  Bull. Chem. Soc. Jpn., 62, 3675—3678 (1989)

Extraction Spectrophotometric Determination of Bismuth(III) with Iodide and Amidines

Alpana GHOSH, Khageshwar Singh PATEL, and Rajendra Kumar MISHRA*
Department of Chemistry, Ravishankar University, Raipur (M. P.), 492010, India
(Received December 22, 1988)

A new simple and rapid spectrophotometric method for the extraction and determination of bismuth(III) is described. The reaction of *N,N'*-diphenylbenzamidines and its 10 derivatives (HA) with bismuth(III) in presence of iodide have been investigated photometrically in chloroform. The value of molar absorptivity of the complexes with these compounds lies in the range $(0.84—1.35)\times10^4$ l mol^{-1} cm^{-1}. Of these, the most sensitive compound *N*-(2-methylphenyl)-*N'*-phenylbenzamidine hydrochloride (MPPBA) was selected for detailed studies. The detection limit of the method is 0.2 μg Bi cm^{-3}. The elements which are commonly associated with the metal e.g. Cu, Ni, Co, Mn, Cr, Zn, Hg, Ti, Zr, Mo, W, V, Al, Sb, etc. do not interfere. The method has been applied for the determination of the metal to soil and ore.

In earlier communications, amidines were used for the extraction and spectrophotometric determination of Sb(III) and Au(III) as halogeno ternary complexes.[1,2] In this paper, *N,N'*-diphenylbenzamidine and its 10 derivatives are reported for extraction and spectrophotometric determination of microgram amounts of bismuth(III) in the presence of iodide ions. The formation of iodobismuthite complex in the water and in the organic solutions is the absence of amidine were examined at the conditions mentioned in the procedure. The value of molar absorptivity of the complex in the aqueous solution is found to be 8500 l mol^{-1} cm^{-1} at 445 nm and its extraction by polar solvents 1-pentanol, methyl isobutyl ketone, ethyl acetate suffers by unstability of the extract at room temperature. Moreover, the classical iodide method commonly used is complicated because it is applicable in sulfurous acid media and suffers form interferences of metal ions e.g. Sb, Pb, Hg, etc.[3,4] Tetrabutyl ammonium ion[5] and dyes[6—9] were claimed to improve the selectivity of classical iodide method, although they suffers from interference of the metal ions. Thiourea is widely used for spectrophotometric determination of metal in perchloric acid medium. However, it is not sensitive and involves the serious interference of Sb.[3,4] Dithizone is employed for the spectrophotometric determination of metal in alkaline solution using cyanide as masking agent to overcome the interference of heavy metals.[10] Recently mucic acid has been used as a colorimetric reagent for the determination of the metal over pH range 4.0 — 5.0 but it is not sensitive.[11]

The present method remarkably enhances the selectivity and sensitivity of the classical iodide method. The complex is stabilized by amidine in the organic solution unlikely to polar solvents e.g., 1-pentanol, MIBK or ethyl acetate. This method also improves the selectivity of other established methods.

Experimental

Apparatus: A Carl Zeiss "SPEKOL" equipped with 1-cm quartz cells were employed for the absorbance measurements.

Reagents: The standard solution and bismuth(III) was prepared by dissolving a weighed amount of bismuth sulfate in dilute sulfuric acid (0.5 mol dm^{-3}) and standardized volumetrically with EDTA using Pyrocatechol Violet as an indicator.[12] A freshly prepared potassium iodide solution (5% w/v) containing ascorbic acid (1% w/v) was employed. A 0.4% (w/v) solutions of amidines in chloroform was used for all extraction work. All chemicals used were analytical grade and their solutions were prepared in deionized water.

Procedure: Place an aliquot of standard bismuth(III) solution containing 25—450 μg of the metal in a 150-cm^3 separatory funnel. To this add 1 cm^3 of 5% KI solution. Adjust the acidity to the required value with 10 mol dm^{-3} H_2SO_4 and dilute to 10 cm^3 with deionized water. Add 10 cm^3 chloroform solution of the reagent. Shake the content of the funnel vigorously for 2 min and allow the phase to separate. Dry the chloroform extract over anhydrous sodium sulfate in a 50-cm^3 beaker. Wash the aqueous layer with 3×2 cm^3 fresh portions of chloroform. Transfer all the extracts to 25-cm^3 volumetric flask and dilute with chloroform to the mark. Measure it at λ_{max} against reagent blank.

