

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM(V) USING N-4-CHLOROPHENYLCINNAMOHYDROXAMIC ACID AND THIOCYANATE

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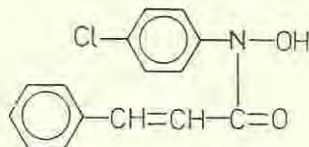
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ABSTRACT. Niobium(V) has been found to react with N-4-chlorophenylcinnamohydroxamic acid (CPCCHA) and thiocyanate to form a golden yellow mixed ligand complex which is quantitatively extractable into chloroform from 3.5 - 6.5 M hydrochloric acid solutions. The complex exhibited a wavelength of maximum absorption at 368 nm with a molar absorptivity of $4.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and the system obeyed Beer's law in the concentration range of 0.12 - 2.73 ppm of niobium. The composition of the complex has been established spectrophotometrically to be 1:1:2 (Nb:SCN⁻:CPCCHA). The effects of diverse ions and of several other experimental variables have been studied to establish the optimum condition for extraction and determination of niobium. On the basis of these studies a simple, precise, sensitive, and a highly selective method has been developed for the determination of niobium(V) by solvent extraction and spectrophotometry. The method has been successfully applied to the determination of niobium in two columbite-tantalite ores and in several synthetic samples corresponding to niobium containing ores, minerals, and alloys.

INTRODUCTION

N-Arylhydroxamic acids have been used as analytical reagents for several metal ions (1,2). These reagents have also been applied for the gravimetric (3,4) and spectrophotometric determination of niobium(V) (4,5). When the niobium(V) hydroxamates are complexed with either thiocyanate or a chromogenic reagent, the sensitivity of determination is further improved coupled with bathochromic shift (6,7) due to mixed ligand complex formation.

One of analytically useful hydroxamic acid analogues is N-4-chlorophenylcinnamohydroxamic acid, CPCCHA (1). This reagent has not been widely applied



to the spectrophotometric investigation of metal ions since its synthesis for the first time in 1969 (8). CPCCHA has been tested for the determination of vanadium (9) and used for the determination of cerium(10). Except these trials, no attempt has been made to exploit the analytical potentiality of CPCCHA in general, and no report has appeared in literature on the use of this reagent for niobium, in particular. Hence, in the present investigation, the reaction of niobium(V) with CPCCHA in presence of thiocyanate in concentrated

hydrochloric acid medium has been studied. The investigation has led to the development of a new, simple, precise, sensitive and highly selective method for the determination of niobium(V) with CPCHA and thiocyanate from hydrochloric acid solutions by solvent extraction-spectrophotometry. The reliability of the proposed method has been ascertained by determining niobium contents of two Ethiopian columbite-tantalite ores and of several synthetic samples.

EXPERIMENTAL

Equipment. A Beckman Medel 24 UV-Visible spectrophotometer equipped with a Beckman recorder and matched 1-cm quartz cells was used for recording the absorption spectra and absorbance measurements.

Standard niobium(V) solution. The solution was prepared by fusing 0.1439 g of niobium pentoxide (Johnson & Mathey, 99%) with 3.6 g of potassium pyrosulphate (Riedel-de Haen) in silica crucible (11). The cooled melt was dissolved in 100 ml of 20% (w/v) tartaric acid (BDH) solution by heating over sand bath. The solution was cooled, transferred to a 1 litre volumetric flask, and diluted to volume with water. The solution was standardized spectrophotometrically (7).

Reagents and solutions. CPCHA was prepared by the condensation of N-4-chloro-phenylhydroxylamine with cinnamoyl chloride at $\sim 0^\circ\text{C}$ in diethylether made alkaline with an aqueous suspension of sodium bicarbonate (8). The product was characterized by melting point and UV; m.p. 193°C , reported (10) 187°C ; UV: $\lambda_{\text{max}}(\text{ethanol}) = 297 \text{ nm}$, $\epsilon_{\text{max}} = 2.44 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, reported (12) for N-phenylcinnamohydroxamic acid, $\lambda_{\text{max}}(\text{ethanol}) = 292 \text{ nm}$, $\epsilon_{\text{max}} = 2.26 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

A 0.005 M stock solution of CPCHA was prepared by dissolving a weighed amount of CPCHA in chloroform by gentle heating and diluting to volume with chloroform.

