

---

## SHORT COMMUNICATIONS

---

### EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF BISMUTH WITH BENZYLDIMETHYLPHENYLAMMONIUM CHLORIDE

K. C. BAYAN and H. K. DAS

Department of Chemistry, Gauhati University,  
Gauhati 781 014, India.

BENZYLDIMETHYLPHENYLAMMONIUM chloride, a quaternary ammonium salt possesses considerable potentiality to find application as a reagent for the determination of a number of metal ions when present in trace amounts in solution. Preparation of the compound is very simple<sup>1</sup>, and its purity can be checked up without much difficulty<sup>2</sup>. Its use for detection of large anions, *viz*  $\text{CrO}_4^{2-}$ ,  $\text{S}_4\text{O}_6^{2-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{I}^-$  was reported long before<sup>3</sup>. Jun Yoshimura and Kaoru Ueno<sup>4</sup> used benzyldimethylphenylammonium chloride for the spectrophotometric determination of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mo}^{5+}$  in  $\text{SCN}^-$  solutions. The metallic  $\text{SCN}^-$  complexes react with the reagent to give coloured species readily extractable into chloroform.

When potassium iodide is added to a dilute sulphuric acid solution containing a small amount of bismuth, a yellow to orange colouration due to the formation of tetraiodobismuthate (III) ion is produced. This complex ion readily forms ion-pair with benzyldimethylphenylammonium ion in the form of an orange precipitate which is highly soluble in 1,2-dichloroethane. In this paper we present a method for the extractive spectrophotometric determination of bismuth ion in micro amounts using benzyldimethylphenylammonium chloride as the reagent and 1,2-dichloroethane as the solvent for extraction.

Absorbance was measured with a Hilger Uvispek photoelectric spectrophotometer in matched quartz cells of 1 cm optical path.

#### Standard solution

The standard stock solution of bismuth was prepared from bismuth (III) oxide (B.P.), which was 2N with respect to sulphuric acid, and contained  $10 \times 10^{-4}$  g of bismuth per ml. of the solution. Solutions of lower concentrations were prepared by dilution of the stock solution with 0.1N sulphuric acid.

#### Reagents

The reagent, benzyldimethylphenylammonium chloride was prepared by mixing equimolar amounts of benzyl chloride and dimethyl aniline, and allowing the mixture to stand until crystallisation occurred. The solid was washed with acetone, dissolved in alcohol and recrystallised.

A 0.01M (0.24%) aqueous solution of benzyldimethylphenylammonium chloride and a freshly prepared 5% aqueous solution of potassium iodide were used as reagents. Sodium hypophosphite were added to the solution of potassium iodide to make it 20% with respect to the hypophosphite.

Standard solutions of diverse ions were prepared from their chloride, nitrate or sulphate; or from sodium, potassium or ammonium salts.

#### Recommended procedure

An aliquot of the bismuth solution containing from 20 to 200  $\mu\text{g}$  of bismuth (III) was made upto 5 ml. with 0.1N sulphuric acid in a separatory funnel. To this 1 ml. of the solution of potassium iodide containing sodium hypophosphite followed by 1 ml. of benzyldimethylphenylammonium chloride solution and 5 ml. of 1,2-dichloroethane was added. The resulting mixture was shaken for 3 minutes and the orange coloured organic layer was separated. Absorbance of the extract was measured at 490 nm against the pure solvent. Amounts of bismuth in unknown solutions were calculated from standard calibration curve.

An aqueous solution of benzyldimethylphenylammonium chloride forms an orange precipitate with tetraiodobismuthate (III) ion—the precipitate being an ion-association complex of the type  $\text{Q}^+[\text{BiI}_4]^-$ , which is completely extractable into 1,2-dichloroethane. The orange coloured extract has maximum absorption at 490 nm and obeys Beer's law over the concentration range of 4 to 40  $\mu\text{g}$  of bismuth (III) per ml. The reagent blank has no absorption at 490 nm. The complex, benzyldimethylphenylammonium tetraiodobismuthate (III) is stable for two hours.

Absorbance values were found to increase when the acid concentration of the aqueous layer exceeded 3N, while lowering of acidity even upto 0.02N was without

any effect upon absorbance values. High absorbances are mainly due to the liberation of iodine which by virtue of being bonded to the iodide ions to give polyiodide ions, usually  $I_3^-$ , form ion-pair with the reagent in the form of a brown precipitate soluble in 1,2-dichloroethane. The extract has considerable absorption at 490 nm. If no reducing agent is used in the determination, the upper limit of acidity of the aqueous layer is restricted to 0.25N only.

Concentration of the potassium iodide solution has to be maintained in between 1% and 3% in case sodium hypophosphite is not used. Allowance upto a concentration of 20% could be provided by employing 1 ml. of a 20% solution of the hypophosphite. The use of a 20% solution of sodium hypophosphite was preferred to avoid interference due to a number of oxidizing ions.

The effect of varying reagent concentrations on extraction of bismuth was studied. A 0.24% solution of benzyldimethylphenylammonium chloride was preferred, since concentrations below 0.15% gave low values of absorbance, while increased reagent concentration produced no significant effect.

