

Design of hydride atomizer system for atomic absorption and its optimization to determination of arsenic in real samples

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Abstract: A simple and well designed hydride metal system for determination of arsenic is being reported. The gaseous stannane is generated by NaBH_4 reduction of arsenic in the acidified sample solution. High sensitivity and low detection limits can be achieved. Low level concentrations of As can also be determined by hydride generation. The range of the method is $1\text{-}30\ \mu\text{g L}^{-1}$ of arsenic. The use of L-cysteine was of particular interest since it not only minimized interferences but also improved sensitivity and signal stability. A simple HNO_3 /L-cysteine method was evaluated for the analysis of digested environmental samples.

Keywords: Hydride metal, Arsenic determination, Water samples.

Introduction

Following the first report on the hydride generation atomic absorption spectrometry (HG-AAS) by Holak (1), the unquestionable advantages of technique led to its application to virtually all elements forming volatile hydrides (2).

For on-line hydride atomization conventional externally heated quartz tube atomizers (QTA) (3-6) are currently almost exclusively employed devices. An exception is the application of the W- coil atomizer (7,8), which was adapted from the initial idea of Berndt and Schaldach (9). The usual design of the conventional externally heated QTA is a T-tube with the horizontal arm (optical tube) of the T aligned in the optical path of the spectrometer. The central arm of the T-tube serves for delivery of hydrides carried by a gas flow from a generator (2). The optical tube is heated either using an electrical resistance device or the acetylene – air flame (700-1100 °C).

Hydride generation techniques are used routinely for the determination of As, Se, and Sb in atomic absorption and atomic emission spectroscopy. Low level concentrations of As can also be determined by hydride generation. The gaseous arsenic is generated

by NaBH_4 reduction of arsenic in the acidified sample solution. High sensitivity and low detection limits can be achieved. The detection limits were further lowered by replacing conventional air-acetylene flame atomizer with more sensitive ones as argon entrained hydrogen diffusion flame, quartz cuvette atomizer, graphite furnace atomizer. Current methodology suffers from several difficulties. These include pH dependency, potential contamination problems, poor standard stability and severe metal interferences. Despite several inherent merits, hydride techniques are rather limitedly used for trace analysis.

In this work a very sensitive and high throughput semiautomatic hydride generation and atomic absorption method for As is described.

Experimental

Apparatus

A Perkin Elmer AAAnalyst double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 5mA was used for the determination of arsenic which was made at 286.3 nm. Measurements were performed in the home made metal hydride generation system.

Reagents

Standard stability—this is a pre-requisite for accurate analysis. In this study, arsenic standards at the part-per-billion level were found to be unstable with acid concentrations typically used such as 1% HNO₃ or 1% HCl. Signals deteriorated in 24 hours. Methods for improving standard stability were investigated in this study.

Contamination—arsenic can be a significant contaminant in analytical reagents. In this work Contamination was not a major problem. However, blanks were always prepared with Careful matching of reagents. Blank absorbances were usually below 0.040 abs.

Metal interferences—hydride generation techniques are sensitive to high concentrations of metals. The use of L-cysarsenic and L-cysteine has shown particular promise in the reduction of these types of interferences. pH dependency—the determination of arsenic by hydride generation has been an undesirable Technique due to the considerable amount of sample preparation that must be performed to adjust the pH within a narrow range. It was the purpose of this study to develop an easier, yet accurate arsenic hydride generation method.

Procedures

Transfer 10 mL of the water sample [or an aliquot diluted with reagent water to 10 mL] into a sample container. Note: For reduced volume analysis, adjust sample and reagent volumes to maintain the required sample to reagent ratios. Add 5 mL of NaBH₄ 5% w/v

and 5 ml of HNO₃ 10% w/v and 5 ml L-cysteine 10% w/v and volume to 50 ml with distilled water. Remove the sample containers from the water bath and cool to room temperature. (During the cool down period proceed with instrument warm up and calibration.)

Construction and Assembled

In the present work we construction and assembled of HG-AAS as follows. Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument setarsenicg recommended by the particular manufacturer should be followed. The use of background correction is recommended, but is not mandatory. Single element hollow cathode lamp or electrodeless discharge lamp and associated power supply.

A quartz cell has an inner of about 0.6 cm and 14-cm long, having perpendicular, 0.4 cm (inner diameter) may be used. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

Inert arsenic-free tubing is used for passage of arsenic vapor from the sample bottle to the absorption cell. Straight glass tubing terminaarsenicg in a coarse porous glass aspirator is used for purging volatile metal hydrid released from the water sample in the BOD bottle. Any pump (pressure or vacuum system) capable of passing air 1 L/min is used. Regulated compressed air can be used in an open one-pass system.