A 5 M standard solution of potassium thiocyanate (Riedel-de Haen) was prepared by dissolving the appropriate amount of the salt in distilled water and standardized by the Volhard's method (13).

A 40% (w/v) stannous chloride solution was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (BDH) in hot concentrated hydrochloric acid (Riedel-de Haen). Fresh solutions of stannous chloride were prepared every week.

Solid magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (BDH) was used to study the effect of the concentration of chloride ions in the aqueous phase.

Solutions of diverse ions. Solution of Ta(V), 1 mg ml^{-1} , was prepared by fusing 0.1221 g Ta_2O_5 (Johnson & Mathey) with 5 g $\text{K}_2\text{S}_2\text{O}_7$, leaching the cool melt with 20 ml of 10% (w/v) tartaric acid and diluting the solution to 100 ml with 15 N H_2SO_4 .

Solution of Ti(IV), 2.4 mg ml^{-1} , was prepared by fusing 0.4 g TiO_2 (BDH) with 4 g KHSO_4 (BDH), leaching the cool melt with 10% (v/v) sulphuric acid and diluting the solution to 100 ml with 10% (v/v) H_2SO_4 .

Rhenium(VII) solution was prepared by dissolving the metal (SPEX) in cold concentrated HNO_3 . The solution was evaporated almost to dryness and residue was dissolved in distilled water to yield 1 mg ml^{-1} Re(VII).

Solutions of Ga(III), 2.5 mg ml^{-1} , Zr(IV), 10 mg ml^{-1} , and Pd(II), 1 mg ml^{-1} , were prepared by dissolving Ga metal (BDH), ZrCl_4 (BDH), and PdCl_2 (SPEX) in cold concentrated HCl, respectively; while solution of Er(III), 2.5 mg ml^{-1} , was prepared by dissolving Er_2O_3 (May & Baker) in hot concentrated HCl.

Solutions of Hg(II), 5 mg ml^{-1} , Cu(II), 5 mg ml^{-1} , and Mn(II), 10 mg ml^{-1} , were prepared by dissolving the respective chloride salts (Riedel-de Haen or BDH) in distilled water. Solution of Pt(IV), 1 mg ml^{-1} , was prepared by diluting 5% (w/w) solution of PtCl_4 (SPEX) with 3 M HCl.

Solutions of Ca(II), Ba(II), Cd(II), Mg(II), Zn(II), Pb(II), Ni(II), Co(II), Sr(II), Y(III), U(VI), La(III), Fe(III), Al(III), Bi(III), Cr(III), Th(IV), Be(II), Tl(I), Ag(I), Li(I), Na(I), Ce(IV), and Rh(III) were prepared by dissolving the respective nitrate salts in distilled water to give 5, 10 or 20 mg ml⁻¹ of the ion in solution.

Tungstate, vanadate, molybdate, acetate, borate, antimony tartrate, arsenate, nitrate, sulphate, fluoride, EDTA, and dichromate solutions were prepared by dissolving sodium, potassium or ammonium salts (BDH or Riedel-de Hean) in distilled water to give 1, 5, 10 or 20 mg ml⁻¹ of the ion in solution.

Solutions of tartaric acid, 100 mg ml⁻¹, oxalic acid (Readel-de Hean), 10 mg ml⁻¹, ascorbic acid (BDH), 100 mg ml⁻¹, boric acid (May & Baker), 20 mg ml⁻¹, and thiourea (Hopkin & Williams), 50 mg ml⁻¹, were prepared by dissolving the solid compounds in distilled water.

Solvents. Chloroform was purified (14) every two days and distilled twice before use. All other solvents were used after a single distillation.

General procedure. An aliquot of the solutions containing 2 to 60 µg of Nb(V) was transferred into a 100 ml separatory funnel. Solutions of concentrated HCl and 40% (w/v) SnCl₂ (5 and 1 ml, respectively) were added and the volume of the aqueous phase was made to 10.8 ml with distilled water. A 1.2 ml aliquot of 5 M KSCN was added to the solution and mixed thoroughly. The aqueous phase was extracted with 10 ml of 5 x 10⁻⁴ M chloroform solution of CPCHA for 4 - 5 min. The chloroform phase was collected in a 50 ml beaker containing about 2 g of anhydrous sodium sulphate and stirred with a glass rod. The aqueous phase was washed twice with 5 ml portions of chloroform. The extracts were dried and transferred into a 25 ml volumetric flask and diluted to volume with chloroform. The absorbance of the coloured solution was measured at 368 nm against reagent blank.

