

SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF BISMUTH AFTER EXTRACTION OF THE IODO COMPLEX BY A HIGH MOLECULAR WEIGHT AMINE

MOHAMMAD AMIN and M.A. KHATTAK

P.C.S.I.R. Laboratories, Peshawar

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An investigation of the complex formed between bismuth and potassium iodide in dilute sulphuric acid solution has been carried out and its extractability by a high molecular weight amine in organic solvent examined. The orange-coloured complex is quantitatively extractable from the aqueous phase into an organic phase of tribenzylamine in chloroform. On the basis of this extractability, a method has been developed for the spectrophotometric determination of bismuth in the presence of many other elements.

Spectrophotometric methods for the determination of platinum,¹ palladium² and rhodium³ by the extraction of the chlorostannous complex with high-molecular-weight amines (HMWA) have been previously reported. In the present work, a study of the bismuthiodo complex in dilute sulphuric acid medium was undertaken. The results of the investigations on the system are reported below.

Experimental

Apparatus and Reagents.—Spectrophotometer Model DU Beckman was used. Standard bismuth solution was prepared from bismuth nitrate (Analar grade) (1 ml=10 γ). Tribenzylamine (TBA) A. 0.2M solution was prepared by dissolving 14.370 g TBA in 250 ml chloroform, and equilibrated with 2N sulphuric acid for 10–15 min. The phases were allowed to separate, the lower organic phase was drawn off and the aqueous phase discarded.

Formation of Bismuth Iodide Complex and Extraction by TBA.—On treatment of bismuth solution with potassium iodide solution, a yellow to orange colour was produced. The coloured complex was extracted quantitatively by shaking with 0.2M tribenzylamine in chloroform. No trace of bismuth was ever found in the aqueous phase. The organic phase was filtered off to remove water droplets and the volume was made up to the mark in 10 ml flask with 0.2M TBA in chloroform.

The absorption spectrum of the coloured complex was determined in aqueous phase and in organic amine phase with respect to their corresponding blanks containing all the reagents. The spectra obtained are given in Figs. 1 and 2. It is evident that a definite maximum occurs at 450 m μ and 490 m μ respectively.

Procedure.—Bismuth solution (1–5 ppm) in 10 ml of 2N sulphuric acid was taken in a 25-ml flask, and 1 ml hypophosphorous acid and 1 ml 10% potassium iodide solution were added.⁴ After shaking for 5 min the volume was made up to the mark with distilled water and the absorption spectrum was obtained by measuring the absorbance in the range of 400–500 m μ at intervals of 10 m μ . The absorption spectrum thus obtained (Fig. 1) shows that maximum absorption occurs at 450 m μ .

Extractability of the Coloured Complex.—The orange-yellow bismuth iodide complex in aqueous phase obtained by the above procedure was transferred to a separating funnel and extracted in two instalments with 10 ml 0.2M TBA in chloroform (previously equilibrated with 2N sulphuric acid). The orange-coloured complex was extracted by shaking the two phases for 2 min. The phases were then allowed to separate and the orange coloured complex had completely transferred to the amine phase: the aqueous phase was tested for bismuth, but no trace was ever found, indicating quantitative extraction of the complex.

The amine phase was filtered off through a small filter paper (to remove suspended water droplets) into a 10-ml flask and the volume was made up to the mark with 0.2M tribenzylamine in chloroform. The absorption spectrum measured against the amine blank is shown graphically in Fig. 2 from where it will be seen that it has a definite absorption maximum at 490 m μ . The spectrum is identical with that obtained in aqueous phase, with the difference that the absorption peak is shifted to a higher wavelength, probably representing the effect of change in solvent.

Calibration and Sensitivity.—Known concentrations of bismuth (1–10 ppm) were extracted by the foregoing procedure, and the absorbance measured at 450 m μ and 490 m μ , for aqueous phase and

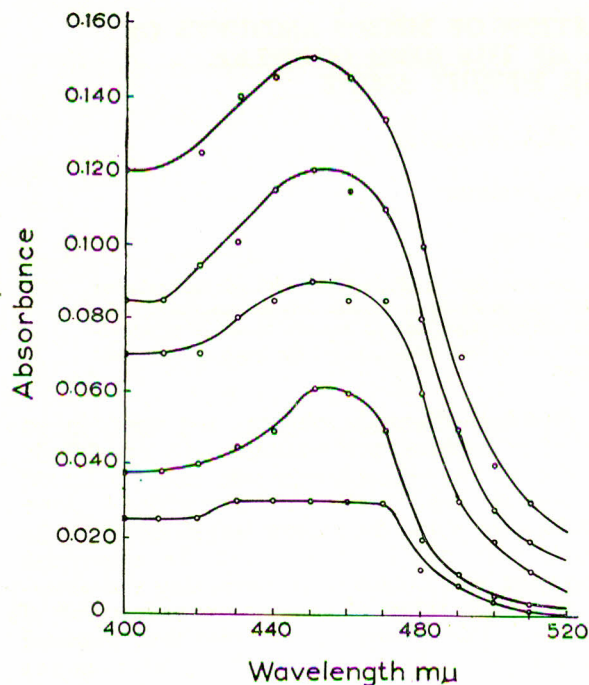


Fig. 1.—The absorption spectrum of bismuth iodide complex in aqueous phase.

