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Extraction-Spectrophotometric Determination of Niobium in Steels and Columbite using Metoclopramide and Thiocyanate*

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A method for the spectrophotometric determination of niobium(V) is proposed, in which niobium(V) is extracted into dichloromethane from 2–3 M hydrochloric acid containing potassium thiocyanate and metoclopramide hydrochloride (MCH). The molar absorptivity of the extracted complex is 2.22×10^4 l mol^{-1} cm^{-1} at 385 nm. Beer's law is obeyed over the range 0.5 to 3.5 μg ml^{-1} of Nb(V). The proposed method permits the determination of niobium(V) at trace levels in the presence of large amounts of other ions. The method has been applied to the determination of niobium in steels and columbite or with high accuracy.

INTRODUCTION

Often, the most sensitive reagents for the spectrophotometric determination of inorganic elements are insufficiently selective. However, there are few reagents with high enough selectivity and sensitivity which can be used as both extraction and spectrophotometric reagents. Enhanced knowledge of complex formation in non-aqueous solvents[1] allows extraction to be carried out with a convenient selective reagent into a low polarity solvent such as chloroform, dichloromethane, 1,2-dichloroethane, toluene; the extraction is made simpler if an ion-association complex is formed.

Affsprung and Robinson[2] proposed the tetraphenyl arsonium cation as a counter ion in the extraction of the anionic Nb(V)-thiocyanate complex into chloroform-acetone and later the critical conditions were improved[3]. 1,2,4,6-tetraphenyl pyridinium perchlorate[4] and dibenzo-18-crown-6[5] in the form KL^+ have also been used for the extraction of the Nb(V)-thiocyanate complex.

In this work, metoclopramide hydrochloride (MCH) is used for the spectrophotometric determination of niobium by extraction of the Nb(V)–SCN–MCH ion-association complex into dichloromethane. Investigation of the optimum conditions and the nature of the extracted species has allowed us to establish a new extraction-spectrophotometric procedure for the determination of niobium in steels and columbite.

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EXPERIMENTAL

Apparatus and Reagents

A Beckmann Model DB spectrophotometer with 1 cm matched silica cells was used for the absorptiometric measurements.

Analytical-grade reagents were used unless otherwise specified. Distilled water was used throughout.

Stock Nb(V) solution (500 μg ml^{-1} of Nb(V) was prepared by reaction of specpure Nb_2O_5 (0.1788 g) with potassium hydrogen sulphate (3.0 g) in a platinum crucible and dissolving the product in 10% m/v tartaric acid solution in a 250 ml calibrated flask. An aqueous 20% solution of potassium thiocyanate was prepared daily to prevent thiocyanic acid polymerisation. An aqueous 0.5% solution of MCH was prepared. Solutions of foreign ions were acidified, if necessary, to prevent hydrolysis.

METHODOLOGY

Preparation of Steel Sample Solution

Place a 0.5–1.0 g of steel sample in a beaker and 30 ml of 20% v/v sulphuric acid and 1.5 ml of orthophosphoric acid, gently heat the mixture and add 1 ml of concentrated nitric acid. Evaporate carefully nearly to dryness and then add 2 ml of concentrated sulphuric acid twice, evaporating the mixture nearly to dryness after each addition, allow the beaker to cool. Dissolve the cooled paste by warming it in 10 ml of 10% m/v tartaric acid. Cool the solution and dilute to 250 ml with distilled water in a calibrated flask. Use suitable aliquots of this solution.

Preparation of Ore Sample Solution

Place in a platinum crucible an appropriate amount of finely ground columbite ore (0.5 g). Add a 30 to 40 fold excess of $KHSO_4$ and subject it to dispersion. Allow the crucible to cool, then dissolve the contents in 10 ml. of 10% m/v tartaric acid. Dilute the solution to 100 ml with distilled water. Use suitable aliquots of this solution.

Extraction of Niobium

Take an aliquot of the stock solution containing 5.0–35.0 μg of Nb(V), in a 100 ml separatory funnel. Add to it 6 ml of 20% potassium thiocyanate, 5 ml of 0.5% aqueous MCH and 5 ml of 10 M hydrochloric acid. Make up the volume of the aqueous phase upto 25 ml with distilled water to make the acid strength 2.0 M. After 2 min. shake the contents of the separatory funnel with 5 ml of distilled dichloromethane for about 3 min. and allow the phases to separate. Recover the yellow dichloromethane layer in a 10 ml standard flask and make up to the mark with distilled dichloromethane. Dry the extract over anhydrous Na_2SO_4 and measure the absorbance at 385 nm against a similarly processed reagent blank.

Calculate the amount of the metal extracted by referring the absorbance to the calibration curve.

RESULTS AND DISCUSSION

Solvent for Extraction and Spectral Characteristics of the Complex

The absorption spectra of the extracted ion-association complex [Nb(V)–SCN^-–MCH^+] and the reagent blank show that the maximum absorbance of the complex in dichloromethane occurs at 385 nm. At this wavelength, the absorbance of the regent blank was very small. Among the several solvents tried, viz., benzene, toluene, o-xylene, o-dichlorobenzene, isoamylalcohol, iso-butanol, carbon tetrachloride, dichloromethane and chloroform, the dichloromethane was found to be the most suitable, giving quantitative extraction readily and providing higher sensitivity for the colour reaction than the other solvents. Under the optimum concentrations of acid, thiocyanate and MCH, 3 min. of shaking was adequate for the quantitative extraction of niobium. A single extraction with dichloromethane was sufficient to remove all Nb(V).