Results and Discussion

Absorption Spectra: The absorption spectra of the ternary complex is chloroform, binary complex in the aqueous solution and that of reagent blank in chloroform are shown in Fig. 1. The maximum absorbance of the ternary and binary complexes lies at 490 nm and 440 nm, respectively. The formation of ternary shows a slight hyperchromic shift and a strong bathochromic shift as shown in Fig. 1. The reagent blank in chloroform shows some absorption at λ_{max} hence it was used as a reference blank for all measurements.

Selection of Extracting Solvents: The influence of various solvents e.g., benzene, toluene, carbon tetrachloride, chloroform, and cyclohexane were examined for the extraction of the complex with *N*-(2-methylphenyl)-*N'*-phenylbenzamidine hydrochloride (MPPBA). The complex is quantitatively extractable into toluene

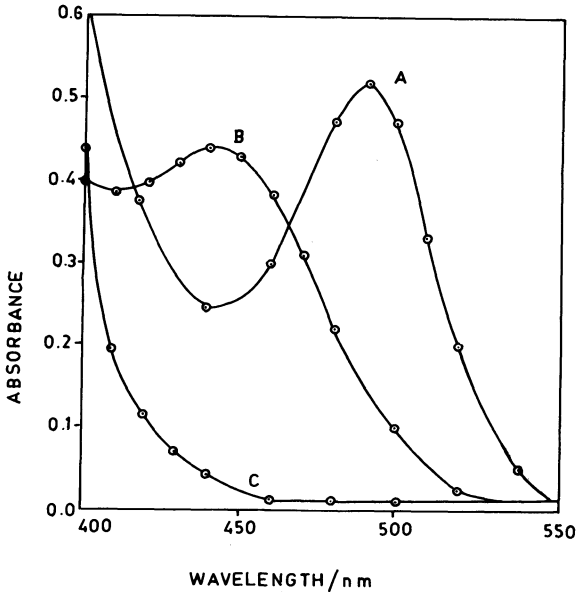

Fig. 1. Absorption spectra of bismuth(III) with iodide in aqueous solution and with iodide and amidine (MPPBA) in chloroform and the reagent blank in chloroform.
(A) $C_{Bi}=3.8\times10^{-5}$ mol dm^{-3}; $C_{KI}=0.03$ mol dm^{-3}; $C_{MPPBA}=0.014$ mol dm^{-3}; $C_{H_2SO_4}=2.0$ mol dm^{-3}. (B) $C_{Bi}=3.8\times10^{-5}$ mol dm^{-3}; $C_{KI}=0.03$ mol dm^{-3}; $C_{H_2SO_4}=2.0$ mol dm^{-3}. (C) $C_{KI}=0.03$ mol dm^{-3}; $C_{H_2SO_4}=2.0$ mol dm^{-3}; $C_{MPPBA}=0.014$ mol dm^{-3}.

and chloroform; whereas partially extracted into aromatic hydrocarbons while no extraction in carbon tetrachloride. The value of molar absorptivity and absorption maximum of the complex in these solvents are: Toluene (λ_{max}-490 nm, $\varepsilon=13400$ l mol^{-1} cm^{-1}), chloroform (λ_{max}-490 nm, $\varepsilon=13500$ l mol^{-1} cm^{-1}). Of these, chloroform is used as a solvent for further extraction work due to high distribution ratio of the reagent in it. Effect of acidity and quantitative extraction of the metal: The effect of acids like sulfuric and hydrochloric acids on the extraction of the metal with iodide and amidines were examined. Hydrochloric acid cannot be used for acidification because of the formation of the chloro complexes which suppress the extraction in the present investigation. Therefore, sulfuric acid has been selected for further extraction work.

The data obtained show that the optimum acidity range for the maximum and constant absorbance of the complex in the organic solution is 0.5—4.0 mol dm^{-3} H_2SO_4. A 100, 200, and 400 μg of Bi(III) is extracted separately as in the procedure. The extract is evaporated, digested with acid treatment and estimated by perchloric acid method. The metal recovered was found to be more than 99%.

