NBSIR 73-260

A Gas Dilution System for Arsine-Air Mixtures

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National Bureau of Standards
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Final Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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ABSTRACT

A gas-blending system originally designed for chlorine-air mixtures was modified for producing arsine-air mixtures in the concentration range from 0.02 to 0.25 ppm. This system has been tested in order to provide accurately known concentrations of arsine-in-air for calibration of analytical monitoring devices. An analytical method has been developed for checking the concentration of arsine in the working standard and consists of the spectrophotometric measurement of an arsine-diethyldithiocarbamate complex in solution.

1. INTRODUCTION

The system originally designed for preparing chlorine-air mixtures [1] has been adapted for producing arsine-air mixtures in the range from 0.02 to 0.25 ppm. The system combines a gas blending unit and an analytical unit. The gas blending unit produces concentrations of arsine by dilution of a relatively high concentration of arsine in nitrogen (i.e. the bulk mixture) with a stream of clean air (i.e. the diluent). The concentration of arsine is measured by absorption of a known volume in a fritted glass absorption tube containing a 0.5 percent solution of the silver salt of diethyldithiocarbamate in pyridine (DDC). The intensity of the color produced is measured spectrophotometrically at 540 nm.

2. EXPERIMENTAL

2.1 Description of Gas Dilution System

A schematic diagram of the system is shown in Figure 1 where the midget impingers of the chlorine system have been replaced with a fritted glass absorption tube. This is an important modification to ensure efficient collection of arsine in the DDC solution. Photographs and additional diagrams of the system are included in NBS Report NBSIR 73-292 and in the operational manual.

2.2 Description of the Analytical System

The analysis of arsine is based on the formation of a coordination complex with the silver salt of diethyldithiocarbamate in pyridine (2,3). The arsine is collected quantitatively in 5-ml of a 0.5 percent solution of this salt in pyridine. The intensity of the color formed is measured spectrophotometrically at 540 nm and the concentration is obtained by comparison with a calibration curve. The sensitivity was found to be adequate for measuring arsine concentrations in the range from 0.02 to 2.0 ppm. As little as 1 to 2 liters of gas sample is required at the 2.0 ppm level to produce a visible red color change.

2.3 Preparation of a Calibration Curve via the Gutzeit Method

A known concentration of arsine was generated and collected in the DDC reagent to prepare a calibration curve. The arsine was generated via the Gutzeit method which depends on the following reaction:

$$As^{+3} + 4\ Zn + 5H^{+} = AsH_3 + 4\ Zn^{2+} + H_2$$

The arsine is produced and absorbed quantitatively. Figure 2 is a schematic diagram of the arsine generating system.

2.4 Preparation of Calibration Curve

A solution of NBS SRM 83C As_2O_3 was prepared by dissolving 0.1328 g of As_2O_3 in 25-ml of 10 percent NaOH solution followed by dilution to 1.0 liter in a volumetric flask. This solution contained 25.1 μg As^{+3}/ml. A 1:10 dilution of this solution was made to provide the stock solution for use in preparing the calibration curve.

From 1 to 10-ml aliquots of the stock As^{+3} solution containing 2.5 μg As^{+3}/ml were added to a glass vial as shown in Figure 2. The vial was capped immediately and the arsine was allowed to bubble through a fine capillary tube for one hour into 5-ml of a 0.5 percent solution of the DDC reagent in pyridine.

It was found that the arsine gas must be bubbled through a fine capillary tube at a relatively slow rate to ensure quantitative absorption in the DDC solution. The DDC-arsine solution was then transferred to a 1-cm cuvette and the absorbance was measured at 540 nm vs. the DDC reagent as a blank. A typical calibration curve is shown in Figure 3.

