Short Communication

Determination of Arsenic in Glycerine by Hydride Generation Atomic Absorption Spectroscopy

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ABSTRACT

A rapid method for the determination of arsenic in glycerine is described. The glycerine sample is diluted and any arsenic present reacted with sodium borohydride and hydrochloric acid to give arsine gas. The evolved arsine is quantitated by atomic absorption spectroscopy in a quartz tube positioned in the flame of a commercial instrument. The method is faster than the colorimetric arsine method recommended by the United States Pharmacopeia and has a precision of 4.4% (RSD) at the 50 μg level (equal to 1.25 μg As/g glycerine).

INTRODUCTION

The official monograph for glycerine in the United States Pharmacopeia (1) sets a limit for arsenic at 1.5 ppm (μg/g). The suggested method for the determination of arsenic (2) involves the evolution of arsine gas using zinc and hydrochloric acid to reduce the arsenic and quantitation by colorimetry. This method is time consuming and tedious as it requires the evolved arsine to bubble slowly through the indicating reagent for 45 min, silver diethyldithiocarbamate, which must be prepared fresh daily.

A much simpler method for the determination of arsenic is hydride generation atomic absorption spectroscopy (AAS) (3). This approach uses very similar chemistry to form arsine, but measurement occurs by decomposition of the arsine gas to arsenic atoms in a heated quartz tube followed by atomic absorption.

EXPERIMENTAL

All experimental work was performed on a Perkin-Elmer (Norwalk, Conn.) 403 atomic absorption spectrometer using a Perkin-Elmer MHS-10 hydride generation attachment, a PE arsenic hollow cathode lamp and a PE Model 56 chart recorder. The MHS-10 (Fig. 1) consists of a reductant solution reservoir, reaction flask, quartz tube, and the necessary plumbing and mounting hardware. The quartz tube is held above the standard 10 cm slot burner and heated by a small, lean air-acetylene flame. Argon is used to purge the cell, and also to provide the pressure which pumps reductant into the sample flask during a determination.

All chemicals used were ACS reagent grade from Fisher Scientific (Pittsburgh, PA). Arsenic standards were prepared from a 1000 μg/g solution also purchased from Fisher. The sodium borohydride in 1% sodium hydroxide solution was filtered through coarse filter paper and found to be stable for at least 2–3 days. Use of a finer filter would extend stability to 3 weeks (4).

The USP arsenic method was performed as written, except that the arsenic standard solutions were prepared from the 1000 μg/g commercial stock solutions.

METHOD

Dilute 1 g of the glycerine sample to 25 mL with deionized water. Transfer 1 mL of the diluted sample to the reaction flask, add 9 mL of 1.5% hydrochloric acid, and allow the system to purge with argon. Depress the plunger to deliver the basic 3% sodium borohydride solution to the reaction

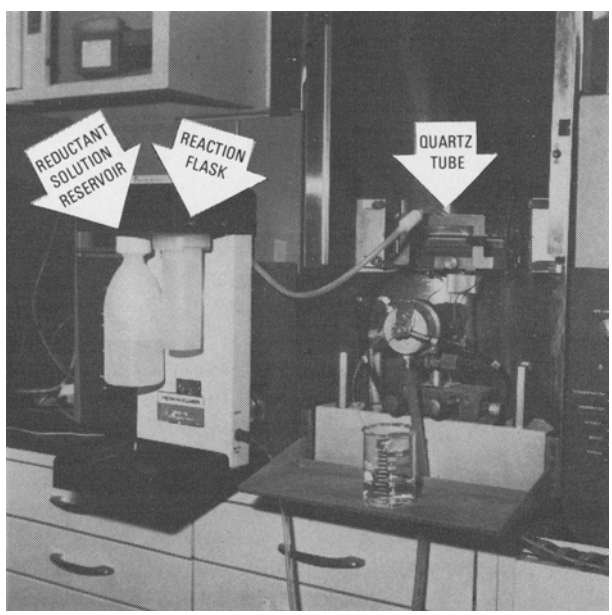

FIG. 1. Photograph of the arsine generation equipment used in this work. The T-shaped quartz tube is positioned in the light beam just above the flame.

