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Rapid and Sensitive Atomic-Absorption Determination of Arsenic by Arsine–Argon–Hydrogen Flame System with the Use of a Zinc Powder Tablet as Reductant

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Determination of arsenic in trace amount is often necessary in connection with pollution. Accuracy of the determination of arsenic can be fairly enhanced by introduction of arsenic as arsine gas into argon-hydrogen flame.[1-4] Chu *et al.*[5] have recently described a flameless atomic-absorption spectrophotometric method for arsenic determination involving chemical conversion of arsenic into arsine. We showed that antimony and selenium can be rapidly determined by introducing stibine or hydrogen selenide gas into argon-hydrogen flame.[6,7]

This paper deals with a method for the rapid, sensitive and accurate determination of arsenic by atomic-absorption spectrophotometry in combination with the argon-hydrogen system. Arsine was rapidly evolved from arsenic(III) or aresenic(V) solutions by reduction with zinc powder tablets, stannous chloride and potassium iodide. With the combined use of these reagents, both optimum hydrochloric acidity and interference of diverse ions in the reduction process could be reduced to a considerable extent.

Experimental

Reagents. All solutions were prepared with Chemicals of analytical reagent grade and deionized water, the aqueous solutions being stored in polyethylene bottles.

Standard Arsenic(III) Solutions: Prepared by dissolving 1.320 g of diarsenic trioxide (As_2O_3) in 10 ml of water containing 4 g of sodium hydroxide, and diluting it to 1000 ml with water. An aliquot of this solution was diluted with water to give a concentration of 0.2 ppm immediately before use.

Standard Arsenic(V) Solution: Prepared by dissolving 2.403 g of potassium dihydrogen arsenate in water and diluting it to 1000 ml with water. An aliquot of this solution was diluted with water to give a concentration 0.2 ppm immediately before use.

Stannous Chloride Solution: Prepared by dissolving stannous chloride dihydrate in 10 M hydrochloric acid to give a concentration of 10%(w/v).

Potassium Iodide Solution: Prepared by dissolving potassium iodide in water to give a concentration of 40% (w/v).

Zinc Tablets 50 g of arsenic-free zinc powder (200 mesh), 4 g of kaolin powder, and 10 ml of water were mixed in a mortar to make a paste. This was moulded into small tablets, 8 mm in diameter, 3 mm in thickness and about 0.5 g in weight, and dried in an electric oven.

Apparatus. The atomic-absorption was measured with a Nippon Jarrell-Ash Model AA-1 EW atomic-absorption spectrophotometer equipped with a Westinghouse arsenic hollow cathode lamp. The apparatus used for generation and collection of arsine was the same as that reported.[6,7]

Recommended procedure: Transfer into a reaction bottle a sample solution less than 20 ml in total volume and

1) W. Holak, *Anal. Chem.*, **41**, 1712 (1969).
2) E. F. Dalton and A. J. Malanoski, *At. Abs. Newslett.*, **10**, 92 (1971).
3) F. J. Fernandez and D. C. Manning, *ibid.*, **10**, 36 (1971).
4) D. C. Manning, *ibid.*, **10**, 123 (1971).
5) R. C. Chu, G. P. Barron, and P. A. W. Baugarner, *Anal. Chem.*, **44**, 1476 (1972).
6) Y. Yamamoto, T. Kumamaru, Y. Hayashi, and R. Tsujino, *Anal. Lett.*, **5**, 419 (1972).
7) Y. Yamamoto, T. Kumamaru, Y. Hayashi, and M. Kanke, *ibid.*, **5**, 717 (1972).

containing not more than 1 μg of arsenic. Add 2 ml of 12 M hydrochloric acid, 1 ml of the potassium iodide solution and 2 ml of the stannous chloride solution. Dilute the mixture to 25 ml with water. Swirl the solution to mix thoroughly and stand it at room temperature for 15—30 min. After adding two zinc tablets, immediately connect the reaction bottle to the collection unit and allow the reaction to take place for 90 sec at room temperature by agitating the mixture with a magnetic stirrer. Turn the four-way stopcock to "sweep" forcing the hydrogen and arsine into the burner mixing chamber, and also introducing argon into the system to sweep the gases into the flame. Simultaneously record the absorption signal on a recorder. Finally return the stopcock to "bypass".

The working conditions are: wavelength 1937 Å, slit-width 0.10 mm, lamp current 15 mA. Flow rates of gases for a standard 10-cm slot burner: argon 8.0 l/min (1.5 kg/cm²G), hydrogen 7.0 l/min (0.4 kg/cm²G) using air-acetylene regulator system, respectively, auxiliary argon 4.0 l/min (2.0 kg/cm²G).

