

Thiodibenzoylmethane as an Extracting & Spectrophotometric Reagent for Bi(III)

B. N. PRABHU & S. M. KHOPKAR

Department of Chemistry, Indian Institute of Technology, Bombay 400076

Received 21 January 1975; accepted 2 May 1975

3-Mercapto-1,3-diphenylprop-2-en-1-one (SDBM) has been used for the simultaneous extraction and spectrophotometric determination of Bi(III). Ten ml of 1×10^{-3} M SDBM in benzene quantitatively extracts 193.6 μg of bismuth at pH 6.0, as an orange-yellow coloured complex which has been measured spectrophotometrically at 470 nm. The system conforms to Beer's law in the concentration range of 2.5-30 $\mu\text{g}/\text{ml}$ of bismuth. The results on the effect of reagent concentration, stability of the complex, period of equilibration have also been investigated. It is possible to extract and determine bismuth quantitatively in the presence of large number of ions with which it is associated. The method is simple, rapid and selective.

THIODIBENZOYLMETHANE derivative, 3-mercapto-1,3-diphenylprop-2-en-1-one, synthesized by Chaston *et al.*¹ was used to extract and determine photometrically copper^{2,3}, thallium and mercury⁴, cadmium⁵, cobalt and nickel^{6,7}, iron⁸ and silver⁹. Bismuth(III) can also be quantitatively extracted as an orange-yellow coloured complex, at pH 5.7-6.5 with 1×10^{-3} M reagent in benzene and measured spectrophotometrically at 470 nm.

Amongst β -diketones, benzoylacetone¹⁰ was used as an extractant, but only in highly alkaline media. The extraction was not quantitative when dibenzoylmethane¹⁰ was used for the extraction. Thioyltrifluoroacetone¹¹ was unsuitable as colorimetric reagent, although it was used for the separation of bismuth from actinium. With thiothenoyltrifluoroacetone¹² as an extractant, the extraction had some limitations. The pH range for quantitative extraction was narrow and ions such as cadmium, iron and bromide were not tolerated. Further copper, chromium, molybdate and selenite were tolerated in smaller proportions. Other extractants from chelating systems are summarized in a recent monograph¹³.

The method proposed in this paper, using thiodibenzoylmethane derivative mentioned above is rapid and simple. The method is more selective than previous methods¹². The pH range for quantitative extraction of Bi(III) is broader and the extraction is possible in nearly neutral region¹⁰. It is possible to extract and simultaneously determine Bi(III) at microgram concentrations in a single operation. The overall time for extraction and determination is only 30 min.

Materials and Methods

Perkin-Elmer model 402 spectrophotometer with matched 1 cm cells and Russian type FEK-57 filter photometer were used. Cambridge pH meter provided with glass and calomel electrode assembly was used for measurements.

3-Mercapto-1,3-diphenyl prop-2-en-1-one (SDBM) was synthesized from dibenzoylmethane (Koch-Light, England) by the procedure of Chaston *et al.*¹. About 0.001M reagent in benzene was used.

A stock solution of bismuth nitrate was prepared by dissolving 2.903 g of bismuth nitrate pentahydrate (BDH AnalaR) in 250 ml distilled water containing 2% nitric acid. The solution was standardized volumetrically with EDTA and was found to contain 4.84 mg of bismuth per ml. The solution of lower concentration (48.4 μg of bismuth per ml) was prepared by appropriate dilution of the stock solution.

Procedure—The pH of an aliquot of bismuth nitrate solution containing 193.6 μg of bismuth was adjusted to 6.0, with 0.01M nitric acid and ammonium hydroxide. The final volume was made up to 25 ml with distilled water and the solution transferred to a separatory funnel and shaken with 10 ml of 1×10^{-3} M SDBM in benzene, for about 5 min in a wrist action flask shaker. The layers were allowed to settle and the organic phase was separated. The absorbance of orange-yellow coloured complex of bismuth was measured at 470 nm against the reagent blank.

Results and Discussion

The absorption spectrum of a solution of Bi(III)-SDBM complex [$\text{Bi(III)} = 1.39 \times 10^{-4}$ M] extracted at pH 6.0, against the reagent blank, showed strong absorbance at 470 nm, while the reagent blank (versus benzene) showed maximum absorbance at 415 nm. Thus the difference in absorbance between the bismuth chelate and reagent blank was maximum at 470 nm. Hence all absorbance measurements were carried out at 470 nm. The absorptivity of the complex was 1.84×10^3 , on the basis of bismuth contents. The sensitivity (Sandell's definition) was 0.114 $\mu\text{g}/\text{cm}^2$ per ml at 470 nm. The complex was stable for at least 72 hr. Beyond this period, the colour faded. It is, therefore, recommended to

measure the complex within 72 hr of extraction. A shaking period of 5 min was adequate for quantitative extraction.

