CHAPTER VIII

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF BISMUTH

RESUME

A sensitive and selective method for extraction spectrophotometric and atomic absorption spectrophotometric determination of bismuth(III) utilising N-p-tolyl-α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) as an extractant is reported. It forms a colourless complex, extractable at pH 5.0 into chloroform. The sensitivity of the method is enhanced by the addition of phenylfluorone in the Bi-PTPMCHA extract, which gives the red colour complex having maximum absorbance at 550 nm and molar absorptivity 3.1×10^4 $lmol^{-1}cm^{-1}$. Beer's law obeyed in the range of 0.33-10.00 ppm of Bi(III).

The present method has been applied for the determination of bismuth in standard metals and alloys. These results were compared with atomic absorption spectrophotometric data.

INTRODUCTION

Bismuth is a toxic metal and its toxic effects on man consist of decreased appetite, weakness, rheumatic pain, diarrhoea and dermatitis (1). Moreover, the metal is chiefly employed for the preparation of hard and easily fusible alloys which are useful as safety plugs in boilers, electrical fuses, solders, etc. which makes the separation and determination of the metal important. Medicinally bismuth salts are used to control diarrhoea and other gastrointestinal diseases.

A large number of organic reagents are available for the spectrophotometric determination of bismuth. Hydroxamic acids have been studied as potential analytical reagents for separation, detection and spectrophotometric determination of metal ions (2-11). N-Phenylbenzohydroxamic acid (PBHA) is employed for polarographic (12), gravimetric (13) and spectrophotometric determination of bismuth (14).

In the present investigation the analytical potentialities of substituted cinnamohydroxamic acids are explored as reagents for extraction spectrophotometric determination of bismuth.

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used were of AnalaR and GR grades of B.D.H. or E. Merck, respectively, unless otherwise specified.

Hydroxamic acids

These are synthesised as described in Chapter II. 0.1% reagent solution of hydroxamic acids were prepared in chloroform.

The standard buffer solutions at desired pH ranges were prepared from 0.2 M sodium acetate and 0.2 M acetic acid and 0.1 M KH_2PO_4 and 0.05 M borax as described elsewhere (15).

The standard bismuth solution was prepared by dissolving requisite amount of bismuth nitrate in double distilled water and its final concentration was determined volumetrically (16).

Phenylfluorone

A 0.01% w/v solution was prepared in pure methanol.

APPARATUS

The spectral measurements were made on Shimadzu UV-VIS-240 spectrophotometer. The pH adjustments were made on Systronics digital pH meter, Model 324, equipped with glass and calomal electrodes.

A GBC-901 atomic absorption spectrophotometer equipped with GBC HG 900 Vapour Generation Assembly and bismuth hollow cathode lamp was used. The 223.1 nm bismuth line and air acetylene flame were used for direct AAS measurements.

EXTRACTION PROCEDURE

2.0 ml aliquot of 2 x 10^{-4} M Bi(III) solution was transferred into a 60-ml separatory funnel. Added a sufficient quantities of distilled water and buffer solution to maintain the pH 5.0 to a total volume of the aqueous phase 20 ml. 10 ml of a 0.1% PTPMCHA solution in chloroform was added and the mixture was shaken vigorously for 10 min. The phases were allowed to separate and the colourless chloroform layer was collected in 25 ml volumetric flask after drying over anhydrous sodium sulphate. Further, the 0.01%, 4.0 ml of phenylfluorone solution was added in the Bi-PTPMCHA extract and 6.0 ml of methanol was added to avoid the turbidity, and the contents were diluted to 25 ml with chloroform. The absorbance was measured at 550 nm against a reagent blank.

Atomic absorption measurements

The chloroform extract was directly aspirated to the flame for AAS measurements.

However, for the lower concentration of bismuth

(0.005-0.06 ppm) the bismuth was determined by the hydride method using GBC HG 900 Vapour Generation Assembly. The following parameters were set : wavelength 223.1 nm, lamp current 10 mA, working range 0.005-0.06 ppm of Bi, sample volume 20 ml, fuel,air acetylene (flow rate 2-3 mm high), inert gas nitrogen at 20 psi.

The chloroform extract of bismuth-hydroxamic acid complex was back extracted with 20 ml 2 M hydrochloric acid and the acidic solution was used for determination of bismuth. The concentration of bismuth was computed from the calibration curve which was prepared in the 0.005-0.06 ppm range using the above method.

RESULTS AND DISCUSSION

The spectral characteristics of bismuth complexes with hydroxamic acids and phenyl fluorone are summarized in Table 1. From the preliminary studies, it is observed that N-p-tolyl-α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the hydroxamic acids studied here. Hence, the optimum conditions for the extraction of bismuth with PTPMCHA has been further investigated.

Effect of pH

The optimal pH for the complete extraction of bismuth with PTPMCHA in chloroform was examined in the pH range 3.0-7.0. It was observed that the extraction was incomplete at lower and higher pH and is maximum at 4.8-5.2 (Table 2), Hence, pH 5.0 was chosen for the extraction purpose.