Procedure for samples. Accurately weighed 0.2g of a well powdered columbite-tantalite ore samples was intimately mixed with 0.5 g of K₂CO₃ and 0.5 g of KNO₃ (2:5:5 weight ratio) in a platinum crucible. The mixture was fused in a muffle furnace at 740-760°C for 15 min. The fused melt was cooled to room temperature and treated with 25 ml of concentrated sulphuric acid. The extract was quantitatively transferred to a 300 ml Kjeldhal flask, evaporated to dryness, and cooled. The residue was dissolved in 80 ml of 25% (w/v) tartaric acid by heating and stirring. The solution was quantitatively transferred to a 100 ml volumetric flask and made up to volume with 5 M sulphuric acid (15,16). A 5 ml aliquot of the solution was diluted to 50 ml with sufficient quantities of 20% (w/v) tartaric acid and concentrated hydrochloric acid to give the final solution that was 2% (w/v) with respect to tartaric acid and 1 M with respect to hydrochloric acid. This solution was used for the analysis.

Stock solutions of synthetic samples of desired composition were prepared by mixing known quantities of the solution of different ions. The solutions were diluted to known volumes (50 ml each) with sufficient quantities of 20% (w/v) tartaric acid and concentrated hydrochloric acid to give the final solutions that were 2% (w/v) with respect to tartaric acid and 1 M with respect to hydrochloric acid. These solutions were used for the analysis.

The niobium content of the sample solutions were determined by the general procedure. For calibration curve, 0.20, 0.40, 0.60, 0.80, and 1.00 ml of 50 µg ml⁻¹ Nb(V) solution were used through the general procedure.

RESULTS AND DISCUSSION

Colour reaction and absorption spectra. Nb(V) was found to react with CPCHA in 7 - 8 M hydrochloric acid medium to give a pale yellow complex extractable into chloroform. The absorption spectrum of the Nb(V)-CPCHA complex

exhibited an intense absorption band at 353 nm with molar extinction coefficient of $3.67 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. 1).

When Nb(V) was extracted with chloroform solution of CPCHA from 3.5- 6.5 M hydrochloric acid medium in presence of stannous chloride and potassium thiocyanate, a golden yellow complex was obtained indicating the formation of a mixed ligand complex. The absorption spectrum of the Nb(V)-SCN-CPCHA complex exhibited an intense absorption band at 368 nm with molar absorption coefficient of $4.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. 1). Thus, the formation of a mixed ligand complex was accompanied by hyper and bathochromic shifts. This colour reaction formed the basis for the development of a new spectrophotometric method for the determination of niobium(V).

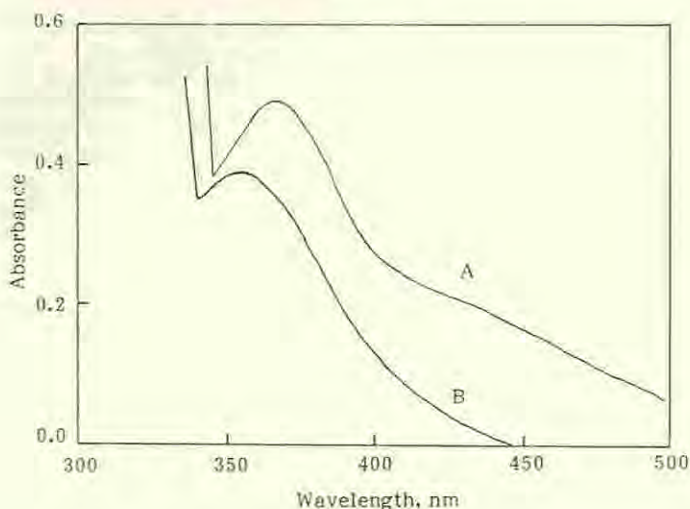


Fig. 1. Absorption spectra of (A) $1.05 \times 10^{-5} \text{ M}$ Nb(V)-SCN-CPCHA and (B) $1.05 \times 10^{-5} \text{ M}$ Nb(V)-CPCHA complexes against reagent blank.

