

Extraction-spectrophotometric Determination of Niobium with Thiocyanate and *N*-Hydroxy-*N,N'*-diphenylbenzamidine

NEENA NASHINE and R. K. MISHRA*

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur-492 010

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Various spectrophotometric methods are reported for the determination of niobium¹. These methods suffer from various disadvantages, such as poor sensitivity, dependence of the absorbance of the complex upon the amount of reagents, interelemental interference of common metal ions etc.

In the present investigation, niobium(V) is selectively extracted as thiocyanate complex with *N*-hydroxy-*N,N'*-diphenylbenzamidine (HDPBA) in chloroform in presence of cetyltrimethylammonium bromide (CTAB). The method is found to be free from interference of almost all ions tested except Mo^{VI}. The interference of Mo^{VI} can be removed by prior extraction. Thus the method enables sensitive and selective determination of niobium in environmental samples.

Results and Discussion

The absorption spectrum of Nb^V-SCN⁻-HDPBA complex in presence of CTAB in chloroform shows an absorption maximum at 390 nm. Maximum and complete extraction of the complex in presence of CTAB is achieved with 8.5×10^{-1} to 8.6×10^{-3} M HDPBA at an optimum acidity of 2.5–4.0 M HCl. At least 0.5–1.0 M of ammonium thiocyanate and $(0.9-1.2) \times 10^{-3}$ M CTAB solutions are required for complete extraction and maximum colour development. Of the various solvents used, chloroform was chosen as solvent due to its superiority. A shaking time of 3 min is sufficient for complete extraction of the complex and the complex is stable upto 2 h at room temperature (25°).

The Nb^V-SCN⁻-HDPBA complex obeys Beer's law upto 1.4 $\mu\text{g ml}^{-1}$ of Nb. The molar absorptivity of the complex calculated in terms of Nb^V is $5.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 390 nm. The Sandell's sensitivity of the method is $1.7 \times 10^{-3} \mu\text{g cm}^{-2}$ and relative standard deviation is $\pm 1.2\%$. The detection limit of Nb^V is 0.07 $\mu\text{g ml}^{-1}$.

The effects of diverse ions studied indicate that

large number of ions do not interfere in the present method. However, Fe^{III} and Mo^{VI} interfere as these are co-extracted along with Nb^V. The interference of Fe^{III} can be eliminated by masking with 10% ascorbic acid solution (1 ml). Mo^{VI} is removed by prior extraction by masking Nb^V with NaF (2 ml; 2%), and Nb determined by demasking with boric acid (3.5 ml; 10%). At least 100-fold molar excess of each can then be tolerated. The following diverse ions (amount in mg are given in parenthesis) do not interfere in the determination of 0.7 $\mu\text{g ml}^{-1}$ of Nb^V, Bi^{III} (1.0); Ti^{IV}, W^{VI} (1.5); Ta^V, Re^{VII}, Sb^{III} (2); V^V, Zr^{IV} (3); Cu^{II}, Co^{II} (3.5); Ag^I, Hg^{II} (4); Al^{III}, Cd^{II}, Cr^{III} (5); Ni^{II}, Zn^{II}, Sn^{IV} (10); ascorbic acid (20%), tartarate (15%); and fluoride (5%).

Application : A known amount of solid sample was digested with aqua regia (5 ml) and HF (15 ml). The process was repeated twice and residue was dried. It was then heated to dryness with concentrated HCl (10 ml). The residue was dissolved in dilute HCl and made upto 100 ml with 6 M HCl containing 2% tartaric acid. The amount of Nb^V present in the sample was determined by the proposed method. The data obtained are compared with the classical thiocyanate method and were found to be comparable and satisfactory (Table 1).

TABLE 1—DETERMINATION OF Nb^V IN SAMPLES

| Sample | Nb found by present method % | Nb found by thiocyanate method % | Relative standard deviation of the present method $\pm \%$ |
|---|------------------------------|----------------------------------|--|
| Ferroniobrium (Bhilai Steel Plant, Bhilai) | 49.1 | 49.5 | 1.2 |
| Aluminium slag (Bharat Co. Ltd., Korba) | 0.01 | 0.02 | 1.1 |
| Cassiterite ore (obtained from Dantewara, Marjum) | 0.38 | 0.39 | 1.2 |
| | 1.97 | 2.03 | 1.1 |

Experimental

A Carl-Zeiss-Jena 'Spekol' spectrophotometer equipped was used for the absorbance measurement.

All chemicals used were of A.R. grade (B.D.H. and E. Merck).

The stock solution of Nb^{V} was prepared by dissolving the metal (0.2010 g) in concentrated H_2SO_4 (100 ml) upon heating. The cold solution was diluted to 500 ml with 3 M H_2SO_4 containing 2% (w/v) tartaric acid. The working standard solution was prepared by appropriate dilution with 6 M HCl containing 1% (w/v) tartaric acid.

Solutions of 5.25 M ammonium thiocyanate and 0.003 M cetyltrimethylammonium bromide (CTAB) were prepared in distilled water. A 0.0035 M solution of *N*-hydroxy-*N,N'*-diphenylbenzamidine² (HDPBA) in chloroform was used. A 10 M HCl was employed for extraction work.

Procedure : An aliquot of the solution containing upto 10 μg Nb^{V} was taken and to it ammonium

thiocyanate (2 ml), HCl (3.5 ml) and CTAB (3.5 ml) were added in 10 ml aqueous phase. This was equilibrated by shaking with HDPBA solution (5 ml) for 3 min. The resulting yellowish pink coloured chloroform extract was separated and dried over anhydrous sodium sulphate (~ 2 g). The aqueous phase was washed with fresh chloroform (2 \times 2 ml). The combined chloroform extract after drying was made upto 10 ml with chloroform. The absorbance of the extract was measured at λ_{max} of the complex against the reagent blank.

References

1. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", 3rd. ed., Interscience, New York, 1958; P. G. RAMAPPA and K. S. RAMCHANDARA, *Asian J. Chem.*, 1989, **1**, 19; B. TAMHINA and A. G. IVSIC, *Solvent Extr. Ion Exch.*, 1987, **5**, 909; M. TARASLWICZ, W. MISIUK and T. H. PUZANOWSKA, *Microchem. J.*, 1988, **37**, 36; D. T. BURNS and D. CHIMPAIEU, *Anal. Chim. Acta*, 1988, **204**, 365; X. WANG, W. MA and Z. SHEN, *Fenxi Shiyanshu*, 1987, **6**, 34; J. AZNAREZ, M. P. CIPRES, L. MARCO and A. FERRER, *Analyst*, 1985, **110**, 1329.
2. K. SATYANARAYANA and R. K. MISHRA, *Anal. Chem.*, 1974, **46**, 1609.