

Spectrophotometric study of binary system Bi(III)-solochrom violet RS and determination of Bi(III)

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Received 25 October 1996; revised 7 July 1997

A simple and direct spectrophotometric method using solochrom violet RS has been developed for determination of Bi(III). The molar absorptivity and the sandell's sensitivity are calculated to be $1.5 \times 10^4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $0.0114 \mu\text{g}\cdot\text{cm}^{-2}$ respectively. The effect of various parameters including time, pH and added reactant volume have been studied. The Beer's law is obeyed over the range 0.42-7.52 $\mu\text{g/ml}$ of Bi(III). The method has been applied for the determination of Bi(III) in various alloys and salt-water samples.

Several azo compounds, azo derivatives of dialchilaminophenol¹, monoazo derivatives of pyrogallol² and 3,3 diazo derivatives of the chromotropic acid³ have been used for spectrophotometric determination of Bi(III). The present work reports the use of the azo compound solochrom violet RS (sodium salt of 2 hydroxynaphthyl-azo-1 phenol-4- sulphonic acid) for spectrophotometric determination of Bi(III). The method has been used for determination of Bi(III) in some alloy samples.

Experimental

A Mettler delta 320 pH-meter and UV- vis Zeiss Jena spectrophotometer were used for measurement of pH and absorbance. All reagents used were of AR grade. BiCl₃ acid solution (10^{-3} M , $2 \times 10^{-3} \text{ M}$, $3 \times 10^{-3} \text{ M}$) and solochrom violet RS aqueous solution (10^{-3} M , $2 \times 10^{-3} \text{ M}$ and $3 \times 10^{-3} \text{ M}$) were prepared. Buffer solutions with pH ranging from 1.81 to 11.92 were prepared according to Britton- Robinson's method.

General procedure

To a known volume of metal ion solution was added the reagent solution (10 ml) in 25 ml calibrated flasks. The pH was then adjusted to 2.87 with the appropriate buffer. The absorbance was measured at 555 nm against a reagent blank after 5 min.

Results and Discussion

The reaction between the Bi(III) and the azo compound results in formation of a complex. This complex shows an absorption maxima at 555 nm, whereas the reagent absorbed negligibly at this wavelength. The effect of time, reactant, volume, and pH on determination of Bi(III) was studied. The optimum time required for development of colour was found to be 5 min at R.T. The effect of concentration of reagent was examined. For 1 ml solution of Bi(III) 10^{-3} M , 5 ml of solochrom violet RS solution 10^{-3} M was sufficient. The absorbance remained practically constant above this value. The formation of the complex was studied over a wide pH range 1.81-11.92 using Britton Robinson buffer solutions. The result indicates that the absorbance was maximum in the acid domain at pH 2.87.

The composition of the complex Bi(III)-solochrom violet RS was established using Job's method of continuous variation and mole ratio method. The mole ratio was found to be 1:2. The stability constant of the complex was calculated using non-isomolar series method, $K = 3.15 \cdot 10^{-12}$ ($pK = 11.50 \pm 0.28$) for a 95% probability at 25°C temperature and ionic strength $\mu=0.2$. The charge on the complex ion was determined by electrophoretic migration method in the presence of a weak solution of potassium nitrate. After 10 min the coloured complex ion migrated towards the anode indicating the complex ion to be negatively charged. Beer's law was obeyed over the concentration range 0.42-7.52 $\mu\text{g Bi(III)/ml}$. The correlation coefficient, r , having the value of 0.9999 indicates a linear dependence of the absorbance on the Bi(III) concentration. The method proposed for determination of Bi(III) is reproducible and accurate, the relative standard deviation being $\pm 1.1\%$, not affected by systemic errors. The molar absorptivity and the Sandell's sensitivity were calculated to be $1.5 \times 10^4 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $0.0114 \mu\text{g}\cdot\text{cm}^{-2}$ respectively.

Interference studies demonstrated that the colour reaction of Bi- solochrom violet RS is specific. Various cations were added individually to a solution of Bi(III) (10^{-3} M) and the limits of molar ratios at which Bi(III) was recognised were Bi(III): Al(III) = 1:30, Bi(III): In(III) = 1:35, Bi(III):V(V) = 1:33.

Table 1—Determination of Bi(III) in some alloys

Alloy	Composition %	% Bi using S.V.R.S.		% Bi using thiourea	
		% Bi.	% error	% Bi.	% error
Solder alloy (Pb, Sn, Sb)	Pb: 78.95-36.8%	0.25±1.2%	4.8	0.25±2%	8
	Sn: 20-60%				
	Sb: 0.80-2.8%				
	Bi: 0.25-0.40%				
Antifriction Y-Sn 83	Sn: 83±1%	0.09±0.8%	2	0.09±1.8%	8
	Sb: 11±1%				
	Cu: 6±0.5%				
	Pb: max 0.5%				
Printing solder alloy	Pb: 83.88-54.38%	0.12±1.0%	8.33	0.12±1.5%	12.5
	Sb: 11.5-16.5%				
	Sn: 4.5-29%				
	Bi: max. 0.12%				

* Average of 4 determinations.

Bi(III):W(VI) = 1:31, Bi(III):Sb(III) = 1:5 and Bi(III):Sb(V) = 1:5.

Determination of Bi(III) in alloy samples

The proposed method has been used for determination of Bi(III) in steel & alloys, residual waters sea organisms and sediments. The Bi(III) ion in the alloy samples (1g for each one) was taken in solution by HNO₃ and H₂SO₄ disintegration and was spectrophotometrically determined both with solochrom violet RS and in the presence of thiourea^{7,8}. The results are presented in Table 1. Since these alloys contain Sb in concentrations that interfere with the Bi(III) determination, the Bi(III) was separated as Bi₂S₃ and then brought back in solution with conc HNO₃. In determination of Bi(III) with thiourea, lead interfered. Therefore, it was separated before the precipitation with H₂S. A few salt-water samples from some geological formations after passing over an anionic exchange were also analysed. Concentrations determined (the average of four determinations) using both our method and the method with dithizone⁹ were:

Sample No. 1 : 0.058 µg/l ± 1.09% and 0.058 µg/l ± 1%.

Sample No. 2 : 0.085 µg/l ± 1.12% and 0.085 µg/l ± 1.3%.

Sample No. 3 : 0.062 µg/l ± 1.00% and 0.062 µg/l ± 1.2%.

The present method for determination of Bi(III) is more sensitive, selective and simple than the earlier known methods. The sensitivity of the present method is comparable to the other methods⁴⁻⁶.

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