Stannous chloride, which was added to stabilize thiocyanic acid in hydrochloric acid solutions (17), has been found to have no effect on both the position and intensity of the absorption band.

The absorption spectrum of CPCHA in chloroform exhibited practically no absorption between 700 and 400 nm and strong absorption below 400 nm. The absorption spectrum of CPCHA in ethanol has also been recorded and showed an intense absorption band at 297 nm with molar absorptivity of $2.44 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Therefore every measurement has been made against a reagent blank.

Several organic solvents, such as, 1-hexanol, amyl alcohol, amyl acetate, chloroform, carbon tetrachloride, benzene, toluene, xylene, chlorobenzene, and 1,2-dichlorobenzene were examined for the quantitative extraction of Nb(V)-SCN-CPCHA complex by following a two step extraction procedure (7). Esters and alcohols were found to be not suitable in that they have been found miscible with the strongly acidic aqueous phase, probably due to the hydrolysis and protonation of the solvents, respectively. Chlorobenzene was not suitable solvent for the extraction because it exhibited slow phase separation, perhaps due to its relatively similar density to the acidic aqueous phase. Benzene, toluene, and carbon tetrachloride gave low absorbance values. Chloroform,

1,2-dichlorobenzene, and xylene were found to be the most effective solvents for the extraction of the complex. Of these solvents chloroform was chosen because it allowed complete extraction with rapid phase separation in one step extraction due to the higher solubility of the reagent in it than in the other solvents.

Effect of acidity. The effect of common mineral acids such as, HNO_3 , H_3PO_4 , H_2SO_4 , and HCl on the extraction of the complex has been studied. Nitric acid has resulted in the decomposition of the complex whereas sulphuric acid and phosphoric acid were found to have bleaching effect as reported (18). Only HCl was found to be adequate for rapid and complete extraction of Nb(V) as the mixed ligand complex.

The optimum acidity range of the aqueous phase for the quantitative extraction of the complex has been found to be 3.5 - 6.5 M HCl (Fig. 2). At lower acidities low absorbance values were obtained due to incomplete extraction, while at higher acidities, again low absorbance values were observed as a result of precipitate formation. The precipitate formation is probably due to the limited solubility of KCl and/or KSCN in the aqueous phase with high salt concentration

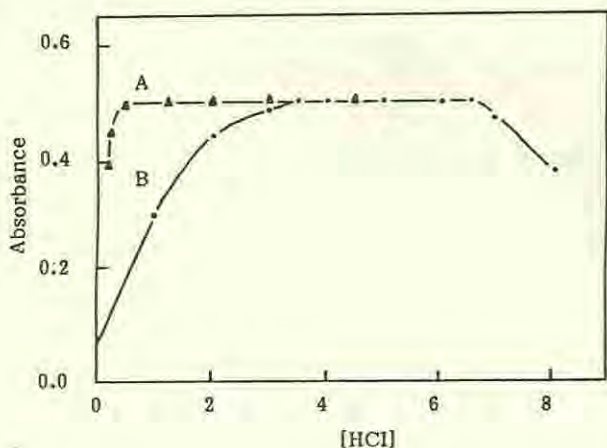


Fig. 2. Effect of HCl concentration of the aqueous phase on the extraction and determination of $24.4 \mu\text{g Nb(V)}$ (A) at 5 M chloride ion and (B) without any added chloride ion.

Effect of chloride ion concentration. The fact that the addition of HCl increases both the acidity and the chloride ion concentration necessitated the study of the effect of chloride ion concentration independently of HCl . The investigation was carried out by holding the HCl concentration constant while varying the chloride ion concentration up to 8 M by the addition of MgCl_2 . The results are shown in Fig. 3. It was found that in the absence of HCl in the aqueous phase, the degree of extraction of the metal was incomplete even at 8 M chloride level, while at 1.2 M HCl , a minimum of 2.5 M chloride was required for the complete extraction of Nb(V) . Excess chloride has been found to have no effect on the extraction of Nb(V) up to 7 M of total chloride, beyond this precipitation occurred in the aqueous phase resulting in a decrease in the degree of extraction of the metal.

