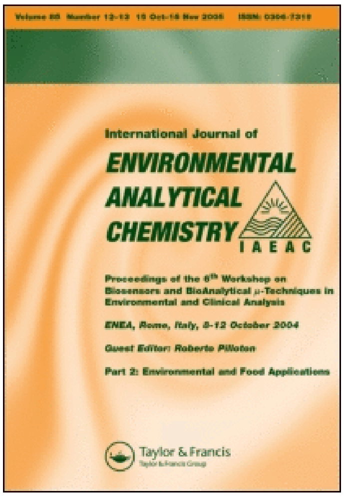

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A New Spectrophotometric Determination of Traces of Arsenic with Silver Acetate in the Presence of Tween-80

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A New Spectrophotometric Determination of Traces of Arsenic with Silver Acetate in the Presence of Tween-80

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A new simple and sensitive procedure for spectrophotometric determination of traces of arsenic has been developed. At pH 5.3, arsine generated usually reacts with silver acetate in the aqueous solution in the presence of Tween-80 to form yellow silver sol, which has an absorption maximum at 420 nm. The molar absorptivity at the wave is found to be $4.8 \times 10^4 \, l \cdot mole^{-1} \cdot cm^{-1}$. Beer's law is obeyed for 0.3–5.0 μg of arsenic in 20 ml absorbing solution. This method has been used in the determination of arsenic in water and wastewater samples and results are found satisfactory.

KEY WORDS: Spectrophotometric determination, arsenic, silver acetate, Tween-80.

INTRODUCTION

There are a number of spectrophotometric methods for the determination of traces of arsenic. A reagent of increasing popularity is silver diethyldithiocarbamate (AgDDTC) in pyridine[1] or in chloroform containing organic bases,[2] which absorb arsine generated in the usual way. This method is as sensitive as that using the molybdenum blue complex and more selective than it, as well as being much simpler to use.

Although the Ag-DDTC technique has been recommended as a standard method, the toxicity of the organic bases and solvents, used militates against its employment and attempts have been made to use aqueous solutions to obsorb arsine. It has been reported[3] that submicro amounts of arsenic can be determined using the reduction of silver and iron(III) ions by arsine in the presence of Ferrozine; however, this method has not been adopted extensively.

Recently, surfactants have been used to increase the sensitivity of many reactions, but no detailed investigation has yet been made of the determination of arsenic. This paper records that arsine reacts with silver acetate to produce colloidal silver, which can be dispersed to form a yellow sol by surfactants and describes the use of this reaction for the spectrophotometric determination of arsenic in some environmental samples such as potable water, wastewater and spring water in the presence of the nonionic surfactant Tween-80.

EXPERIMENTAL

Reagents

Unless stated otherwise, all reagents used were of analytical grade quality. Double glass distilled water was used for solution preparation and other purposes.

Standard arsenic solution. Dissolve 0.132 g of arsenic trioxide in 2 ml of 1 N sodium hydroxide, dilute with water, make slightly acid with hydrochloric acid, and dilute to 100 ml. The solution contains 1.00 mg of arsenic per ml. From this stock solution prepare a standard solution containing 1.00 or 10.0 μg of arsenic per ml.

Silver acetate solution—0.1%(*W*/*V*). Dissolve 0.1 g silver acetate in water and make up to 1 l with water. Keep the solution in the dark.

Tween-80 *solution*—0.25%(*V*/*V*). Transfer 2.5 ml Tween-80 into water, dilute to 1 l with water and mix well. Do not shake the solution before use. Store in a dark bottle.

Sodium acetate buffer—pH 5.3. Dissolve 136 g of sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in water, add 57 ml of glacial acetic acid and dilute to 1000 ml with water. Adjust the pH of this buffer solution to 5.3 using a pH-meter.

Absorbing solution. Mix 1.4 ml of silver acetate solution, 4.0 ml sodium acetate buffer and 0.9 ml of Tween-80 solution and dilute with water to 20 ml. According to this proportion, prepare sufficient solution to be satisfied for a week of use. This solution should be mixed well when it is prepared and not shaken before use to avoid foaming. It should be stored in a dark bottle.

For the arsine evolution, the following reagents were used: 15% potassium iodide solution in water, a 40% stannous chloride solution in concentrated hydrochloric acid, a 1 + 1 sulfuric acid solution, 10% lead acetate solution in water and granular zinc free from arsenic of 20 mesh.

Equipment

The arsine evolution apparatus was prepared by connecting one end of a 4 mm i.d. glass tube at an angle of 90° to a 24/40 ground adapter. The glass tubing was bent at a 90° angle at a distance of 10 cm from the adapter. The adapter, which was connected to a scrubber containing glass wool impregnated with 10% lead acetate solution, was placed on a 150 ml 24/40 ground glass flask and the outlet tube of the scrubber was adjusted to reach the bottom of a 20 ml absorption tube, containing 20.0 ml of the absorbing solution.

The absorbance was measured in a 3 cm cell using a model 721 spectrophotometer, produced by the Shanghai Analytical Instrument Works.

Normal precautions for trace analysis were taken throughout.