Results and Discussion

In the conventional method for arsenic determination by colorimetry, granular zinc metal is used as the reducing agent. Evolution of arsine has to be continued for about half an hour because the reaction proceeds gradually. Holak[1] used granular zinc for arsine generation and collected the arsine by freezing in a liquid nitrogen trap. It was then introduced into an air-acetylene flame after being brought to room temperature and swept with nitrogen. The procedure required considerable time. It was found[2-4] that it is not necessary to wait for the reaction to complete since almost all the hydrides are formed during the early period of the reaction when smaller granular zinc (20 mesh) is used. We have reported[6,7] that zinc powder tablets are effective for rapid and quantitative evolution of stibine and hydrogen selenide.

We also found that the use of the zinc tablets together with stannous chloride and potassium iodide considerably accelerate the reduction even in a lower acidic medium. Conditions were investigated for the quantitative production of arsine by use of a mixture of reagents.

The mechanism of the conversion of trivalent and pentavalent arsenic into arsine appears to be very complicated. It is therefore of interest to investigate the role of potassium iodide and stannous chloride in the overall reduction process. It is known[8] that both potassium iodide and stannous chloride are highly effective not only for the complete reduction of arsenic from the pentavalent to the trivalent state, but also for the suppression of the interference of diverse metal ions in the overall reduction process. A potassium iodide solution (0—3.0 ml) and a stannous chloride solution (0—6.0 ml) were added respectively to arsenic(III) and arsenic(V) solutions, each containing 1.0 μg of arsenic with a final acidity of 2 M. It was found that potassium iodide and stannous chloride enhanced to a great extent the recovery of arsenic as arsine from the trivalent state (KI with 0.8% $SnCl_2$, 4-fold; $SnCl_2$ with 1.6% KI, 3-fold) when at least 0.3 ml of the potassium iodide and 0.5 ml of the stannous chloride solutions were added. Thus the potassium iodide or stannous chloride concentration was usually kept at 1.6% or 0.8%. As a result, the same values in the atomic-absorption signal were obtained when evolution of arsine took place either from trivalent arsenic or pentavalent arsenic state.

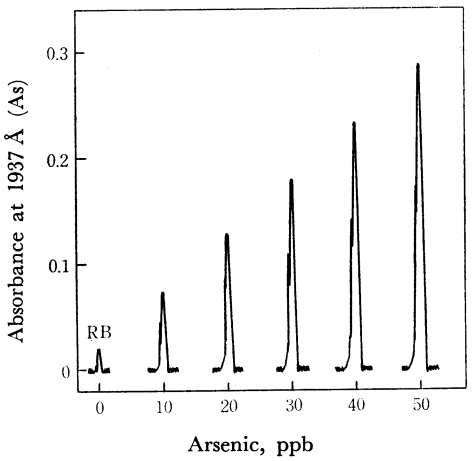

Fig. 1. Absorption signal *vs.* concentration of arsenic. (RB is a reagent blank)

The optimum range of acidity was about 1.5—2.5 M in hydrochloric acid. Addition of at least one zinc tablet was enough to obtain a highest and constant recovery of arsenic as arsine.

After addition of the reagents no distinct evolution took place appreciably for a few seconds, during which time we could connect the reaction bottle to the gas collection unit without any loss of arsine. Arsine was vigorously generated by grinding the tablets by agitating the mixture with a magnetic stirrer. A constant and maximum sharp signal was obtained for only one minute gas sampling. The calibration curve was constructed by the procedure described above by use of arsenic(III) standard solution. An example is shown in Fig. 1. An appreciable value of absorbance is observed in the reagent blank. This can be attributed to the arsenic contained in the zinc tablets as impurities. The same results were obtained by using the arsenic(V) solution as a standard. The sensitivity for 1% absorption of the signal was estimated to be 0.001 ppm of arsenic and the linearity of absorption *vs.* concentration was good over the range 0.01—0.05 ppm. The precision was estimated to be 3% from the results of ten solutions with 1 μg of arsenic. The effect of diverse cations on the reduction process was studied using a solution containing 1.0 μg of arsenic(III). The following ions did not interfere at the 250 ppm level: chromium(III), manganese(II), iron(III), aluminium, cobalt(II), nickel(II), copper(II), zinc, silver, cadmium, mercury(II), sodium, potassium, magnesium, and calcium. The maximum permissible amount of the other ions was as follows: lead and antimony(III) 10 ppm, selenium 0.4 ppm.

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8) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed., Interscience, New York (1959), p. 289.