A similar study was carried out to determine the minimum acid concentration required for complete extraction of Nb(V) at constant concentration of chloride

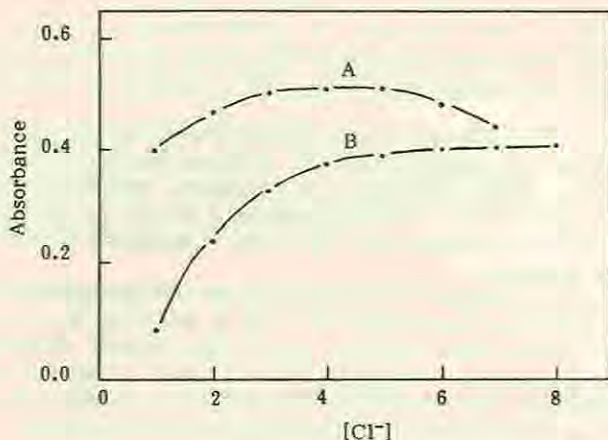


Fig. 3. Effect of chloride ion concentration on the extraction of 24.4 μg Nb(V) at (A) 1.2 M HCl and (B) 0.0 M HCl.

ions. Results obtained (Fig. 2) show that at 5 M chloride level the minimum concentration of the acid, as HCl, for the quantitative extraction of Nb(V) was found to be 0.4 M.

Thus, it appears that both the free acid and chloride ion profoundly influence the degree of extraction of the complex and their concentrations must be controlled carefully. Hence hydrochloric acid was found to be the most effective reagent as source of both H^+ and Cl^- ions.

Effect of thiocyanate. The effect of the concentration of thiocyanate ion on the extraction and determination of Nb(V) has been studied over a wide range. The optimum thiocyanate concentration for the quantitative extraction of Nb(V)-SCN-CPCHA complex ranged from 0.1 to 1.5 M with respect to potassium thiocyanate. At lower thiocyanate concentrations, the absorbance decreased due to the incomplete formation of the mixed ligand complex, while at higher concentrations of thiocyanate, formation of the complex was retarded resulting in decreased absorbance values.

Effect of the concentration of stannous chloride. Stannous chloride required for stabilizing the thiocyanic acid in HCl medium (17) was found to have no adverse effect up to 0.22 M, higher concentrations resulted in low absorbance values due to precipitation of salts in the aqueous phase.

Effect of the amount of CPCHA. A 1 to 8 molar ratio of the metal to the ligand, CPCHA, was found to be necessary for the complete extraction of Nb(V) as Nb(V)-SCN-CPCHA complex. A 100-fold molar excess of the ligand, CPCHA, has been found to have no adverse effect on the extraction of the complex. Nevertheless, a large excess of the reagent resulted in an unwanted high absorbance value of the blank which caused difficulties in zero adjustment of the instrument. In practice a 20-30 fold molar excess of CPCHA was used.

Effect of the volume of the aqueous phase. It has been found that the volume of the aqueous phase can be varied from 10 to 50 ml with respect to a fixed volume of 10 ml of the organic phase without any significant variation in the absorbance or extraction efficiency of Nb(V)-SCN-CPCHA complex. However, more repetitive extractions were necessary for the complete extraction of Nb(V) from larger volumes of the aqueous phase.

Extraction time and stability of the complex. The coloured Nb(V)-SCN-CPCHA complex required 4 - 5 min shaking time for complete extraction. The stability of the complex was studied by storing the solutions in a cool dark place. Exposure to laboratory fluorescent light or diffuse day light at intervals of measurement has been found to have no effect. The complex was stable for 52 h at room temperature. After 52 h the absorbance values were found to decrease with time, which may be due to the decomposition of the extracting solvent chloroform (14) or the complex or both.

