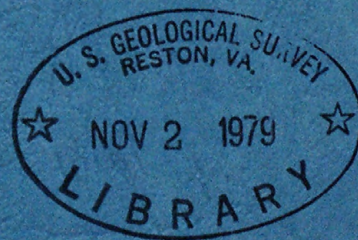


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DETERMINATION OF ARSENIC IN GEOLOGIC MATERIALS  
USING SILVER DIETHYLDITHIOCARBAMATE





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DETERMINATION OF ARSENIC IN GEOLOGIC MATERIALS  
USING SILVER DIETHYLDITHIOCARBAMATE

by

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## ABSTRACT

A colorimetric method is herein described for the determination of arsenic in a wide variety of geologic materials. The method has a detection limit of 1 ppm and no serious interferences. As many as 50 samples can be analyzed per man per day using relatively simple apparatus.

## INTRODUCTION

The U.S. Geological Survey has need for sensitive, rapid, interference-free methods for detecting various elements of geochemical interest in a wide variety of materials. Arsenic is one such element because of its role as a pathfinder element for hydrothermal ore deposits of Au, Ag, and Cu.

At present, As is commonly determined by an adaptation of a test described by Almond (1953). Although quite rapid and convenient, the method is lacking in sensitivity and reproducibility. A number of flame atomic-absorption techniques have been published recently that have great sensitivity, but poor reproducibility and numerous interferences. Some of these drawbacks have been resolved through improvements in the chemical preparation of samples and various automated sampling devices (Fishman and Spencer, 1977), but at the expense of simplicity of method and apparatus. Graphite-furnace techniques suffer from the same limitations. The molybdenum-blue method of Onishi and Sandell (1953) is quickly eliminated on the basis of being too laborious for rapid, routine analysis as well as being subject to serious interferences from Si and P.

A recent modification by Marshall (1978) of the silver diethyldithiocarbamate (AgDDC) method seems to best meet the above-mentioned criteria of simplicity, rapidity, and freedom from interference. The aqua regia-HF acid digest serves the multiple purpose of destroying organics, dispelling sulphur, and allowing for a large sample size while not necessitating specialized equipment, as is the case for perchloric acid digests. This variation of the procedure is quickly carried out with nothing more specialized in the way of equipment than fritted gas-dispersion tubes and a standard spectrophotometer. As many as 50 samples can be analyzed per man per day to a sensitivity of 1 ppm.

#### MATERIALS

AgDDC reagent is prepared by mixing a chilled 200-ml solution of 4.5 g sodium diethyldithiocarbamate (NaDDC) with a chilled 200-ml solution of 3.4 g  $\text{AgNO}_3$  while stirring vigorously. The resulting precipitate is vacuum filtered, washed twice with 100-ml portions of chilled demineralized water, and dried in a desiccator. In 250-ml of reagent-grade chloroform, 0.625 g of this product is dissolved along with 0.41 g 1-ephedrine (F. W. 165.24) (available through Aldrich Chemical Co., Inc.<sup>1/</sup>; Kopp, 1973). The iron solution was made with 7 g of ferrous ammonium sulfate hexahydrate per 100 ml of water and a pinch of ascorbic acid to prevent oxidation to the ferric state. Arsine was bubbled through the AgDDC solution by means of gas-dispersion tubes (B porosity) obtained from Ace Glass, Inc.<sup>1/</sup> A Bausch & Lomb<sup>1/</sup> spectronic 100 was used to read the complex-bearing chloroform solutions.