Effect of Reagents, Time, Temperature, and Volume of Aqueous Phase: The effect of the concentration of reagents on the extraction of Bi(III) with KI and MPPBA were studied. The extraction is quantitative when the concentration of MPPBA in chloroform is higher than 0.009 mol dm^{-3}. The concentration of potassium iodide should be between 0.0075 to 0.09 mol dm^{-3} in aqueous solution. The function of ascorbic acid added is to prevent the oxidation of iodide as well as to remove any oxidizing materials present in aqueous solution. The order of addition of reagents is not critical. A shaking time of 1 min was sufficient for complete extraction of the metal and further extraction upto 10 min did not cause any adverse effect. The absorbance of the extract was stable for at least 5—6 h at room temperature (25±2 °C). The effect of dilution upon extraction of the metal with MPPBA was examined. The results indicates that the absorbance of the extraction remained unchanged when the volume ratio of organic phase to aqueous phase was 2:1 to 1:10. The reaction temperature of the medium is critical and it should be between 20 and 30 °C. Beyond this temperature the color intensity of the complex decreases.

Optimum Concentration Range, Sensitivity, and Precision of the Method: A linear calibration graph passing through the origin was obtained by the recommended procedure over concentration range 1—18 μg Bi cm^{-1} with MPPBA. The detection limit of the method was determined by taking known microgram amount of the metal in total aqueous phase (5 ml) containing 0.2 ml KI and 1 ml sulfuric acid (10 mol dm^{-3}) and it was shaken with a few drops of chloroform solution of amidine. The experiment was repeated until the orange color of the organic phase has been appeared. The detection limit of the method is 0.2 μg Bi cm^{-3}. The molar absorptivity of the complex obtained by this method is 1.35×10^4 l mol^{-1} cm^{-1}. The relative standard deviation of the method for 10 replicate measurements at 150 μg Bi 10 cm^{-3} was ±1.2%.

Effect of Amidines: The effect of substitution in *N*-phenyl ring of the amidine on the color intensity of the extract was examined (Table 1). The introduction of CH_3 or Cl groups in amido N-ring except 2-CH_3 decrease the color intensity of the complex. The breaking of the conjugation as seen with benzyl and octyl groups greatly suppress the color of the complex. The increase in degree of substitution also causes adverse effect. The position of substituents enhances the color intensity in the order: *p*-<*m*-<*o*-.

Composition of the Complex: Bismuth(III) reacts with iodide in sulfuric acid medium to give colored iodo complex which is extracted as iodo-ternary complex with reagent MPPBA into chloroform. The metal to ligand ratio was determined by plotting log *D* (distribution ratio) versus log *M* molar concentration of the reagents and which give slope of 3.9 and 1.8 for iodide and amidine respectively (Fig. 2). The reaction mechanism can be expressed as following:

Table 1. Spectral Data of Iodobismuth Complex with Various Amidines in Chloroform

	$C_6H_5-C(=N-R')-N(R)-H$ R	R′	λ_{max} nm	ε l mol^{-1} cm^{-1}	Sandell's sensitivity μg cm^{-2}
1	C_6H_5	C_6H_5	490	12200	0.017
2	2-$CH_3C_6H_4$	C_6H_5	490	13500	0.015
3	3-$CH_3C_6H_4$	C_6H_5	490	11320	0.021
4	4-$CH_3C_6H_4$	C_6H_5	490	10500	0.020
5	2,5-$(CH_3)_2C_6H_3$	C_6H_5	490	10275	0.020
6	2-ClC_6H_4	C_6H_5	490	10620	0.019
7	3-ClC_6H_4	C_6H_5	490	10450	0.020
8	4-ClC_6H_4	C_6H_5	490	10100	0.020
9	2,5-$(Cl)_2C_6H_3$	C_6H_5	490	8360	0.025
10	$CH_3(CH_2)_7$	C_6H_5	490	9000	0.023
11	$C_6H_5CH_2$	C_6H_5	490	9360	0.022

Table 2. Determination of Bismuth(III) in Complex Materials

Sample No.[a]	Bismuth found (ppm) Present method	Bismuth found (ppm) Thiourea method	Relative standard deviation of the present method[b]
a	37.0	39.0	±1.2%
b	12.5	14.0	±1.1%

a) a: Soil sample obtained from Sonakhan Mines. b: Galena sample obtained from Zawar Mines, Udaipur.
b) Average of six determinations.

