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A SENSITIVE METHOD FOR THE DETERMINATION OF ANTIMONY BY NON-DISPERSIVE ATOMIC FLUORESCENCE SPECTROMETRY

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A sensitive method for the determination of antimony by non-dispersive atomic fluorescence spectrometry is described. Antimony is converted to stibine utilizing sodium borohydride reduction, and atomized in a hydrogen-argon-entrained air flame. The detection limit of antimony is 3 ng, and the analytical working curve is linear in the range of three decades of concentration from the detection limit.

The advantages and disadvantages of non-dispersive atomic fluorescence spectrometry have been discussed by many workers1-9). Up to now many efforts have been made to obtain high sensitivity. These are as follows: (1) The use of high intensity light sources such as high intensity hollow cathode lamps and microwave excited electrodeless discharge lamps; (2) The combination of a cesium-tellurium solar-blind photomultiplier with an ultraviolet filter; (3) The development of various focusing optics using mirror systems; and (4) The use of synchronous, phase sensitive amplifiers.

Dagnall et. al.10) and Kolihová et. al.11) have reported that antimony has eight and nine atomic fluorescence spectral lines, respectively, in the ultraviolet spectral region. Therefore, antimony is considered to be one of the elements most suitable for non-dispersive atomic fluorescence spectrometry.

In the previous paper12), we described a sensitive method for the determination of arsenic by non-dispersive atomic fluorescence spectrometry coupled with a gas sampling technique. In this paper the application of the coupled system to the determination of antimony is described.

Experimental. The experimental arrangement of the apparatus, described in the previous work12), was used. An antimony electrodeless discharge lamp (EMI Electronics Ltd.) was used as a light source, and was maintained with a Microtron 200 microwave generator (2450 ± 25 MHz) and a Model 210L resonant cavity (Electro Medical Supplies Ltd.) which was operated at 36 W. The discharge was initiated with a high frequency Tesla vacuum tester.

A hydrogen-argon-entrained air flame was supported on a three slot burner head. The burner head was situated as described previously[12), so as to pass the light beam from the light source parallel to the burner slots. All measurements were performed with a hydrogen flow rate of 1.7 l/min and an argon flow rate of 5.7 l/min, respectively.

Atomic fluorescence radiation was detected by a solar-blind photomultiplier (HTV R166). A John Fluke power supply (Model 412B) was used to provide high voltage (700 V) for the photomultiplier. The signals from the photomultiplier were fed into a lock-in amplifier (Princeton Applied Research Corp., Model HR-8) which was phased with a reference signal from a mechanical light chopper (Chopping frequency: 110 Hz).

A 1000 ppm commercially available standard solution (Kanto Chemical Corp. Inc.) made from antimony trichloride was used as an antimony stock solution. More dilute standard solutions were prepared by appropriately diluting the stock solution so that they contained about 7 % hydrochloric acid. A 3 % sodium borohydride solution was prepared just before use, by dissolving sodium borohydride (MERCK reagent for synthesis). Hydrochloric acid used in this work was of analytical reagent grade.

The stibine generator which is the same as that used in the previous work[12), is shown in Fig. 1. The electro-magnetic valves in Fig. 1 were adjusted to pass argon through a by-pass tube. A sample solution containing antimony and hydrochloric acid was transferred into a reaction flask. The solution was diluted to about 50 ml with de-ionized water. The acidity of the solution was kept at about 4 N with respect to hydrochloric acid. After 1.5 ml of a 3 % sodium borohydride solution had been placed on the glass boat shown in Fig. 1, the atmosphere in the reaction flask was replaced with argon, by adjustment of the valves to pass argon through the reaction flask. The valves were again set at the initial position to pass argon through the by-pass tube. The sodium borohydride solution was added while the solution being agitated with a magnetic stirrer. After 45 seconds, the switch of the valves was turned on, allowing argon to flow through the reaction flask and carry the stibine gas evolved into the burner. The atomic fluorescence signals were recorded on a recorder (Hitachi, Model 056), and the peak heights were measured.

Results and Discussion. The detection limit, defined as the quantity of antimony for which the signal-to-noise ratio was equal to 2, was found to be 3 ng.