Procedure

Pipet 25.0 ml of sample containing not more than 5.0 μg arsenic into a clean generator bottle. Add successively, with thorough mixing after each addition, 7 ml of sulfuric acid, 1 ml of potassium iodide and 2 ml of stannous chloride. Allow 15–30 min for reduction of arsenic to the trivalent state.

Add 5 g zinc to the generator and connect the scrubber-absorber assembly immediately. Make certain that all connections fit tightly.

Allow the evolution and absorption of arsenic to proceed for 50 min, at room temperature, out of direct sunlight. Pour the solution from the absorber directly into a 3 cm cell and measure the absorbance of the solution at 420 nm, using the reagent blank as the reference. Prepare a calibration curve for the range 0.3–5.0 μg arsenic in 20.0 ml.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of colour produced and a reagent blank are shown in Figure 1. The absorption maximum of the product is at 420 nm. The absorbance of the reagent blank is constant at this wavelength. All absorbance measurements are therefore made at 420 nm. The molar absorptivity, $\varepsilon = 4.8 \times 10^4 \cdot \mathrm{l \cdot mole^{-1} \cdot cm^{-1}}$, is much greater than that obtained with the Ag-DDTC method $[\varepsilon = (1.2 - 1.6) \times 10^4\ \mathrm{l \cdot mole^{-1} \cdot cm^{-1}}]$.

Selection of silver salts and surfactants

In order to obtain a sensitive and stable result, several combinations of silver salts and surfactants were tested. For example, silver nitrate-polyvinyl alcohol (mix 2 ml of 0.1 M $AgNO_3$ with 1 ml of 1% polyvinyl alcohol solution, dilute to 20.0 ml with water at pH 6.0), silver nitrate-acetone-trimethylamine-Triton X 100 (mix 1 ml of 0.1 M $AgNO_3$, 3 ml of acetone, 0.5 ml 1% trimethylamine with 1 ml of 1% Triton X 100 and dilute to 20.0 ml with water), silver nitrate-trimethylamine-polyvinyl alcohol (mix 1.0 ml of 0.1 M $AgNO_3$, 0.4 ml of 0.2% trimethyl-amine with 1.0 ml of 0.2% polyvinyl alcohol and dilute to 10.0 ml with water), silver sulfate-trimethylamine-polyvinyl alcohol (mix 1.0 ml of saturated at room temperature Ag_2SO_4, 0.4 ml of 0.2% trimethylamine with 1.0 of 0.2% polyvinyl alcohol and dilute to 20.0 ml with water) etc. However all these absorbing solutions gave rise to unstable dark brown colors.

Because silver acetate is souble to water and its anion is colorless and nonoxidizing, it was decided to use it as the chromogenic reagent. Many surfactants as polyvinyl alcohol. Gum arabic, Tween-80, sodium lauryl sulfate, and Triton X 100 were tested as dispersants in the presence of trimethylamine. But they gave high reagent blanks, and unstable absorbances.

In a medium buffered to pH 5.3 with only Tween-80 was found to give a low reagent blank and stable absorbance. Therefore in all further

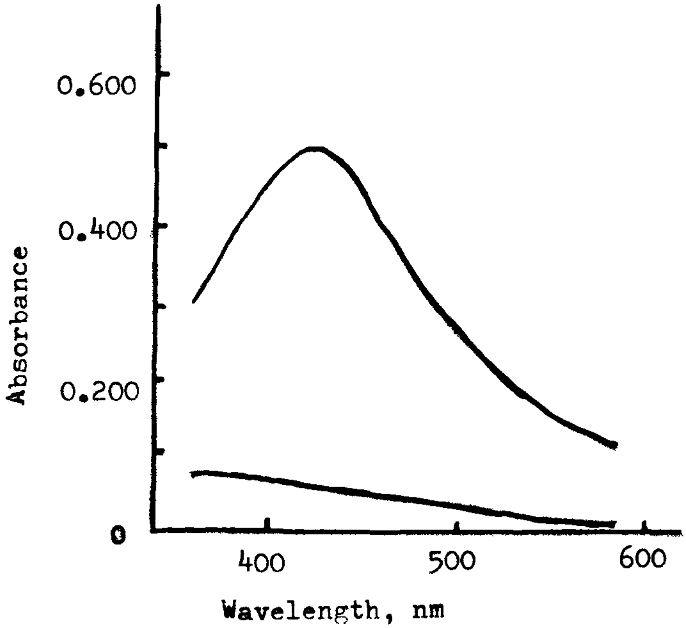

FIGURE 1. Absorption spectra (3 cm cell, pH 5.3). A 5.0 μg As vs. reagent blank; B. Reagent blank vs. water.

work silver acetate was employed as a chromogenic reagent and Tween-80 as a dispersant.

When alcohol is added, the absorbance of the solution is lowered, and the reagent blank is raised. Tween-80 therefore should be free from alcohol.

Effect of variables

A pH study of the absorbing solution showed that the coloured solution had a constant absorbance over the pH range 5.0–6.0. Outside these limits, the resulting absorbance values are lower. However, in more acidic solution, the absorbance of reagent blank is high, and for this reason a pH of 5.3 was selected.