The extraction of bismuth into benzene solution of SDBM was studied over the pH range of 1.0-8.0. At pH 5.7-6.5, bismuth was extracted quantitatively in a single extraction. Below and above this pH range, the extraction efficiency decreased. No extraction occurred above pH 8.0. Therefore all extractions were carried out at pH 6.0.

Different amounts of bismuth were extracted as usual and determined at 460, 470 and 480 nm. It was observed that the orange-yellow coloured Bi(III)-SDBM chelate adhered to Beer's law in the concentration range of 2.5-30 µg/ml of bismuth at 470 nm.

The effect of varying concentration as well as the varying volumes of the reagent was studied. Thus about 193.6 µg of bismuth were extracted at pH 6.0, with 10 ml of 2.5×10^{-4} to $1.5 \times 10^{-3} M$ of reagent. Similarly extractions were carried out, with volumes varying from 2.5 to 25 ml of $1 \times 10^{-3} M$ reagent. In all such absorbance measurements, the reagent blank of appropriate concentration was used. It was observed that the extraction of bismuth was quantitative with 10 ml of $1 \times 10^{-3} M$ SDBM in benzene.

Salting-out agents such as ammonium, sodium, potassium, magnesium nitrates (0.5-3M) and calcium and lithium nitrates (1-4M), had no effect on the extraction of Bi(III).

Effect of diverse ions—The tolerance limit for several ions were investigated. The tolerance limit was set, as the amount of foreign ion, in the presence of which, the error in the recovery of Bi(III) is less than $\pm 2\%$. It was seen that ions such as alkali, and alkaline earth metals, rhenate, nitrate, nitrite, thiocyanate and sulphate are tolerated in ratios greater than 1:100 of metal to foreign ion. Thallium, beryllium, fluoride, iodide, thiosulphate, ascorbate, malonate, thiourea and molybdate are tolerated in the ratio of 1:25. Uranium, bromide iodide and tartarate are tolerated in the ratio of 1:5. The ions tolerated in the ratio of 1:3 are chromium, manganese, gallium, selenite and vanadate. The

ions tolerated in the ratio 1:1 are thorium, lead, cobalt and nickel. Since large amounts of sequestering agents, such as potassium cyanide, sodium fluoride and ammonium thiocyanate were tolerated, the interference of some of the ions such as cadmium, copper, silver was eliminated with cyanide, zirconium with fluoride, ruthenium and gold with thiocyanate. The interference of iron was eliminated by prior extraction with acetylacetone¹³. Some of the anions such as arsenate, citrate, oxalate, phosphate and EDTA, however, showed strong interference.

Results are accurate within $\pm 1\%$. From ten determinations, with 193.6 µg of bismuth, the absorbance of the complex was found to be 0.170 ± 0.001 . The relative standard deviation was $\pm 0.85\%$. It was possible to simultaneously extract and spectrophotometrically determine bismuth in microgram concentrations, in the presence of various elements such as copper, cadmium, silver, etc. which are generally associated with it.

References

1. CHASTON, S. H. H., LIVINGSTONE, S. E., LOCKYER, T. N., PICKLES, V. A. & SHANNON, J. S., *Aust. J. Chem.*, **18** (1965), 673.
2. UHLEMANN, E., SCHUKNECHT, B., BUSSE, K. D. & POHL, V., *Anal. Chim. Acta*, **56** (1971), 185.
3. UHLEMANN, E. & MULLER, H., *Anal. Chim. Acta*, **41** (1968), 311.
4. UHLEMANN, E. & SCHUKNECHT, B., *Anal. Chim. Acta*, **69** (1974), 79.
5. SCHUKNECHT, B., RUBISCH, G. & UHLEMANN, E., *Anal. Chim. Acta*, **69** (1974), 329.
6. UHLEMANN, E. & MULLER, H., *Anal. Chim. Acta*, **48** (1969), 115.
7. UHLEMANN, E. & SCHUKNECHT, B., *Anal. Chim. Acta*, **63** (1973), 236.
8. MULYE, R. R. & KHOPKAR, S. M., *Z. anal. Chem.*, **272** (1974), 283.
9. MULYE, R. R. & KHOPKAR, S. M., *Anal. Chim. Acta*, **76** (1975), 204.
10. STARY, J. & HLADKY, E., *Anal. Chim. Acta*, **28** (1963), 227.
11. HAGEMANN, F., *J. Am. chem. Soc.*, **72** (1950), 768.
12. SOLANKE, K. R. & KHOPKAR, S. M., *Anal. Lett.*, **6** (1973), 31.
13. DE, A. K., KHOPKAR, S. M. & CHALMERS, R. A., *Solvent extraction of metals* (Van Nostrand-Reinhold, London), 1970.