In Fig. 2 the analytical working curve for antimony is shown. The working curve is linear from the detection limit up to 5μg of antimony. Kolihová et. al.11) have shown the analytical working curves for the sensitive antimony fluorescence lines in the hydrogen-oxygen-argon flame, using an antimony high intensity hollow cathode lamp as a light source. The solar-blind photomultiplier used in this work responds only to radiation of wavelengths less than 320 nm. However, the antimony fluorescence lines reported by Kolihová et. al. are within the spectral response of the detector. As shown in Fig. 2, the shape of the analytical curve in the high concentration region is somewhat different from that anticipated from the results reported by Kolihová et. al.11). The difference is possibly caused by the non-linear relationship between the production rate of stibine gas and the

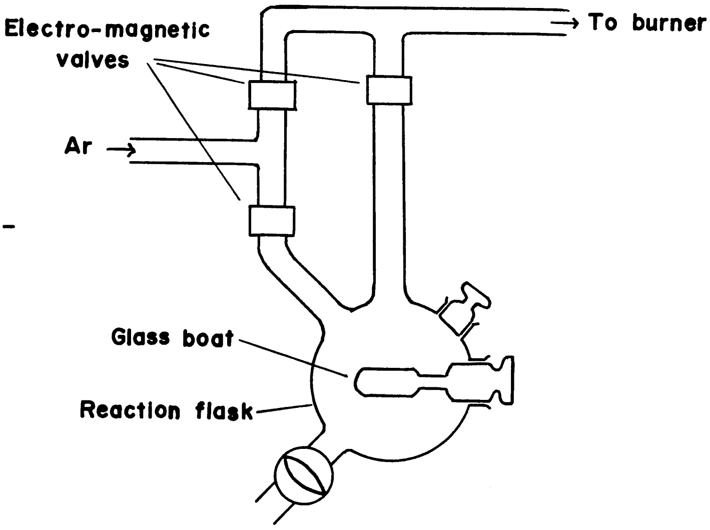

Fig. 1. Stibine generator

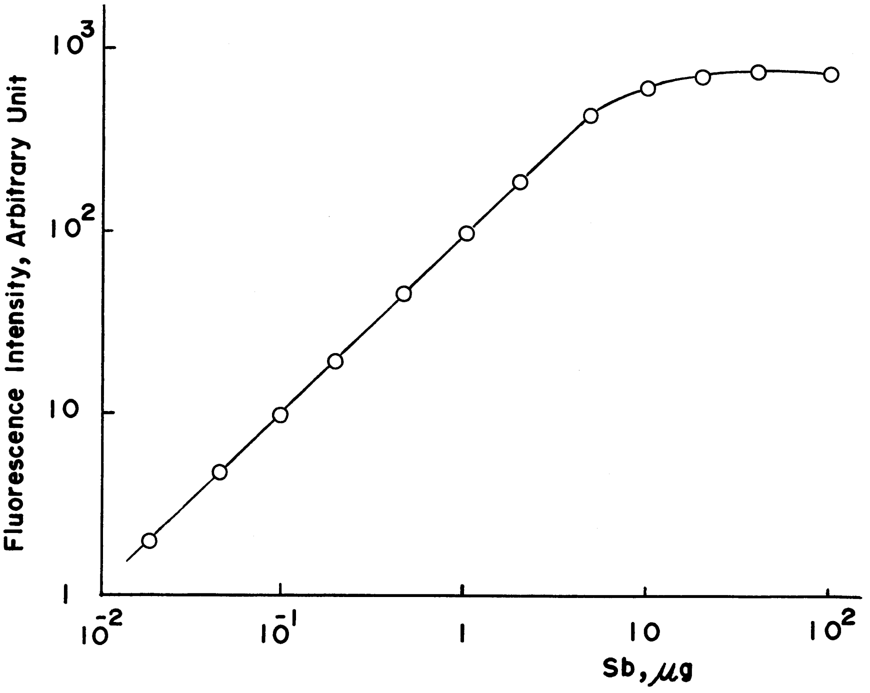

Fig. 2. Analytical working curve for antimony

concentration of antimony.

With the non-dispersive system used in this work, the limiting noise was due to the OH band emission (280-320 nm) from the flame. The noise level decreased to about a tenth when a screen was placed between the flame and the detector. However, no appreciable change of the noise level was observed when a screen was placed between the light source and the flame. This suggests that the improvement of the detection limit will be achieved with an improved non-dispersive system combined with a filter such as a chlorine filter$^{8)}$.

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