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A NEW SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY WITH SILVER-DIETHYLDITHIOCARBAMATE AND o-PHENANTHROLINE MIXTURE IN CHLOROFORM

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Antimony(III) is spectrophotometrically determined by reaction between stibine and a mixture of silver diethyldithiocarbamate and o-phenanthroline in chloroform. The red color appears in the chloroform phase, and the color developement may be due to the formation of colloidal silver by reduction with stibine. The method is fairly sensitive and selective.

A minute amount of arsenic(V) can be spectrophotometrically determined by the red color developed through the reaction of arsine (AsH_3) with silver diethyldithiocarbamate(Ag•DDTC)-pyridine mixture. This method, being originated by Vasak and Sedivec$^{1)}$, has been widely accepted as a conventional means for the determination of arsenic$^{2)}$ in water. In their study$^{1)}$, it was observed that stibine (SbH_3) developed a different shade of color and phosphine(PH_3) did not interfere. In the arsenic determination, it was later pointed out by Bode and Hachmann$^{3)}$ that a chloroform solution of a certain organic base such as ephedrine, brucine, piperazine and o-phenanthroline, was available instead of pyridine. In the view of these aspects, we have established a new spectrophotometric method for determination of antimony by introducing stibine gas into a chloroform solution in which Ag•DDTC and o-phenanthroline were dissolved.

Experimental

Reagents: All the solutions were prepared from analytical reagent grade chemicals and deionized water, and all the aqueous solutions were stored in polyethylene bottles.

Standard antimony(III) solution: Dissolve 1.0 g of antimony chloride in a small amount of 4 N hydrochloric acid and the solution was diluted to 500 ml with 4 N hydrochloric acid. The factor of this stock solution was determined by titration with potassium bromate using methyl orange as indicator.

Absorbing solution: Dissolve 500 mg of Ag•DDTC and 200 mg of o-phenanthroline in 100 ml of chloroform. Stand the mixture overnight for dissolution.

Zinc: Use granular zinc metal (about 1 mm in diameter) whose arsenic content should be below 0.01 ppm.

Apparatus: Absorbance measurements were carried out with a Hitachi model 101 spectrophotometer, using glass cells (10 mm pass-length). The apparatus for evolution and absorption of stibine is shown in Fig. 1.

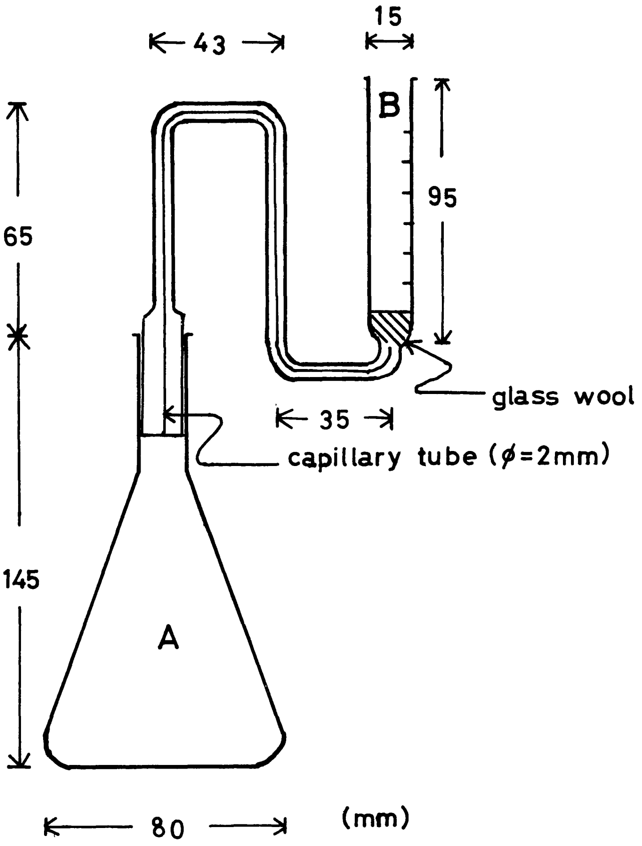

Fig. 1. Apparatus for evolution of stibine

General procedure: Transfer 0 - 20 ml of antimony(III) solution containing no more than 40 μg to the Erlenmeyer flask (A). Add 15 ml of (1 + 1) sulfuric acid and dilute to 50 ml with water. Swirl the solution to mix. After standing the flask (A) in a water bath (30°C) for 15 min , quickly add 5 g of the granular zinc to the antimony solution, immediately insert the stopper and allow the gas to bubble in 5 ml of the chloroform solution in the absorbing tube (B) for an hour. Measure the absorbance of the chloroform solution at 520 nm using a chloroform solution of Ag•DDTC-o-phenanthroline mixture as reference.