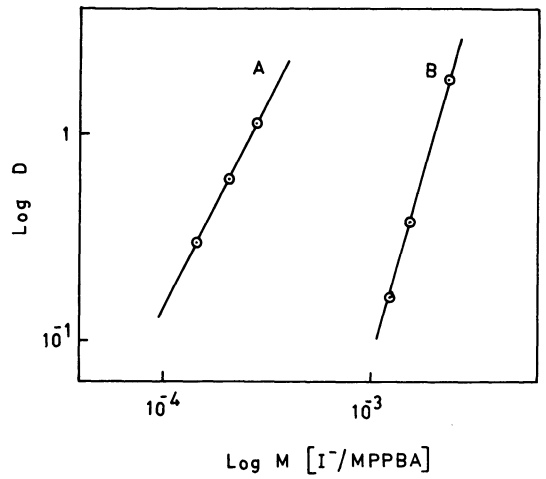

Fig. 2. Determination of composition of the complex in chloroform by curve-fitting method.
C_{Bi}=9.6×10^{-5} mol dm^{-3}; $C_{H_2SO_4}$=2.0 mol dm^{-3}. (A) log D vs. log [MPPBA]; C_{KI}=0.03 mol dm^{-3}. (B) log D vs. log [I$^-$]; C_{MPPBA}=0.014 mol dm^{-3}.

$$Bi^{3+} + 4I^- + H^+ + 2HA_o \rightleftharpoons \{[BiI_4][H(HA)_2]\}_o$$

where subscripts o and HA denote the organic phase and amidine respectively.

Effect of Diverse Ions: The effect of diverse ions in the determination of 175 μg Bi(III) was studied. The complex was extracted as described in the recommended procedure. Interference was considered to occur if the error in the absorbance exceeded ±2%. The tolerance limit of various diverse ions (in mg) are summarized in parentheses as: Cd, Pb (0.7); Ag (1); Sb (3); V, W (4); Hg, Cu, Re (5); Mo, La (30); U (50); Al (70); Ti (80); Th (90); Zr, Cr (100); Be, Mn (120); Zn, Co (200); Ni (300); Br$^-$, $C_2O_4^{2-}$ (50); PO_4^{3-}, Cl$^-$ (80); EDTA (80); NH_2CSNH_2 (50).

Application of the Method: The method has been applied for recovery of the metal to soil and galena samples. A weighed amount of the sample (5 g) is digested with aqua regia (10 cm^3) and dried sample is treated with 5 cm^3 of concentrated hydrochloric acid to remove excess of nitrate ions. It is evaporated upon dryness and then treated with 3—4 cm^3 of concentrated sulfuric acid. The dry residue is then dissolved in water, filter and make up to 50 cm^3 with deionized water. Bi is prior separated by cupferron extraction as described in the literature.[3] The metal content of the sample is determined by standard addition method as described in the procedure. The results indicated that this method is reproducibly applicable to these samples for recovery of the metal.

We are thankful to Ravishankar University for providing fellowship to one of them (A. G.).

References

1) A. Golwelker, K. S. Patel, and R. K. Mishra, *Intern. J. Environ. Anal. Chem.*, **33**, 185 (1988).
2) K. S. Patel and K. H. Lieser, *Anal. Chem.*, **58**, 1547 (1986).
3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed., Interscience, New York (1959).
4) N. M. Lisicki and D. F. Boltz, *Anal. Chem.*, **27**, 1722 (1955).
5) K. Hasebe and M. Taga, *Talanta*, **29**, 1135 (1982).

6) A. Dimitrova and A. Shishov, *Bolg. Akad. Nauk.*, **32**, 1679 (1979); *Chem. Abstr.*, **92**, 190733m (1980).
7) V. E. Poladyan, S. F. Pakhol Chuck, L. M. Avalsovich, and A. M. Andrianov, *Ukr. Knim. Zh.*, **51**, 743 (1985); *Chem. Abstr.*, **103**, 167062d (1985).
8) N. L. Shestidesyataya, P. P. Kish, and A. V. Merenich, *Zh. Anal. Khim.*, **25**, 1547 (1970).
9) Qi-Heng Lu Xu Song and Jin Yao, *K'O Hsuch Tung Pao*, **25**, 302 (1980); *Chem. Abstr.*, **95**, 17501y (1981).
10) H. A. Mottola and E. B. Sandell, *Anal. Chim. Acta*, **25**, 520 (1961).
11) A. Gonzalez, C. Baluja-Santos, and F. Bermejo-Martinez, *Analyst*, **111**, 547 (1986).
12) A. I. Vogel, "A Text book of Quantitative Inorganic Analysis," 3rd ed, Longman, London (1982).