2.5 Preparation and Analysis of Arsine Bulk Mixtures

The initial attempt to prepare an arsine bulk mixture consisted of adding arsine gas at a partial pressure of 5-10 mm Hg to a cylinder and filling the cylinder with air to 1000 psi. Analysis of the arsine concentration was performed within several days after initial preparation. The results indicated that the arsine concentration had decreased considerably after initial preparation. Another arsine-in-air mixture was prepared containing

3000 ppm arsine according to the respective partial pressures of arsine and air added. Subsequent analysis after two weeks indicated that the arsine concentration was reduced to less than 0.5 ppm. As a result of these measurements, it was concluded that arsine-in-air mixtures in cylinders were not suitable as working standards. The decrease in arsine concentration is believed to be caused by the oxidation of AsH_3 by O_2 in the added air as follows:

$$4AsH_3 + 3O_2 = 4\underline{As} + 6H_2O.$$

2.6 Preparation of a Bulk Mixture of Arsine in O_2-Free Nitrogen

Efforts were then directed to the preparation of a mixture of arsine with O_2-free nitrogen to provide a working standard. The procedure consisted of first preparing a relatively high concentration of arsine in O_2-free nitrogen (< 5 ppm O_2). Arsine was added at a partial pressure of approximately 15 mm and filled to 200 psi with O_2-free nitrogen. The mixture was allowed to stand for 24 hours. Then the cylinder pressure was reduced to 50 psi and refilled to 1200 psi with O_2-free nitrogen. Subsequent analysis of this mixture yielded a result of 75 ppm. To prepare arsine mixtures via previously described dynamic dilution systems in the concentration range from 0.02 to 0.25 ppm, it was desirable to prepare a bulk mixture having an arsine concentration of about 2.0 ppm. This was accomplished by successive volumetric dilution of the 75 ppm arsine bulk mixture with O_2-free nitrogen. After each dilution the arsine concentration was analyzed and the results tabulated in Table 1. The good agreement between the calculated arsine values obtained by dilution and the observed measured values indicates no detectable effect of added oxygen-free nitrogen on arsine.

Table 1

Dilution of Bulk Mixture from 75 to 2 ppm with O_2-Free Nitrogen

Conc. of Bulk Mixture (arsine-in-nitrogen) ppm	Calc'd Conc. of Bulk Mixture after Dil. ppm	Meas. Conc. of Bulk Mixture after Dil. (mean, ppm)
75	35.0	34.1
35	6.9	7.8
6.9	4.2	4.4
4.2	2.0	2.0

3. RESULTS

3.1 Stability of Arsine-in-Nitrogen Bulk Mixtures

An important requirement of the bulk mixture is that it remain stable over a reasonable length of time. For this reason the arsine concentration was monitored over a period of several months to determine any change in concentration. The results shown in Figure 4 indicate a decrease in arsine concentration of 56 percent over a period of 4 1/2 months (i.e. 2.0 to 0.88 ppm). In view of the limited stability, it is recommended that bulk mixtures of arsine-nitrogen be analyzed each time they are used to prepare mixtures by the gas dilution procedure.

3.2 Evaluation of the Performance of the Dilution System

To prepare arsine concentrations in the range from 0.02 to 0.25 ppm, the bulk mixture was diluted with air using the previously described dynamic dilution system. The arsine concentrations were monitored to determine any change in the arsine concentration due to oxidation by the oxygen present in the diluent air. The concentration of arsine at the sample port outlet, C_x, was calculated as follows:

$$C_x = C_{bulk} \frac{F_{bulk}}{F_{bulk} + F_{air}}$$

where

C_x = concentration of arsine.

C_{bulk} = concentration of bulk mixture.

F_{bulk} = flow rate of bulk mixture.

F_{air} = flow rate of diluent air.

Calculated values were compared with the measured values of the concentration levels chosen. The results are tabulated in Table 2 and plotted in Figure 5.