Effect of reagent concentration

To investigate the influence of the concentrations of PTPMCHA on the extraction of bismuth, the extraction was carried out with various amounts of PTPMCHA in chloroform. It was observed that 10 ml of 0.1% PTPMCHA in chloroform gives the complete extraction of bismuth. However, a 10 ml of 0.15% PTPMCHA in chloroform could be used without any difficulty (Table 3).

TABLE 1

Spectral characteristic of bismuth substituted cinnamohydroxamic acids with phenylfluorone

Bi(III) : 3.33 ppm

Hydroxamic acids : 0.1%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, 4 ml in MeOH

Shaking time : 10 min

pH : 5.0

Solvent : $CHCl_3$+ MeOH (3:2)

Colour of complex : Red

Compd No.	Cinnamohydroxamic acid	λ max nm	Molar absorptivity $l\ mol^{-1} cm^{-1}$	Sandell's Sensitivity $\mu g\ cm^{-2}$
I	N-Phenyl-α-phenyl p-methoxy-	550	2.9×10^4	0.0072
II	N-p-Tolyl-α-phenyl-p-methoxy-	550	3.1×10^4	0.0067
III	N-m-Tolyl-α-phenyl-p-methoxy-	550	3.0×10^4	0.0070
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	550	2.8×10^4	0.0075
V	N-Phenyl-α-phenyl-	550	2.8×10^4	0.0075
VI	N-p-Tolyl-α-phenyl-	550	2.9×10^4	0.0072
VII	N-m-Tolyl-α-phenyl-	550	2.9×10^4	0.0072
VIII	N-p-Chlorophenyl-α-phenyl-	550	2.7×10^4	0.0077
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	550	2.8×10^4	0.0075

TABLE 2

Effect of pH on the extraction of bismuth

Bi(III) : 3.33 ppm

PTPMCHA : 0.1%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, 4 ml in MeOH

Shaking time : 10 min

Solvent : $CHCl_3$ + Methanol (3:2)

λmax : 550 nm

Colour of complex : Red

pH	Absorbance	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
3.0	0.00	-	-
4.0	0.09	5.6×10^3	18
4.5	0.31	1.9×10^4	63
4.7	0.43	2.7×10^4	90
4.8	0.49	3.1×10^4	99.9
5.0	0.49	3.1×10^4	99.9
5.2	0.49	3.1×10^4	99.9
5.4	0.40	2.5×10^4	83
5.5	0.30	1.8×10^4	61
6.0	0.11	6.9×10^3	22

TABLE 3

Effect of reagent concentration

Bi(III) : 3.33 ppm

Phenylfluorone : 0.01%, 4 ml in MeOH

Shaking time : 10 min

pH : 5.0

Solvent : $CHCl_3$+ MeOH (3:2)

λmax : 550 nm

Colour of complex : Red

PTPMCHA (0.1%) ml	Molar concentration of PTPMCHA (M)	Absorbance	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
3.0	0.0083	0.29	1.8×10^4	59.1
5.0	0.0139	0.43	2.7×10^4	87.7
6.0	0.0167	0.46	2.8×10^4	93.8
7.0	0.0195	0.47	2.9×10^4	95.8
10.0	0.0278	0.49	3.1×10^4	99.9
15.0	0.0417	0.49	3.1×10^4	99.9
20.0	0.0556	0.49	3.1×10^4	99.9

Effect of phenylfluorone concentration

Varying amounts of phenylfluorone solution in methanol were added in the bismuth hydroxamate. It was observed that 4.0 ml of 0.01% solution of phenylfluorone in methanol was adequate for the complete colour development (Table 4). A further excess of phenyl fluorone decreases the colour intensity of the complex.

Effect of shaking time and stability

Extraction of bismuth complex is rapid under the recommended conditions. The complex is stable for several hours.

Beer's law

The coloured system obeys Beer's law in the range of 0.33-10.0 ppm of bismuth(III). The molar absorptivity was found 3.1×10^4 l $mol^{-1} cm^{-1}$ with a photometric Sandell's sensitivity 0.0067 $\mu g\ cm^2$.

Effect of diverse ions

Different amounts of diverse ions were added to a fixed amount of bismuth and the bismuth was extracted according to the procedure. Most of the metal ions associated with bismuth do not interfere, except for Ce^{4+}, U^{6+}, Hg^{2+} and Ti^{4+}. The interference from large amounts of Ce^{4+}, U^{6+} and Hg^{2+} can be tolerated by

TABLE 4

Effect of phenylfluorone concentration

Bi(III) : 3.33 ppm

PTPMCHA : 0.1%, 10 ml in $CHCl_3$

Phenylfluorone : 0.01%, in MeOH

Shaking time : 10 min

pH : 5.0

Solvent : $CHCl_3$ + MeOH (3:2)

λ max : 550 nm

Colour of complex: Red

Concentration of phenyl fluorone in ml	Absorbance	Molar absorptivity $l\ mol^{-1} cm^{-1}$	% E
1.0	0.34	2.1×10^4	69.3
1.5	0.37	2.3×10^4	75.4
2.0	0.40	2.5×10^4	81.6
2.5	0.42	2.6×10^4	85.6
3.0	0.49	3.1×10^4	99.9
4.0	0.49	3.1×10^4	99.9

