41	35.25
12.0	0.429	3.50	35.04
15.0	0.543	4.47	35.77

^aThe amount of arsenic was calculated using the calibration curve data for the acidified inorganic arsenic standards, because the Lewisite samples were treated similarly and analyzed at the same time.

^bThese values are probably erroneous because the measurements were made at or near the lower detection limit of the method for quantitative analysis and therefore, the percent As value was discarded in calculating the average, standard deviation, and percent relative standard deviation values.

^cAverage % As = 35.6
 $\sigma = 0.45$

% Relative
 Standard
 Deviation = 1.3

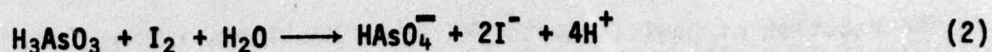
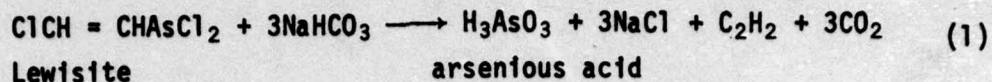
reaction with thio Michler's ketone (TMK), and arsine hydride generation. The following discussion outlines the procedures and summarizes the advantages and disadvantages of each.

1. Iodometric Titration.

The principle of this procedure is the conversion of Lewisite to Arsenious acid, the oxidation of this with iodine, and the detection of excess iodine with starch indicator solution^{9,10,11}. Equations 1 and 2 outline these steps:

¹⁰ L. M. Rice and E. E. Danner, TDMR 761, "Methods of Analysis of L Prepared by the Cuprous Chloride and Mercuric Chloride Processes," 20 September 1943, UNCLASSIFIED.

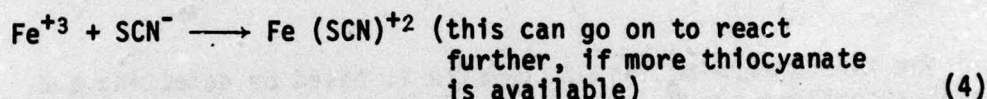
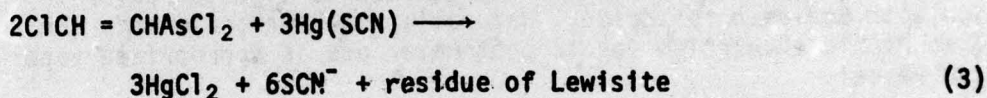
¹¹ Quality Assurance Directorate, US Army Edgewood Arsenal, #136-305-3, "Procedure for the Chemical Analysis of the Chemical Agent Lewisite (L)," 15 June 1964, UNCLASSIFIED.



This procedure has several advantages, in that it is relatively simple and requires no special equipment. Furthermore, by selective use of solvents, it can distinguish organic from inorganic arsenic compounds. The titration experiences interference from any species more readily oxidized than arsenious acid. The least amount of agent detectable by this method ranges from 10 to 100 µg. Overall, the iodometric titration is best suited for purity and composition analyses of neat or concentrated agent.

2. Colorimetric

The colorimetric determination of Lewisite involves the reaction of Lewisite with mercuric thiocyanate and subsequent reaction of the freed thiocyanate with an iron (III) solution to produce an intensely red-colored ferric thiocyanate complex. Equations 3 and 4¹²:



While this is slightly more sensitive than the iodometric titration, it is also more prone to interference.¹³ Many anions compete with iron for the thiocyanate, including bismuth, cadmium, cobalt, copper, nickel, and zinc. Phosphite, fluoride, oxalate, nitrate, and chloride compete with thiocyanate for iron. A major advantage of the procedure is that it is readily adaptable to automated analyzers.

¹² C. S. Ashcraft and K. W. Clark, EATM 321-5, "Rapid Colorimetric Method for Determination of Agents Phosgene, Lewisite, Hydrogen Cyanide, and Cyanogen Chloride," November 1966 UNCLASSIFIED

¹³ I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, Quantitative Chemical Analysis, 4th ed., Macmillan, London, 1969, pp. 1049-1052.

3. TMK.

The reaction of Lewisite with TMK (thio Michler's ketone; 4,4'-bis(dimethylamino)thiobenzophenone) is used primarily for detection rather than quantitative analysis of Lewisite.¹⁴ It is used in such devices as the XM 256 chemical agent detector kit for rapid identification of the presence of Lewisite in air samples down to 9 mg Lewisite per m³ air with minimal interference from other agents or common pollutants. Apparently, the precise nature of the reaction is poorly understood.

4. Arsine Hydride Generation.

The arsine hydride generation procedure is similar to FAAS^{15,16}. Arsenic is reacted in a closed vessel with sodium borohydride, and the arsine hydride produced is passed through a vapor cell placed in the path of an arsenic emission beam, the decrease of this being due to absorbance of arsenic. This procedure is very sensitive, being able to detect down to 10-30 ppb (ng As/L). It shows preferential reactivity to As (III); consequently Lewisite samples must be digested prior to reaction with sodium borohydride. Naturally, the method demands the use of an Atomic absorption spectrophotometer and an appropriate vapor reaction vessel.

5. FAAS

The FAAS determination of Lewisite is based on detecting and measuring absorbance due to arsenic at 193.7 nm. This spectral region is relatively free of other elemental lines, although broad-band background absorption is a problem, and there must be correction for it. FAAS detects mass or quantity rather than concentration of a species; its lower detection limit is expressed in terms of the least amount that can be measured. For normal arsenic samples this is somewhere on the order of 10-100 pg As.¹⁶ The procedure has the advantages of being very sensitive and relatively free of interferences. No special sample preparation is required. It does not distinguish among the various arsenic-containing species, as does iodometric titration. As with the arsine hydride generation procedure, it requires the availability of an atomic absorption spectrophotometer plus a heated graphite furnace.

¹⁴ L. D. Strauch, R. M. Gamson, R. B. Turner, H. L. Stroterhoff, M. P. Sullivan, and G. B. Sonneman, ED-TR-76121, "XM 256 Chemical Agent Detector Kit, the Detection of Lewisite," March 1977, UNCLASSIFIED

¹⁵ R. D. Wauchope, At. Absorp. Newsl., 15, 64, 1976.

¹⁶ K. G. Brodie, American Laboratory, 9 (3), 73, 1977.

IV. CONCLUSIONS

The use of flameless atomic absorption spectrophotometry in the determination of Lewisite has been validated. There is no need for special sample treatment or handling, rather, direct injection of alkaline samples is possible. The method seems best suited to the routine monitoring of samples for the presence of Lewisite.

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