Table 1. Analytical characteristics of the proposed method

Concentration range ($\mu\text{g L}^{-1}$)	1-30
Slope	0.0113
Intercept	0.0011
Correlation coefficient (r)	0.9992
% RSD (n=3) ^a	1.10
LOD ($\mu\text{g L}^{-1}$) ^b	0.15

^a Arsenic concentration was 5 $\mu\text{g L}^{-1}$ for which the R.S.D. was obtained.

^b Limit of detection. Calculated as three times the S.D.(3 σ) of the blank signal.

Table 2. Recovery of arsenic from spiked products before digestion

Sample ^a (%)	Sample ^a	Arsenic (II)found ^b	Recovery
Mineral water 1	0	N.D. ^c	96.0%
	1	0.96(± 0.03)	
Mineral water 2	0	N.D	95.0%
	6	5.7 (± 0.02)	
Canned fish 1	125	127.7(± 4.1)	102.2%
Canned fish 2	150	152.3(± 4.5)	101.5%
Pineapple juice 1	25	25.2(± 1.9)	100.8%
Pineapple juice 2	50	49.4(± 2.1)	98.8%

a) All values are mg Kg⁻¹

b) Average of three determinations found by the proposed method.

c) Not detected

Table 3. The total arsenic content of canned products (after digestion)

Type of sample	Content of arsenic (mg Kg ⁻¹) ^a
Canned fish (b)	18(±1.7)
pineapple juice(c)	5(±1.8)

^a Averages of three determinations ± standard deviation.^b After 8 months after production^c After 6 months after production

Results and Discussion

A calibration curve was constructed by 10 ml of sample standard solutions. Table 1 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for arsenic was linear from 1-30 µg L⁻¹. The limit of detection was sufficiently low.

Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Turn on the instrument and circulaarsenic pump. Adjust pump rate to 1 L/min or as required. Allow system to stabilize. Trearsenic each standard solution container individually, and immediately attach the container to the aeration apparatus. The absorbance, as exhibited either on the instrument or recording device, will increase and reach maximum

within 10 sec. As soon as the maximum response is obtained, approximately one minute, open the bypass value (or optionally remove aspirator from the sample container if it is vented under the hood) and conarsenicue aeration until the absorbance returns to its minimum value. Close the by-pass value, remove the aspirator from the standard solution container and conarsenicue aeration. Repeat until data from all standards have been collected.

For the optimization of parameters, we do instrumental and chemical parameters. By variation of position of cell, maximum absorption achieved and by one variable at a time method, chemical parameters were optimized. The optimum concentration of NaBH₄, L-cystein and HNO₃, were achived 0.5%, 0.1% and 0.1% (w/v) respectively.

Application to Real Samples

To evaluate the analytical applicability of the proposed method, it was applied to determine arsenic in Mineral water samples and also in canned products.

The water sample was prepared from (Kohrang mineral water factory, Shiraz, Iran). The canned fish was prepared from (Saele factory, Iran) and the fruit juice samples were prepared from (Shani factory, Iran).

These samples were spiked with standard stock solution of arsenic (II) and determined by the proposed optical membrane. The results are shown in Table 2. This proposed method also was applied to the determination of arsenic in different canned products (fruit juice and fish). Prior to the determination, samples were digested and diluted. The results are given in Table 3.

References

1. Holak W., Anal, Chem., 1969, 41, 1712.
2. Dedina J., Tsalev D.L., Hydride Generation Atomic Absorption Spectrometry, Wiley& Sons, Inc., Chichester, 1995.
3. Korkmaz D.K., Ertas N., Ataman O.Y., Spectrochim. Acta, part B, 2002, 57, 571.
4. Korkmaz D.K., Dedina J., Ataman O.Y., J.Anal.At.Spectrom., 2004, 19, 255.
5. Korkmaz D.K., Demir C., Aydin F., Ataman O.Y., J. Anal.At.Spectrom. 2005,2046.
6. Kratzer J., Dedina J., Spectrochim. Acta, part B, 2005, 60, 859.
7. Riberiro A.S., Arruda M.A.Z., Cadore S., Spectrochim. Acta, part B, 2002, 57, 571.
8. Riberiro A.S., Arruda M.A.Z., Cadore S., J. Anal.At.Spectrom., 2002,17,1516.
9. Berndt H., Schaldach G., J. Anal.At.Spectrom., 1988, 3, 709.