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<sup>1/</sup>Use of company and brand names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

## PROCEDURE

A 1-g sample is placed in a Teflon beaker followed by 2 ml  $\text{HNO}_3$ , 6 ml  $\text{HCl}$ , and 15 ml  $\text{HF}$ . The mixture is heated to dryness at  $110^\circ\text{C}$  and transferred to 16x150-mm disposable test tubes with 10 ml of 1 M  $\text{HCl}$ . After mixing and centrifuging, a 5-ml aliquot is transferred to a 25x150-mm test tube along with 5 ml of 1 M  $\text{HCl}$ . One milliliter of 1-percent iron solution is added to help insure a constant rate of hydrogen evolution from sample to sample (Bhargava and others, 1972; Marshall, 1978). One milliliter of 40-percent  $\text{KI}$  and 1 ml of 20-percent  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  are added, and the solution is mixed and left to stand for 10 minutes to allow reduction of available As and potential interfering ions to go to completion. Four to six pieces of mossy zinc are dropped into the solution, and the arsine-generation assembly is connected (Fig. 1). The resulting arsine is allowed to bubble for 30 minutes through 3 ml of  $\text{AgDDC}$  solution contained in 12x75-mm disposable culture tubes. The  $\text{AsDDC}$  complex is read on the spectrophotometer in the aforementioned culture tubes at 540 nm.

## STANDARDS

The 1,000- $\mu\text{g}/\text{ml}$  stock solution is made by dissolving 1.3 g arsenic trioxide in 20 ml 1 M  $\text{NaOH}$ , adding 500 ml water, 30 ml 1 M  $\text{HCl}$ , and diluting to 1 L. Prepare 100- $\mu\text{g}/\text{ml}$  standards from the stock by dilution with water.

Make a standard series (preferably with freshly made  $\text{AgDDC}$  as the blank and low standard are cleaner) in triplicate by pipetting 0, 0.1, and 0.5 ml of 10- $\mu\text{g}/\text{ml}$  standard and 0.1-, 0.25-, and 0.5-ml 100- $\mu\text{g}/\text{ml}$  standard into 25x150-mm culture tubes. Add 10 ml 1 M  $\text{HCl}$  and carry each standard through the normal procedure as above. These standards will correspond to 0, 2, 10, 20, 50, and 100 ppm in the samples. Plot the results on graph paper as in Fig. 2. On succeeding days, a single standard in triplicate will confirm whether or not all is well.