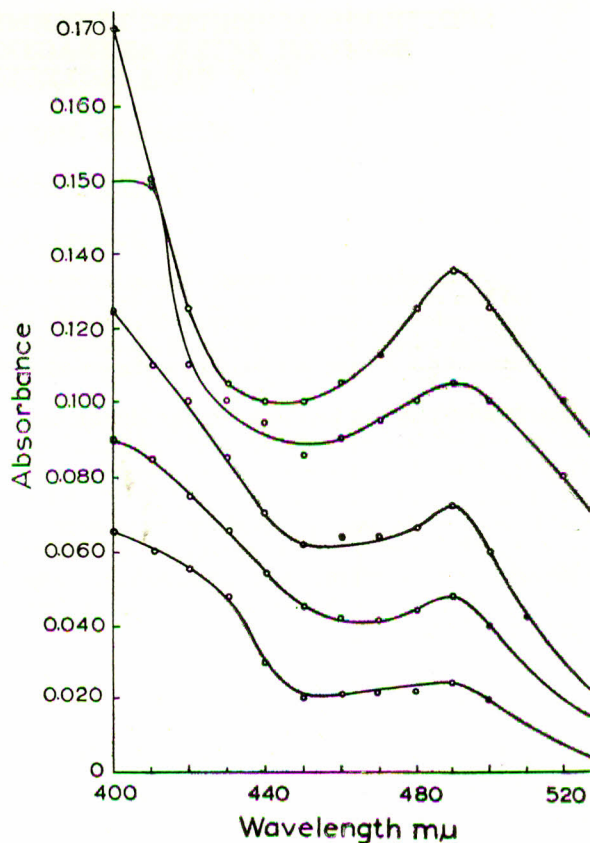


Fig. 2.—The absorption spectrum of bismuth iodide complex after extraction by 0.2M tribenzylamine in chloroform.

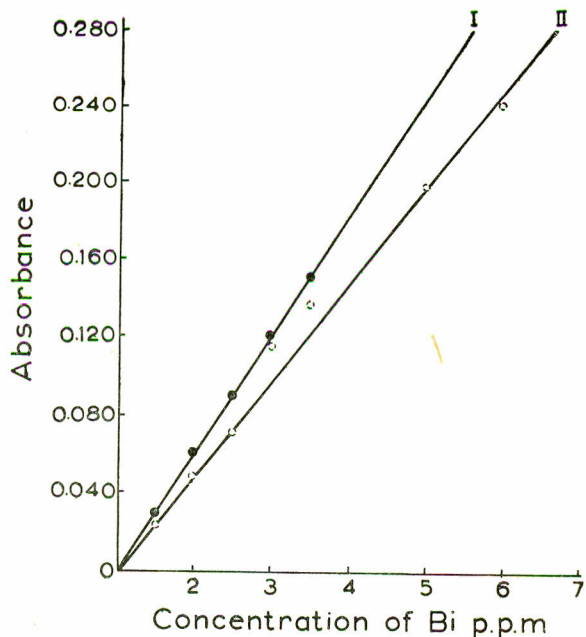


Fig. 3.—Standard curves for bismuth iodide complex: I, aqueous phase; II, extracted by 0.2M tribenzylamine in chloroform.

organic amine phase, respectively. Beer's law was closely obeyed in the above range. The amine-extracted complex showed twofold increased sensitivity for the same amount of bismuth iodide complex in the aqueous phase.

Effect of Sulphuric Acid Concentration.—The addition of sulphuric acid is essential to prevent the precipitation of bismuth as hydroxide. The best concentration of the acid for complex formation lies in the range of 1–2N. A higher concentration of the acid decreases the absorbance of bismuth iodide complex.

2N Sulphuric acid (10 ml) was sufficient to produce maximum colour intensity with 1 ppm bismuth solution.

Stability of the Complex.—The bismuth iodide complex was found stable in aqueous as well as in the organic phase. The stability of the complex depended on the acid concentration. In 2N sulphuric acid, the complex gave constant absorbance readings in aqueous as well as in TBA.

phase after 24 hr. The stability in organic amine phase was however found to be better, as it gave constant absorbance even after a fortnight.

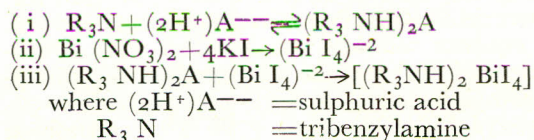
Interferences.—It was observed that Ni, Zn, Al do not interfere upto 2.5 mg for 5 ppm bismuth. Interference by Fe(III), Mn, Cu and Ag (1 g each) was studied, and the results are as follows:

Foreign elements	Bi added	Bi found
Ni 2.5 mg	5 ppm	5 ppm
Ni 5 mg		5.3 „
Ni 10 mg		5.6 „
Ni 20 mg		5.8 „
Zn 2.5 mg		5.0 „
Al 2.5 mg		5.0 „
Fe(III) 1 g		∞ „
Mn 1 g		Nil
Cu 1 g		Nil
Ag 1 g		Nil

(∞ = Beyond the range of the standard curve)

Discussion

The coloured complex formed between bismuth (II) and a soluble iodide in an acid solution is easily extractable into tribenzylamine, hence the species is anionic and "liquid anion exchange" occurs between the complex and amine. The overall extraction of the species may be represented as



The orange-coloured complex possesses definite absorption maximum at 450 m μ and 490 m μ in the aqueous and amine phase, respectively.

The absorption spectra of the coloured species in aqueous and organic amine phase indicate that the curves are more or less identical, with the difference that the absorption peak is shifted by 40 m μ from a lower to a higher wavelength in the organic amine phase. While this bathochromic shift can be attributed to the effect of change of solvent from aqueous to organic amine phase, it should be pointed out that there had not been such a marked shift in absorption bands in other extraction of similar nature.^{1,2,3} The fact that the species exists in the same form as in aqueous phase is open for further investigations and discussions. However, in the extraction of brucinium iodobismuthite with chloroform,⁵ the shift from higher to lower wavelength has been reported to be of 35 m μ and it may appear that the shift in the present case may be a characteristic of this complex.

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