Table 2

Comparison of Calculated and Observed Arsine Concentrations from Sampling Manifold

Conc. of Bulk Mixture 2.04 ± .02 ppm

AsH_3 flow rate ℓ/min	Air flow rate ℓ/min	Dilution factor	Calc'd conc. ppm	Obs. conc. ppm
0.053	0.718	0.07290	0.149	0.148
0.153	2.83	0.05129	0.105	0.103
0.053	2.83	0.01840	0.038	0.040
0.030	2.83	0.01049	0.021	0.025

4. CONCLUSION

It can be concluded from these results that an arsine-in-nitrogen bulk mixture can be diluted with air in the previously described dynamic system with sufficient accuracy to produce arsine concentrations in the sampling manifold in the range from 0.02 to 0.25 ppm. The overall error in concentration will depend upon the accuracy of the concentration of the bulk mixture and the flow measurements.

5. REFERENCES

1. E. E. Hughes, W. D. Dorko, E. Scheide, J. K. Taylor, Gas Generating Systems for the Evaluation of Gas Detecting Devices, NBS Report NBSIR 73-292, October 1973.

2. O. P. Bhargava, J. F. Donavan, and W. G. Hines, Anal. Chem. 44, 2402-(1972).

3. T. Kaneshige, M. Takizawa, and H. Nagai, Jap Anal. 13, 780-(1964).

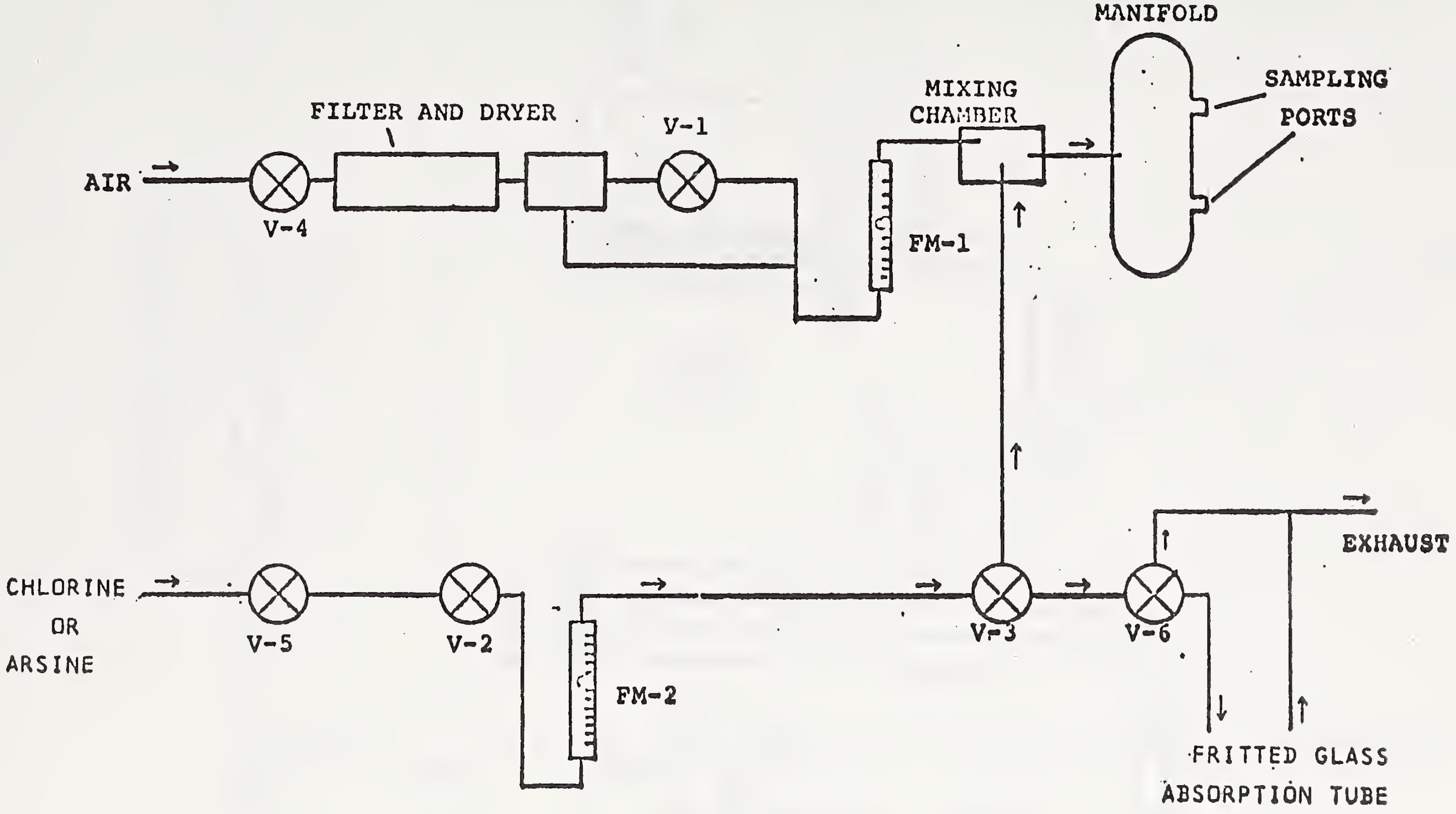

Figure 1. Gas Dilution System

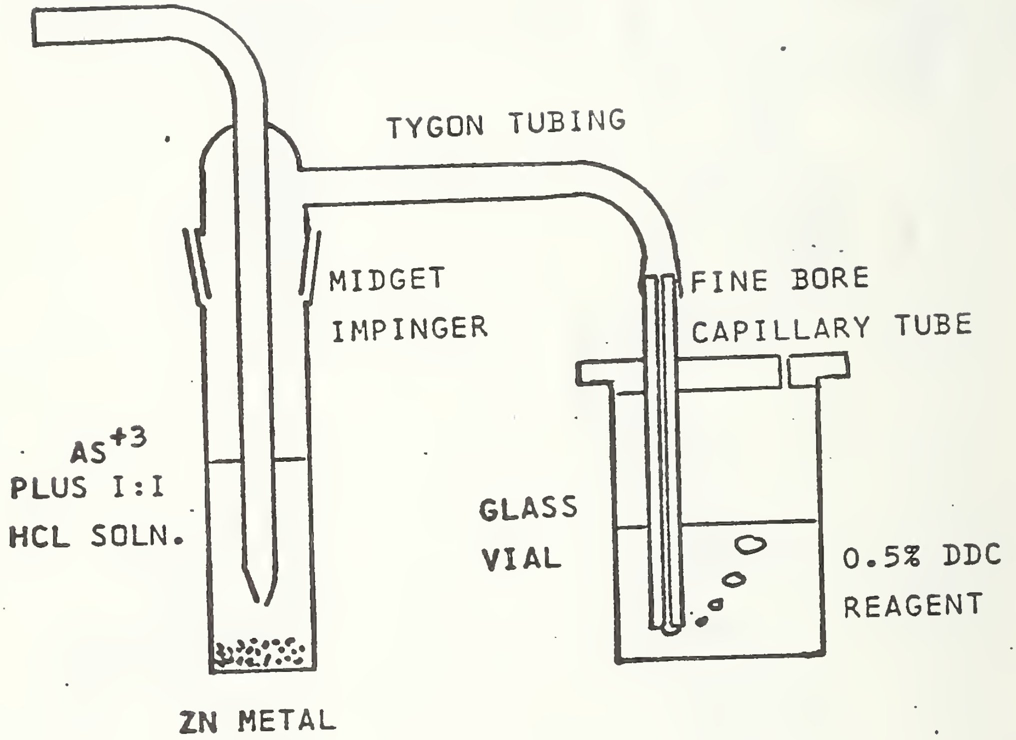

Figure 2. Arsine Generation System