TABLE 5

Effect of cations and anions on the extraction of Bismuth(III)

Bi(III) : 3.33 ppm
PTPMCHA : 10 ml, 0.1% in $CHCl_3$
Phenylfluorone : 4 ml, 0.01%, in MeOH
Shaking time : 10 min

pH : 5.0
Solvent : $CHCl_3$+MeOH (3:2)
λmax : 550 nm
Colour of Complex : Red

Ions	Added as	Amount added (mg)	Absorbance
Ag^{+}	$AgNO_3$	25	0.49
Ba^{2+}	$BaCl_2$	30	0.50
Sr^{2+}	$SrCl_2$	30	0.48
Ca^{2+}	$CaCl_2$	25	0.49
Cu^{2+}	$CuSO_4$	25	0.50
Pb^{2+}	$Pb(NO_3)_2$	25	0.49
Cd^{2+}	$CdSO_4$	25	0.48
Mg^{2+}	$MgSO_4$	25	0.49
Fe^{3+}	$FeCl_3$	25	0.50
Sn^{2+}	$SnCl_2$	25	0.48
Sb^{3+}	$K(SbO)C_4H_4O_6\cdot\frac{1}{2}H_2O$	25	0.49
Hg^{2+*}	$HgCl_2$	20	0.50
Ti^{4+b}	TiO_2	20	0.50
Zr^{4+}	$ZrOCl_2$	20	0.50
Hf^{4+}	$HfOCl_2$	20	0.48
Ce^{4+*}	$(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$	20	0.99
Nb^{5+}	Nb_2O_5	20	0.50
Ta^{5+}	Ta_2O_5	20	0.50
V^{5+}	NH_4VO_3	20	0.50
Mo^{6+}	Na_2MoO_4	25	0.49
U^{6+*}	$UO_2(CH_3COO)_2$	25	0.49
Al^{3+}	$Al(NO_3)_3$	25	0.49
Zn^{2+}	$ZnCl_2$	25	0.49
SO_4^{2-}	Na_2SO_4	30	0.49
Cl^{-}	NaCl	25	0.50
F^{-}	NaF	25	0.50

* Masked with $SnCl_2$. b. Masked with NaF.

masking with tin chloride and Ti^{4+} with sodium fluoride. The data are given in Table 5.

Composition of the complex

The stoichiometry of the complex was determined by the slope ratio method (17). The stoichiometry of Bi-PTPMCHA complex was determined by taking fixed amount of bismuth and gradually increasing the amount of reagent (L_1) keeping the concentration of phenylfluorone constant. The slope of the plot of log D_M vs - log (L_1) was found 3.0, confirms the metal to ligand (PTPMCHA) ratio 1:3.

The stoichiometry of Bi-PTPMCHA-phenylfluorone complex was determined by taking the fixed amount of bismuth solution and PTPMCHA and gradually increasing the amount of phenylfluorone (L_2). The slope of the plot of log D_M vs - log (L_2) was found 1.0; confirms the metal to ligand (phenylfluorone) ratio 1:1. Hence, the overall metal (Bi) to ligand ratio is 1::2:1.

REFERENCES

1. Oehme, O.W.,"Toxicity of Heavy Metals in the Environment, Part II", Marcell Dekkar, New York (1979).
2. Agrawal, Y.K. and Roshania, R.D., Bull. Soc. Chim. Belgs., 89, 159 (1980).
3. Agrawal, Y.K. and Patel, S.A., Rev. Anal. Chem., 4, 237 (1980).
4. Agrawal, Y.K., Rev. Anal. Chem., 5, 3 (1980).
5. Agrawal, Y.K., Anal. Chem., 47, 940 (1975).
6. Agrawal, Y.K., Analyst, 98, 147 (1973).
7. Agrawal, Y.K. and Kapoor, H.L., Ann. Di Chimica, 66, 117 (1976).
8. Agrawal, Y.K., Russ. Chem. Rev., 48, 1773 (1979).
9. Menon, K.S. and Agrawal, Y.K., Analyst, 109, 27 (1984).
10. Fritz, J.S. and Sharma, J., J. Chromatog., 25, 153 (1966).
11. Agrawal, Y.K. and Mehd, G.D., Rev. Anal. Chem., 6, 185 (1983).
12. Das, J. and Shome, S.C., Anal. Chim. Acta, 24, 37 (1961).
13. Chwastowska, J. and Minczewaki, J., Chem. Analz. (Warsaw), 9, 791 (1964).

14. Patke, S.K., Ph. D. Thesis, M.S.University of Baroda, Baroda (1981).

15. Dean, J.A., "Lange's Handbook of Chemistry", 12th ed., McGraw Hill Book Company, New York (1979).

16. Welcher, F.J., "The Analytical Uses of Ethylene diamine tetraacetic acid", D. Van Nostrand (1965).

17. Branko, T. B. and Jerome O.W., Anal. Chem., 45, 1519 (1973).