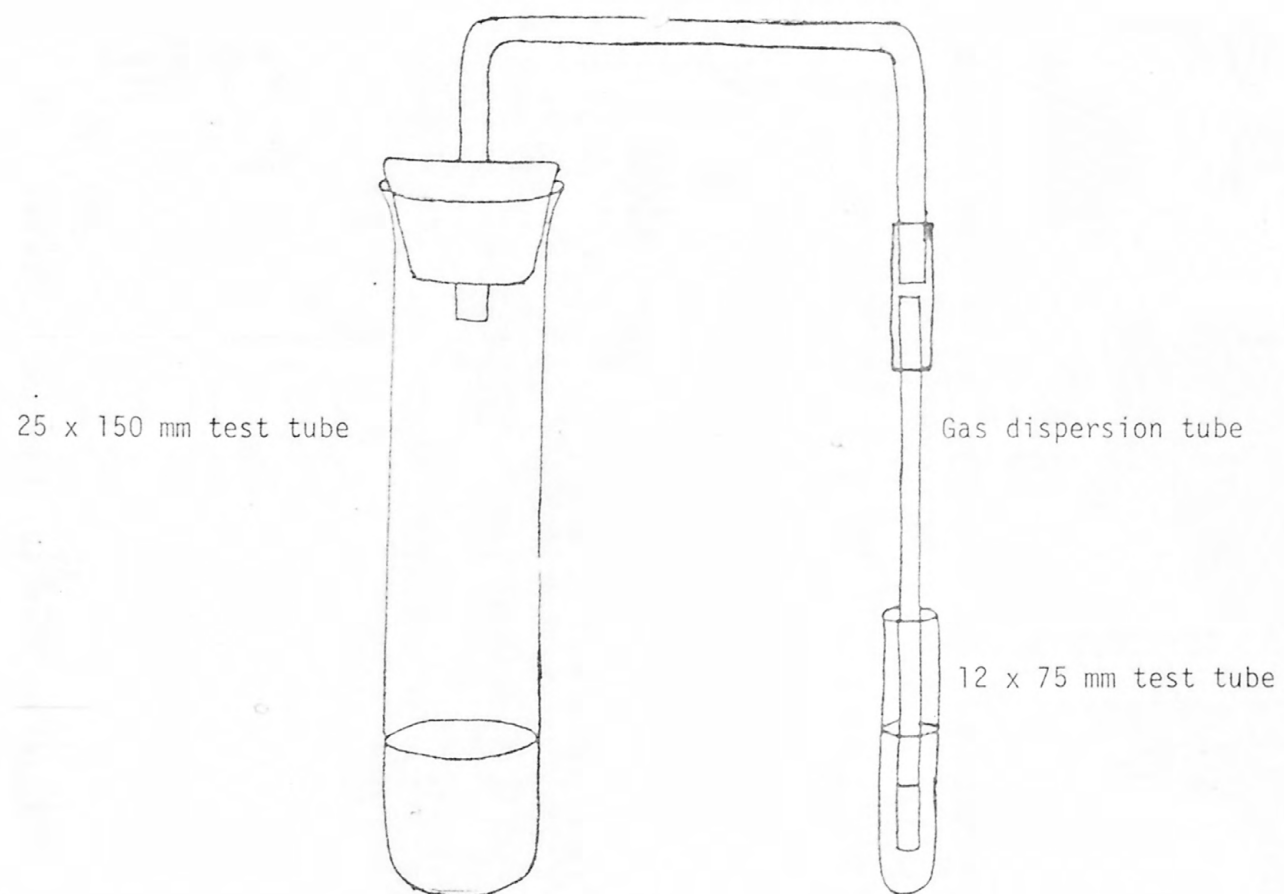


FIG 1.--Arsine evolution apparatus.