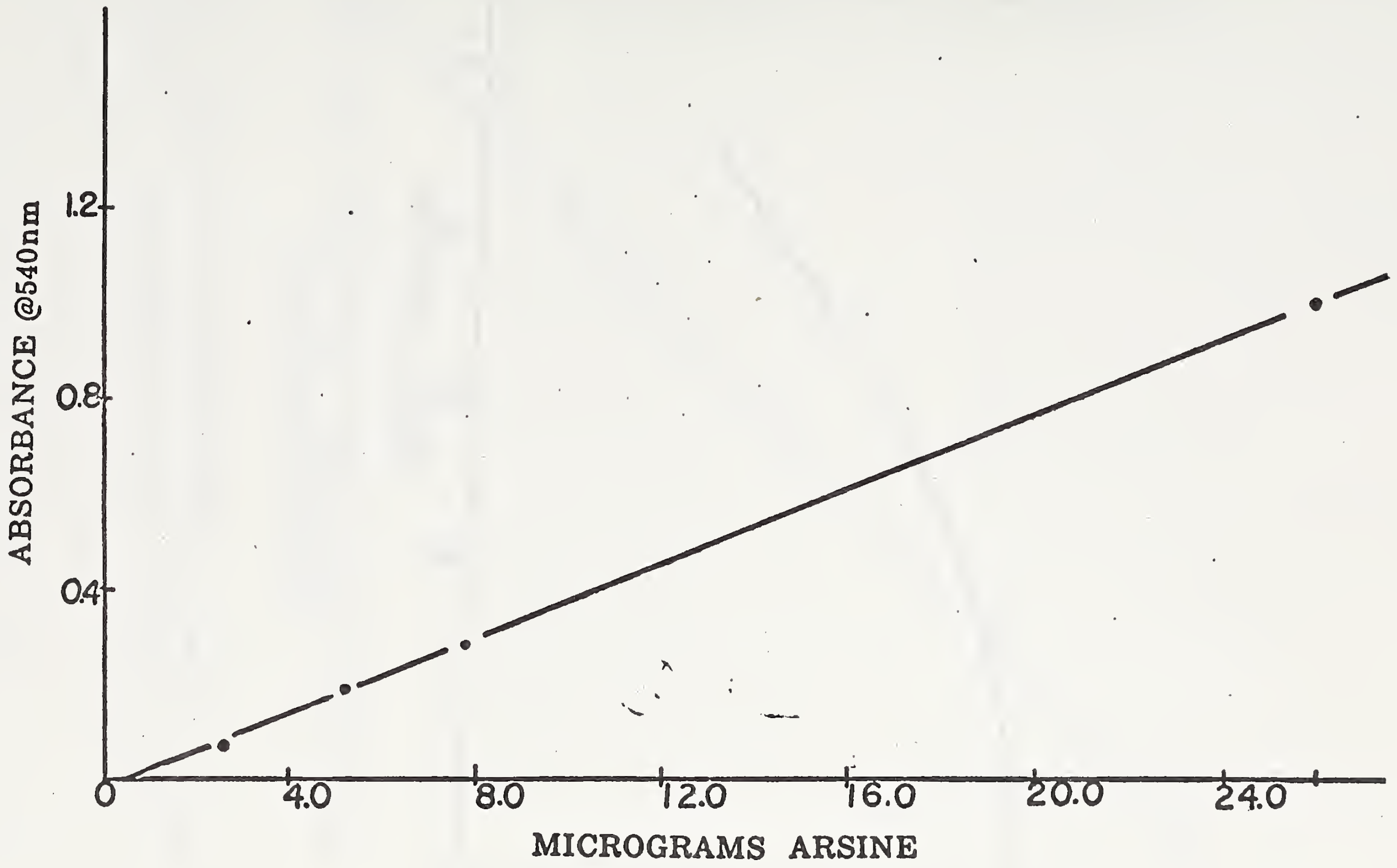

Figure 3. Spectrophotometric Calibration Curve

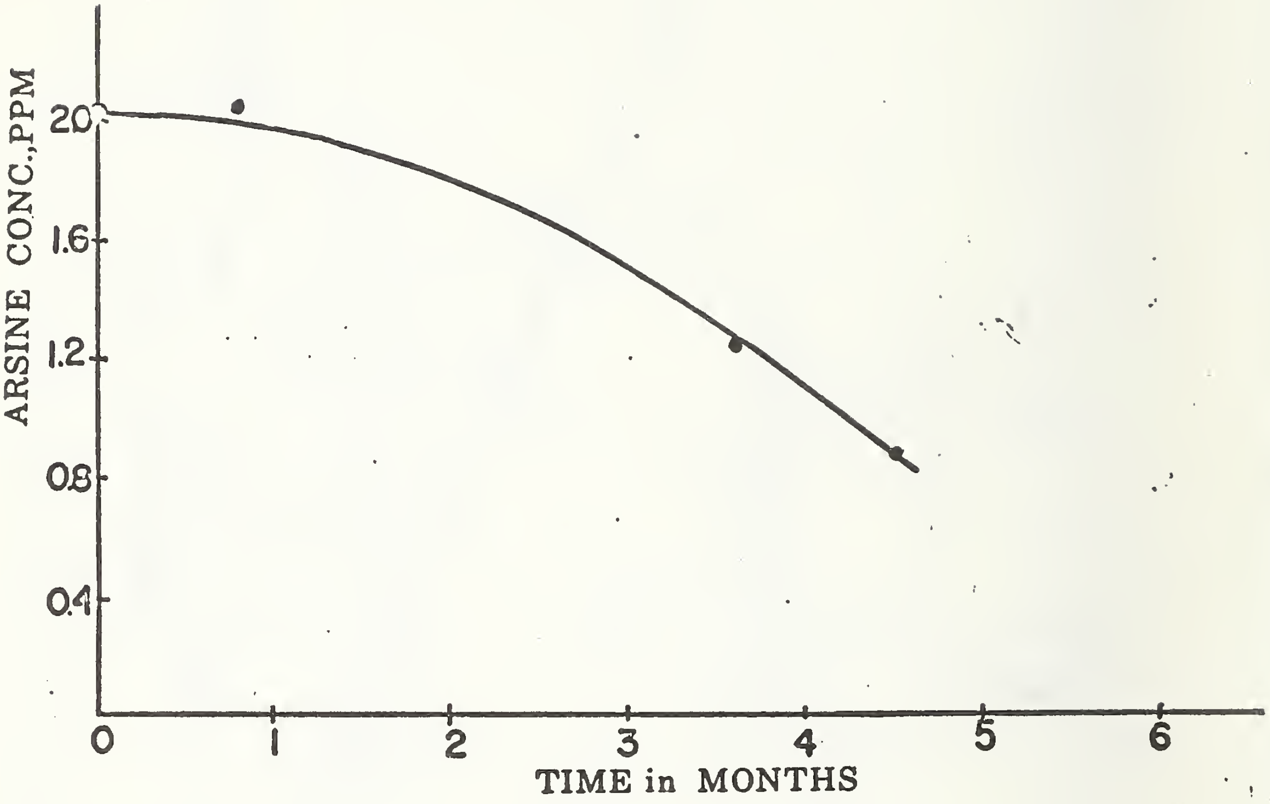

Figure 4. Change in Concentration of an Arsine-Nitrogen Mixture

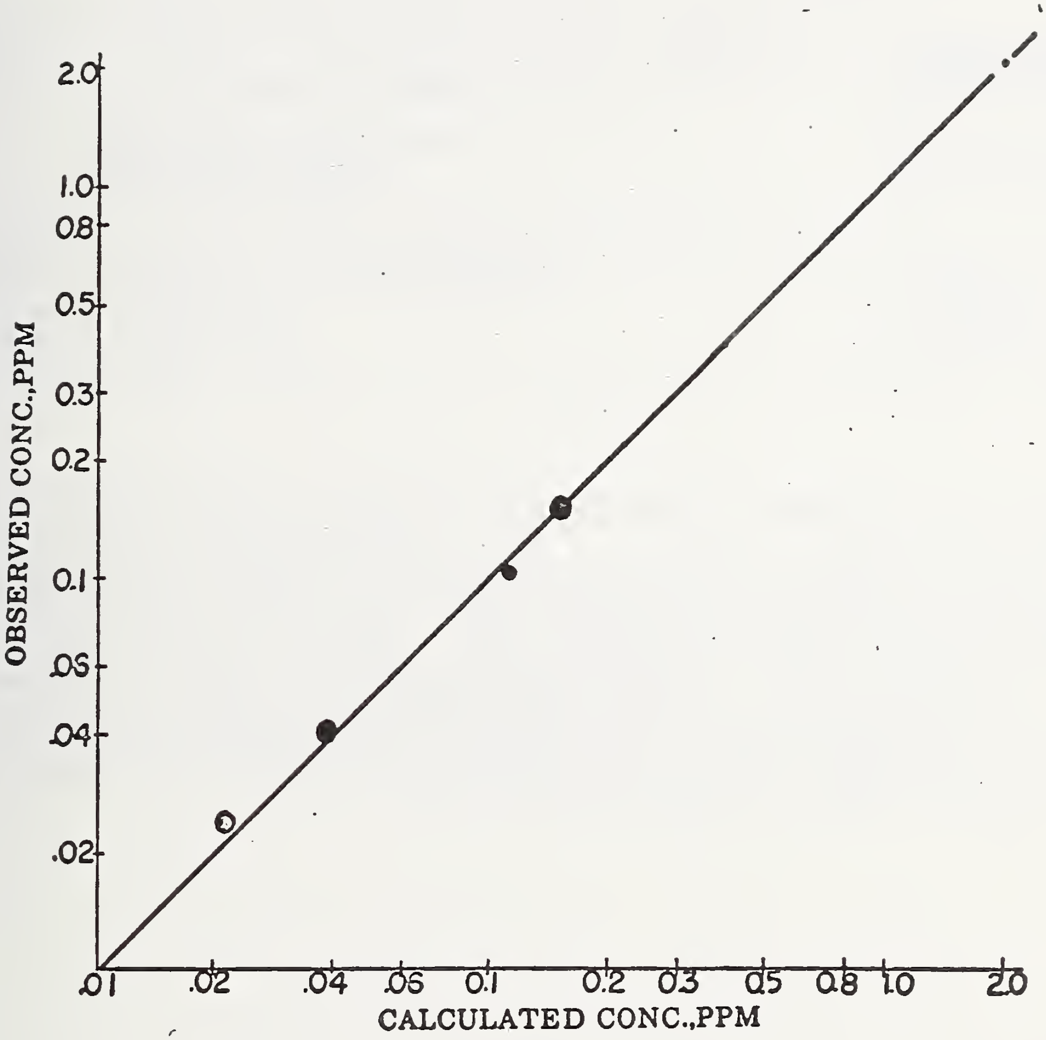

Figure 5. Performance of Arsine Dilution System

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR 73-260	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

A Gas Dilution System for Arsine-Air Mixtures

5. Publication Date
October 1973

6. Performing Organization Code

7. AUTHOR(S) P.A. Pella, E.E. Hughes, and J.K. Taylor

8. Performing Organ. Report No.
NBSIR 73-260

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

National Institute for Occupational
Safety and Health
Cincinnati, Ohio 45202

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A gas-blending system originally designed for chlorine-air mixtures was modified for producing arsine-air mixtures in the concentration range from 0.02 to 0.25 ppm. This system has been tested in order to provide accurately known concentrations of arsine-in-air for calibration of analytical monitoring devices. An analytical method has been developed for checking the concentration of arsine in the working standard and consists of the spectrophotometric measurement of an arsine-diethyldithiocarbamate complex in solution.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Arsine; gas-blending; gutzeit method; spectrophotometry.

18. AVAILABILITY ☒ Unlimited

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Washington, D.C. 20402, SD Cat. No. C13

☐ Order From National Technical Information Service (NTIS)
Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)
UNCLASSIFIED

20. SECURITY CLASS (THIS PAGE)
UNCLASSIFIED

21. NO. OF PAGES
14

22. Price

USCOMM-DC 29042-P74

AMERICAN REVOLUTION BICENTENNIAL 1776-1976