The effect of foreign ions was studied by adding different amounts of foreign ions to 50  $\mu$ g of bismuth (III) and determining the bismuth following the recommended procedure. It was found that  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Ag^+$ ,  $Au^{3+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Mn^{7+}$ ,  $V^{5+}$ ,  $As^{3+}$ ,  $Sb^{3+}$ ,  $Mo^{5+}$ ,  $W^{6+}$ ,  $Pb^{2+}$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $S_4O_8^{2-}$ ,  $SO_3^{2-}$ ,  $NO_3^-$ ,  $CNS^-$ ,  $S_2O_3^{2-}$ ,  $ClO_4^-$ ,  $C_2O_4^{2-}$ , citrate, tartrate and acetate ions even in amounts five times that of bismuth did not interfere, and a good recovery of bismuth (within 4% error in microgram level) was achieved. Equal amounts of  $Pt^{4+}$ ,  $Pd^{2+}$  and  $Cr^{6+}$ , however, interfered. Interference due to  $Cr^{6+}$  (upto a five fold excess) could be avoided by making the aqueous layer more acidic (eg., 2N).

The method thus proved to be simple and rapid, and yet provided a good recovery of bismuth in trace concentrations in presence of most of the common ions. When compared with the existing standard spectrophotometric method for the determination of bismuth using potassium iodide alone, the present method is found to be far more superior in selectivity and accuracy. The present method will be very helpful in estimating bismuth in trace concentrations from ores and minerals when interfering ions, viz  $Pt^{4+}$  and  $Pd^{2+}$  are absent.

The authors express their sincere thanks to Professor N. N. Siddhanta for having accorded permission to work in the Chemistry Department of

Gauhati University, and Dr N. K. Baishya for his help in carrying out this work.

8 February 1983; Revised 31 May 1983

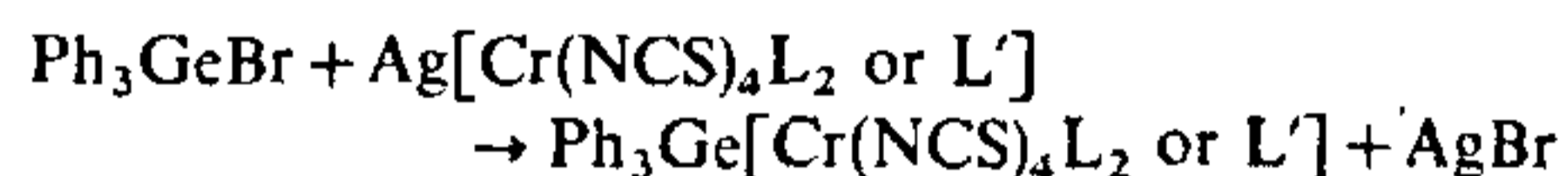
1. Ryan, D. E., *Can. J. Chem.*, 1956, 34, 1683.
2. Blagoveshchenskaya, Z. I., *Izvest. Vyschikh Ucheb. Zavedenii, Tekhnol, Tekstil. Prom.*, 1960, No. 6, 116.
3. Yatsimirskii, K. B. and Blagoveshchenskaya, Z. I., *Trudy Komissii Anal. Khim., Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 1954, 5, 90.
4. Jun Yoshimura and Kaoru Ueno, *Mem. Fac. Sci. Kyushu Univ., Ser. C., Chem.*, 1961, 4, 63.

### SOME TRIPHENYLGERMANIUM DERIVATIVES OF MIXED LIGAND THIOCYANATOCHROMATE (III)

R. K. SRIVASTAVA\* and T. N. SRIVASTAVA,  
Chemistry Department, University of Lucknow,  
Lucknow 226 017, India.

\* Present address: Inorganic Chemistry Division,  
Regional Research Laboratory, Jorhat 785 006, India.

IN continuation of our studies<sup>1,2</sup> on  $(R_3M)_3 [Cr(NCS)_6]$  or  $R_3M[Cr(NCS)_4L_2]$  type of compounds, some triphenylgermanium derivatives have been prepared and characterized. Triphenylgermanium bromide and  $Ag [Cr(NCS)_4L_2]$  or  $Ag [Cr(NCS)_4L']$  were prepared by reported method<sup>1-3</sup>. Triphenylgermanium complexes were prepared according to the following reaction -



L = aniline, urea, dimethylformamide, ammonia or pyridine.

L' = 1, 10-phenanthroline or ethylenediamine.

In a typical reaction, triphenylgermanium bromide (5 mmol) in acetone (25 ml) was refluxed for 4 hr on a water bath with an acetonic suspension of the silver complex (6 mmol) in 25 ml. The precipitated silver bromide was rejected and the excess solvent was distilled off from the filtrate under reduced pressure. The treatment of the residual viscous mass with diethyl ether followed by petroleum ether (40-60°C) yielded a coloured pure crystalline complex. The product was washed with petroleum ether (40-60°C) and dried in vacuum. No further purification was needed.