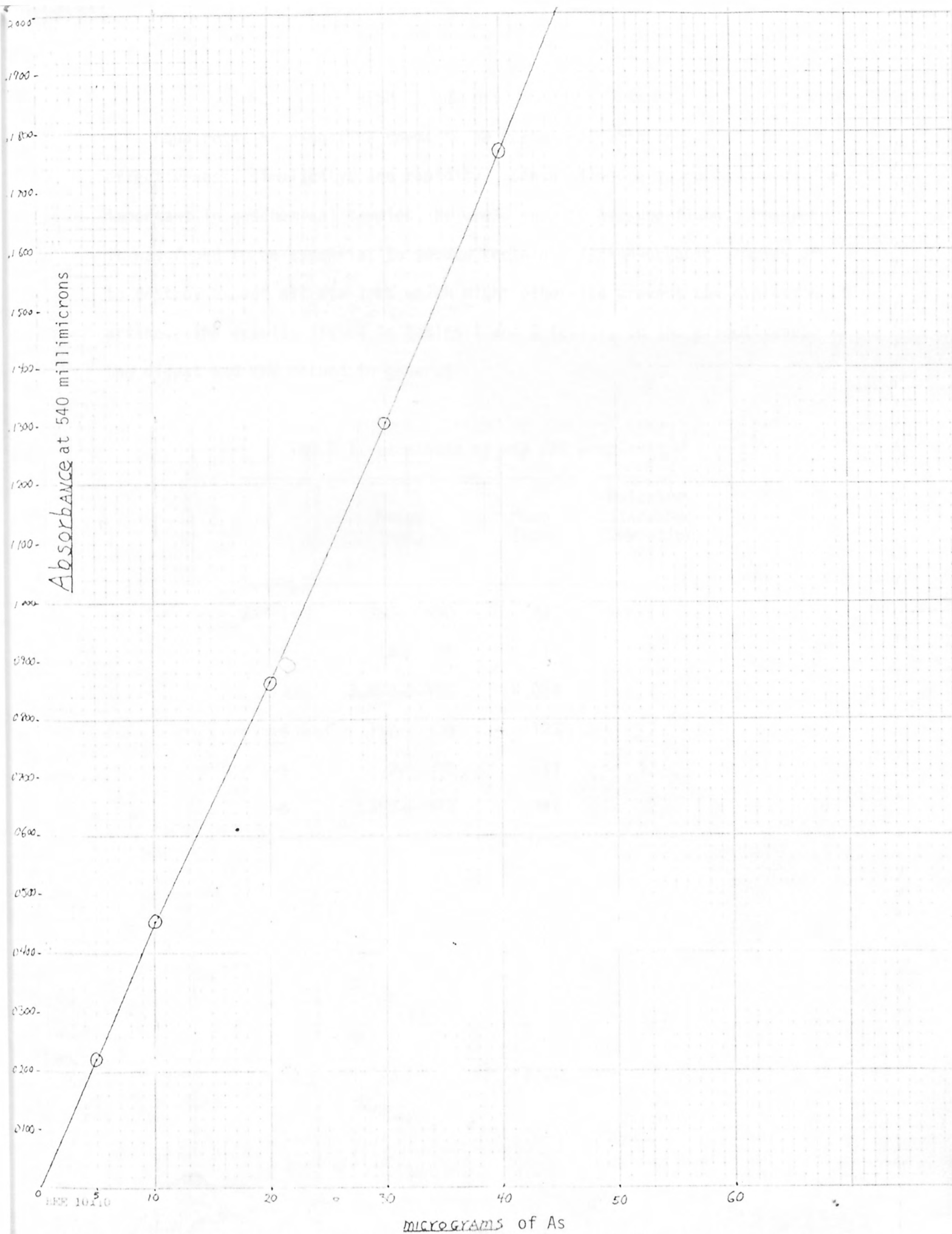


FIGURE 2.--Standard curve for arsenic using the silver diethyldithiocarbamate method.

## RESULTS AND DISCUSSION

Aqua regia-HF digestion seems to be most ideal with regard to its effectiveness, simplicity, and rapidity. Since silicate-bound As may not be important in geochemical samples, HF would seem to be superfluous; however, it was found to be essential to subdue frothing of high-organic samples and to destroy excess nitrate ions which might otherwise prevent the evolution of arsine. The results listed in tables 1 and 2 testify to the effectiveness of the digest and the method in general.

TABLE 1.--*Analysis of six GXR samples*

	Range (ppm)	Mean (ppm)	Relative Standard Deviation (%)
GXR-1	360- 490	432	12
-2	18- 21	19	7
-3	3,600-4,400	4,020	7
-4	110- 130	123	7
-5	9- 12	11	13
-6	350- 370	362	2



TABLE 2.--*Comparison of results*

	Mean <sup>a</sup> (ppm)	Mean <sup>b</sup> (ppm)	Mean <sup>c</sup> (ppm)	Mean <sup>d</sup> (ppm)
GXR-1	432	332	315	436
-2	19	18.2	20	23
-3	4,020	4,564	3,470	3,980
-4	123	89	75	103
-5	11	10	10	12
-6	362	329	250	297

<sup>a</sup> This method.

<sup>b</sup> Sanzolone, Chao, and Welsch, 1979.

<sup>c</sup> Allcott and Lakin, 1978.

<sup>d</sup> Terashima, 1976.

AgDDC dissolved in  $\text{CHCl}_3$  1-ephedrine was chosen over the pyridine solution not only to avoid the offensive odor of the latter solvent, but also to provide the necessary sensitivity to detect  $0.5 \mu\text{g}$  of As. The AgDDC must be fresh; otherwise it is difficult to dissolve or comes out of solution by the action of gases bubbling through it, thus producing cloudy blanks and standards.

A number of elements have been reported as having a negative interference on this method. Metallic interferences most often mentioned are Cu, Co, Ni, Cr, and Mo; and these probably interfere with the reduction and arsine-generation steps. Sufficient stannous chloride should solve these problems as Marshall's studies seem to confirm. He obtained quantitative recoveries with as much as  $2,000 \mu\text{g}$  of these elements present. In addition, it was found that the method modification here described would bear considerably more Sb, Te, and Hg than Marshall's studies indicate. Possibly the difference in complexing solutions is responsible for this discrepancy. Selenium was found to be the most severe interference, causing a considerable suppression of As values with as little as  $50 \mu\text{g}$  of the elements present. Even so, if one compares the concentration of these elements necessary to cause a significant interference with their crustal abundance, it is apparent that only exotic geochemical samples would present a problem.

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