Effect of Experimental Variables

The effect of KSCN and MCH on the extraction of Nb(V) was studied. It can be seen that 6–15 ml of 20% KSCN and 5–12 ml of 0.5% aqueous MCH were required for the maximum recovery of Nb. The addition of more than 15 ml or 20% KSCN and 12 ml of 0.5% MCH were ineffective with respect to complete recovery of Nb(V). At volumes less than 6 and 5 ml of KSCN and MCH, respectively, the extraction of Nb(V) was not quantitative. Hence 6 ml of KSCN and 5 ml of MCH were used in subsequent work. The order in which the reagents are mixed is not critical but owing to hydrolysis of the metal ion at higher pH the dilution must be made after addition of HCl and KSCN.

The effect of hydrochloric acid on the extraction of Nb was investigated by taking 20 μg of Nb(V), 6 ml of 20% KSCN, 5 ml of 0.5% MCH and varying the volume of 10 M HCl. The results indicate that optimum acid range is 0.8–2.8 M. Outside this range the absorbance readings are low. Hence 2.0 M HCl concentration was maintained in all further work.

The wavelength of maximum absorption and the absorbance of the coloured extract was not affected by changes in ionic strength between 0.1 and 1.0 M with respect to sodium chloride and potassium nitrate. Variation in temperature between 20 and 40°C did not affect the absorbance values. The volume of the aqueous phase could be varied from 10 to 100 ml, with a 10 ml organic phase without any adverse effect on extraction efficiency.

Molar Absorptivity, Sensitivity, Beer's Law Range and Precision

The molar absorptivity and photometric sensitivity for the yellow ion-association complex at 385 nm are 2.22×10^4 l mol^{-1} cm^{-1} and 0.002 μg cm^{-2} of Nb(V) respectively. The system obeys Beer's law in the concentration range 0.5–3.5 μg ml^{-1}. The optimum concentration range for determination evaluated from Ringbom plot is 0.8–3.2 μg ml^{-1}.

The precision of the method was evaluated from ten separate evaluations on sample containing 2 mg l^{-1} of Nb. The relative standard deviation was 0.5%.

Effect of Foreign Ions

The effect of several elements most frequently associated with niobium in steels and ores was studied. The tolerance limits in the determination of 20 μg of Nb(V) are shown in Table 1. Molybdenum interferes seriously, therefore, it was removed by prior extraction using MCH and SCN$^-$ as extractants in the presence of ascorbic acid, while masking Nb(V) with NaF. Niobium was determined by demasking F$^-$ with boric acid. Large amounts of Fe(III) interfere and to avoid it the following procedure was used.

To a portion of the sample solution containing 20 μg of Nb(V) in a 100 ml separatory funnel, 5 ml of concentrated HCl was added and

TABLE 1

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 20 μg OF Nb(V) WITH MCH AND KSCN

Foreign ion	Tolerance limit[a]/μg Without masking agent	With masking agent	Masking agent
Ni(II), Mn(II), Cd(II), Ca(II), La(III), Ce(III), U(VI), Mg(II), Zr(IV), Th(IV), Zn(II), Fe(II), Al(III), NO_3^-, PO_4^{-3}	2500	—	—
Cr(III), Co(II)	150	—	—
Fe(III)	100	2000	10% m/v ascorbic acid
Fe(III)	100	20000	Extract with IBMK.
F$^-$	250	—	—
Ta(V), Cu(II), V(V), Sb(III)	150	200	10% m/v tartaric acid
Ti(IV), Mo(VI), Sn(IV), Sn(II)	6	50	0.01% m/v NaF[b]

[a] Amount causing an error not exceeding 2% in the absorbance of 20 μg of Nb(V).
[b] Fluoride ions in excess must be at a concentration less than the above tolerance limit (250 μg).

extracted with 10 ml of isobutylmethylketone (IBMK) with mechanical shaking for 3 min. After leaving the phases to separate, the organic phase was discarded. Niobium was extracted with dichloromethane as outlined in the above procedure and measured the absorbance of the extract at 385 nm against reagent blank.

The tolerance limit for Ta(V) was about ten times the amount of Nb(V) and hence the method can be applied to the determination of Nb(V) in ores such as columbite.

Composition of the Ion-association Complex

The stoichiometry of the complex was investigated by Job's method of continuous variations, mole ratio method and equilibrium shift method. A 1 : 1 molar ratio of MCH^+ to Nb(V) was found. The equilibrium shift method gave a ratio of 1 : 3 for Nb(V) to SCN^- which is in agreement with the anionic complexes of Nb(V) and thiocyanate reported[4] as $NbOX(SCN)_3^-$. Hence the ion-association complex corresponds to $NbOCl(SCN)_3^-MCH^+$.

Application of the Method

The sample solutions of steels and columbite ore were prepared as described before. An aliquot of the sample solution containing up to 20 μg Nb(V) was transferred into a 100 ml separatory funnel.10M HCl was added to bring the solution to 5M HCl and Fe(III) was extracted with 10 ml of IBMK by mechanical shaking for 3 min. Discarding the organic phase, the aqueous phase was subjected to the procedure for the extraction of Nb(V) described above and the absorbance was measured.

The method has been applied to the determination of Nb(V) in columbite, standard steel (BCS), special stainless steel, mild steel (MBH Reference Materials, England) and the results obtained are presented in Table 2.

TABLE 2

RESULTS OF THE DETERMINATION OF NIOBIUM IN STEELS AND COLUMBITE

Sample	Niobium concentration %		Relative standard deviation %
	Certified	Found[a]	
13×12731, 18/8 stainless steel[b]	1.10	1.095	1.4
13×14216, special stainless steel[b]	0.25	0.248	0.8
BCS 457 mild steel...	0.016	0.015	1.4
BCS 261/1 columbite...	0.91	0.91	1.2
Columbite	24.4	24.37	1.7

[a] Average value and relative standard deviation for eight replicate determinations.

[b] MBH Reference Materials, England.

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