TABLE I

Precision of Atomic Absorption Spectrophotometric Method for Arsenic in Glycerine at 50 ng Level

	Volume in reaction flask	
	1 mL	10 mL
Number of replicates	10	6
Mean peak-height (mm)	111	86.5
Standard deviation (mm)	11.5	3.8
Relative standard deviation (%)	10	4.4

TABLE II

Comparison of the Atomic Absorption Spectrophotometric and Colorimetric (USP) Methods for Arsenic in Glycerine

Arsenic concentration added (μg/g)	Concentration found (μg/g) AAS (this work)	USP method Analyst 1	Analyst 2	Analyst 3	Analyst 4
0	0.03	0.06	0	0.04	0.05
0.1	0.08	0.10	0.12	0.11	0.11
0.5	0.46	0.61	0.48	0.51	0.51
1.0	1.1	1.07	1.06	0.90	0.43
7.0	7.4	7.03	7.04	7.03	3.36

flask. Release the plunger after the peak maximum on the chart recorder has been reached. Measure an acid blank, and the standards in the same way. Standards may be prepared by adding microliter volumes of a 1 μg/ml stock solution to 10 mL of HCl directly in the reaction flasks. Standard concentrations should cover the range between 0 and 10 ng/mL in the reaction flask. Measure the height of the peaks for the standards and plot or calculate the calibration curve.

RESULTS AND DISCUSSION

Before settling on the details of the method just described, several variations were examined. For example, the final version uses aqueous arsenic standard solutions. It was determined experimentally that using standards containing glycerine at the same concentration as the sample (matrix matching) was unnecessary; there was an insignificant difference in the slopes of the two calibration curves. The effect of different volumes in the reaction flask was not insignificant. If a reaction volume of 10 mL is used the precision is much better than for a 1 mL reaction volume (Table I). In addition, the calibration curve slope (sensitivity) for 1 mL is higher. The decisions to use aqueous (no glycerine) standards and the 10 mL reaction volume were based on maintaining the simplicity of the method, as well as good figures of merit. The dilution of the glycerine sample is required to be within the linear range of the method. No attempt was made to analyze undiluted glycerine.

The method described in Experimental has a linear calibration curve in the concentration range of 0.1-3 μg/g As in glycerine. On an absolute scale, it has a detection limit of ca. 2 ng for a signal-to-noise ratio of 3.

To see how well this method compares to the USP method, glycerine samples were spiked with arsenic and analyzed by both methods. The results, shown in Table II, are in good agreement. The results of analyst number 4 (USP method) for the two highest arsenic concentrations are quite low—probably because of leakage in the arsine generator. Such leakage is a common problem with that method, especially when a ball-joint apparatus (6) is used. I have not observed leakage problems with the AAS method.

The primary advantage of the AAS method is its rapidity. The AAS and USP methods are comparable in terms of accuracy and precision—certainly adequate for ascertaining whether a sample meets the USP specification. The USP method, however, requires an individual apparatus (6) for each sample, reference and blank. The analyst is therefore limited to a finite number, ca. 6-10, of determinations per analysis session. If one is lost, e.g., leakage, it is not recoverable without starting all over. In addition, the elapsed time for each batch is ca. 1 hr. In that same hour, the analyst using the AAS method could do about 20 determinations.

LIMITATIONS

This method is limited to finished (i.e., refined, distilled) glycerine. Crude glycerine may contain metal ions and/or reducible organic compounds which can interfere with formation of the arsine. For example, it is well known that metal ions such as nickel interfere (3,5). It is likely that the USP method is similarly limited, as it utilizes similar arsine generation chemistry.

ACKNOWLEDGMENT

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