Results and Discussion

This technique has been used for generation of arsine in the conventional method for determination of arsenic. The procedure can be easily utilized to produce stibine from antimony (III) solution and to introduce the stibine gas into the chloroform solution containing Ag•DDTC -base mixture. The procedure for generating stibine gas should be continued at least for 45 min to obtain complete recovery of antimony. Effect of various bases on coloration was investigated. The bases used here were brucine, piperazine, 2,2'-bipyridine and o-phenanthroline. Examples of the absorption spectra are shown in Fig. 2. These spectra were obtained according to the recommended procedure described above.

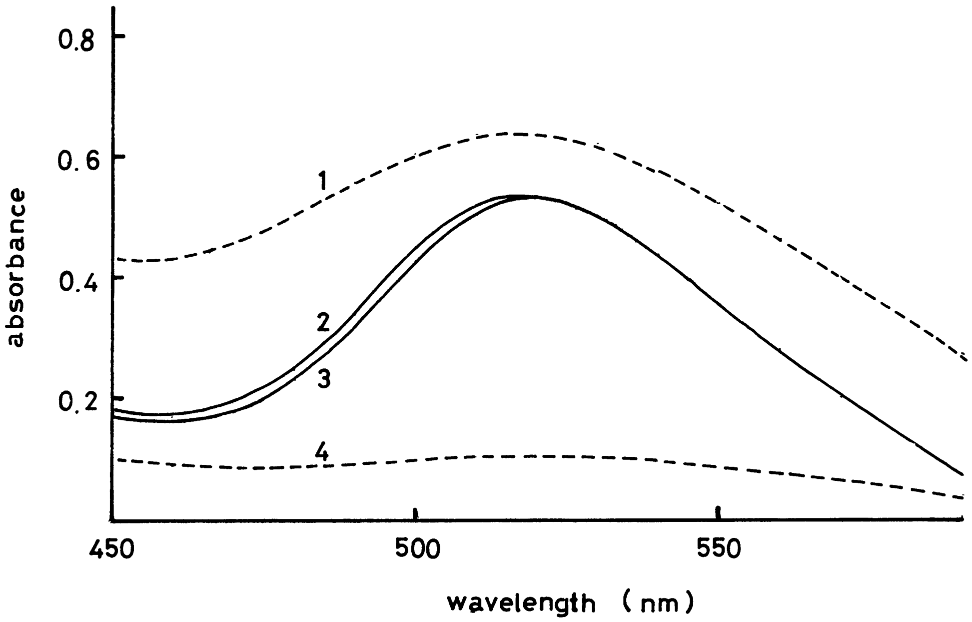

Fig. 2. Absorption Spectra

1. Brucine, As 20 μg 2. Brucine, Sb 20 μg
3. o-Phenanthroline, Sb 20 μg
4. o-Phenanthroline, As 20 μg

When brucine was used as base, stibine and arsine gave similar absorption spectra, but o-phenanthroline behaved quite selectively to antimony. As pointed out by Bode and Hachmann$^{4)}$, in the case of arsenic, the red color that appeared in the chloroform solution is due to colloidal silver suspension formed by the reaction between Ag•DDTC and arsine. From this point of view, the spectra (curve 2 and 3 in Fig. 2) may be assigned to a product formed through the similar reaction by the strong reducing power of stibine. As to solvent, chloroform was found to be the most favorable for the dissolution of both Ag•DDTC and o-phenanthroline. The preliminary study incicated that the sensitivity was 0.008 μg of antimony for 0.001/cm^2 absorption unit. A plot of absorbance vs. the amount of antimony gives a straight line over the range of 2 - 40 μg of antimony. The reproducibility of the proposed method was estimated from the results of five determinations, each with 4 μg/ml for antimony in the chloroform solution. The mean absorbance value was 0.530 with a relative standard deviation of 3.8 %. Apparent molar absorption coefficient for antimony with this system was calculated to be 1.6 x 10^4. The color intensity is fairly stable for several hours and the change of absorbance with the time of standing the solution was -3 %/hr. As to the effect of diverse ions, many common elements did not interfere with the determination. However, the presence of copper(II), chromium(III) and iodide, when their amount was about 200 fold excess in weight to antimony, depressed appreciably the evolution of stibine gas.

References

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