Tests at pH 5.3 using 20 ml of a solution containing 5.0 μg of arsenic with varying amounts of the silver acetate and Tween-80 showed that the maximum absorbance is reached, when amounts of the reagents lie between 1.0–2.5 and 0.7–1.2 ml respectively. The amount of silver acetate is recommended to use 1.4 ml. As the volume of Tween-80 was increased there was a tendency for foam to form and for the absorbing solution to overflow from the tube. For this reason the use of Tween-80 is preferred.

Examination of the effects of temperature on colour development showed that the absorbing solution has constant absorbance in the temperature range 15–30°C. However at temperatures higher than 35°C, the absorbance of reagent blank increases; 20°C was therefore adopted.

The generation of arsine should be carried out for 50 minutes to ensure complete transference of arsenic to the absorbing solution at 20°C.

Although the colour intensity remains virtually constant for 48 hr it is advisable to measure the absorbance 1 hr after end of the reaction.

When sunlight shines directly on absorbing solution, the absorbance of the reagent blank is raised significantly and the solution becomes grey and cloudy as a consequence of which the results of the measurement are lowered evidently. In order to obtain reliable results and a clear solution, it is essential that the experiment should be conducted in dark or at least out of direct sun light.

The corrected absorbance values correspond to six-electron transfer in the reaction of arsine with silver as shown by the equations

$$AsH_3 + 6Ag^+ \longrightarrow 6Ag^0 + As^{3+} + 3H^+$$

followed by the dispersion of Ag^0 with surfactants.

Thus arsenic in amounts as low as 0.3 μg and as high as 5.0 μg per 20 ml of absorbing solution has been determined using a 3 cm cell. The absorbance is directly proportional to the amount of arsenic analyzed. The average relative standard deviation is of the order of ±5.3% about 5.0 μg of arsenic and increase up to ±8.8% at the 0.3 μg level. When the volume of the water sample is increased to 50 ml, the limit of detection in this method is 6 ppb arsenic.

Effect of foreign ions

This method may be applied to solutions not containing large amounts of certain reducible heavy metals which would be likely to interfere with the evolution of arsine, iron, chromium and molybdenum may be present in moderate amounts, they increase the rate of evolution of hydrogen. Low results are obtained in the presence of oxidizing agents such as nitric acid, hydrogen peroxide, because they inhibit the evolution of arsine, selenium is not evolved and is reduced to the element. Hydrogen sulfide does not interfere in this procedure as it is removed by the lead acetate scrubber used in other arsine generation methods.

The effect of foreign ions on determination of 4.0 μg of arsenic was examined. The following ions, when present up to the amounts (in 25 ml) shown in brackets, do not interfere:

Na^+(100), K^+(100), NH_4^+(100), Be^{2+}(1), Mg^{2+}(100), Ca^{2+}(50), Sr^{2+}(5.0), Ba^{2+}(5.0), Cd^{2+}(1.0), Cu^{2+}(1.0), Pb^{2+}(1.0), Co^{2+}(1.0), Ni^{2+}(1.0), Mn^{2+}(1.0), Hg^{2+}(1.0), Sn^{2+}(800), Al^{3+}(25), Fe^{3+}(10), Bi^{3+}(1.0), Sb^{3+}(0.5), Se(IV, 0.1), Te^{4+}(1.0), Ge^{4+}(1.0), Mo(VI, 3.0), Cr(VI, 10), Cl^-(1000), NO_3^-(50), ClO_4^-(100), SO_4^{2-}(1000), PO_4^{3-}(1000).

Samples analyzed

The method has been applied to the determination of arsenic in water samples.

For potable water, place directly 50 ml sample into the flask which generates arsine, carry out the analysis according to the previous procedure.

For wastewater and sewage containing organic matter it is necessary to digest samples with nitric acid and sulfuric acid. Transfer a sample containing not more than 5.0 μg arsenic to the 150 ml flask, which is to be used for the generation of arsine, add 2.5 ml of concentrated sulfuric acid, and then add 5 ml of conc. nitric acid and mix well. Heat gently at first and then more strongly until the solution boils; digest at this temperature until all organic matter is destroyed, adding more nitric acid if necessary. Cool, dilute the solution with 50 ml of water and boil until fumes of sulfur trioxide are given off. Repeat this operation twice to expel all the nitric acid. Dilute the solution in the flask with water, and finish the determination according to the directions in the general procedure.

The results of determination of arsenic for some water samples are listed in Table I.

Data in Table I are an average of triplicate or more measurements, give all results or standard deviations.

TABLE I

Determination of arsenic in water and wastewater

	Present method			Ag-DDTC method		
Sample	As found, ppm	Standard derivation	Degree of freedom	As found, ppm	Standard derivation	Degree of freedom
Well water						
1	0.02	0.001	2	0.01	0.001	2
2	0.22	0.012	2	0.24	0.016	2
Reservoir water	0.02	0.001	3	0.01	0.001	2
Electroplating wastewater	0.48	0.02	2	0.47	0.02	2
Coking wastewater						
1	0.13	0.005	3	0.13	0.007	2
2	0.23	0.01	3	0.22	0.01	2
3	75	2	2	74	3	2

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