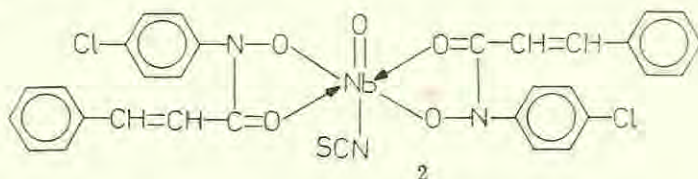
Stoichiometry of the complex. The stoichiometry of the complex was determined by different spectrophotometric methods. The continuous variations (19, 20) and the mole ratio (21) methods were employed to determine the ratio of Nb(V) to CPCHA while the ratio of Nb(V) to SCN⁻ was determined by the extraction method (22). In the continuous variation method the maximum absorbance for the complex was observed at the mole fraction of 0.33 of Nb(V), which corresponds to a 1:2 ratio of Nb(V) to CPCHA.

The result of the continuous variations method was supported by the result of the mole ratio method which also gave a 1:2 ratio of the Nb(V) to CPCHA.

The ratio of Nb(V) to thiocyanate was determined by the extraction method (22) in which the quantity $\log [A/(A_{\max} - A)]$ was plotted against $\log [\text{SCN}^-]$, where A is the absorbance at an equilibrium concentration of thiocyanate and A_{\max} is the absorbance at optimum concentration of thiocyanate. The plot yielded a slope of 1.14 which indicates the ratio of Nb(V) to SCN⁻ to be 1:1 in the Nb(V)-SCN-CPCHA system.

Thus, the overall stoichiometry of the Nb(V)-SCN-CPCHA complex has been established as 1:1:2 (Nb:SCN⁻:CPCHA). This result is in agreement with the compositions reported (6,23) for Nb(V) complexes with some other hydroxamic acids.

From the extractability of the complex into a non-polar solvent, consideration of the presence of Nb=O group (6,11,23-25), and the stoichiometry, structure 2 is proposed for the complex:



Evaluation of photometric parameters. The concentration range obeyed by Beer's law has been determined and the optimum concentration range in which photometric analysis error is minimum has been evaluated from the Ringbom's plot (26).

The molar absorptivity, the sensitivity of the method (27), the limit of determination (28), and the precision of the method as determined from the relative standard deviation of six measurements are summarized in Table 1.

In general, the data in Table 1 show that the method is highly sensitive and reproducible and can be applied to the analysis of niobium at trace levels.

Effect of diverse ions. The effects of diverse ions on the extraction and determination of Nb(V) have been investigated to evaluate the selectivity of the proposed method by adding known quantities of the desired ion to a solution containing 20 μg of Nb(V). The extraction and determination of the metal ions were made according to the general procedure described earlier. The tolerance limit of diverse ions which cause an error less than 2% are given in Table 2.

Table 1. Photometric characteristics of the complex.

λ_{\max} , nm	368
ϵ_{\max} , $M^{-1} \text{ cm}^{-1}$	4.75×10^4
Sensitivity, $\mu\text{g cm}^{-2} \text{ Nb(V)}$	1.96×10^{-3}
Concentration range from Beer's law, $\mu\text{g ml}^{-1} \text{ Nb(V)}$	0.12 - 2.73
Optimum concentration range from Ringbom's plot, $\mu\text{g ml}^{-1} \text{ Nb(V)}$	0.13 - 1.76
Limit of determination, $\mu\text{g ml}^{-1} \text{ Nb(V)}$	0.02
Relative standard deviation, (n = 6), %	0.95

Table 2. Tolerance limit of diverse ions in the determination of 20 $\mu\text{g Nb(V)}$.

Ion	Tolerance limit, μg	Direction of interference
Fe^{3+}	80	*
Na^+ , K^+ , Li^+ , Be^{2+} , Ca^{2+} , Mg^{2+}		
Ba^{2+} , Sr^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+}		
Mn^{2+} , Pb^{2+} , Cr^{3+} , Ce^{4+} , Th^{4+}	20 each	*
UO_2^{2+} , La^{3+}	16 each	a
Al^{3+}	12	b
Tl^+	10	a
Co^{2+}	5	b
Hg^{2+}	5	a
Ga^{3+} , Y^{3+} , Er^{3+}	5 each	*
Rh^{3+}	4	b
Ag^+	2.5	a
Bi^{3+}	1.5	b
Pd^{2+}	1	b
Cu^{2+} , Pt^{4+}	1 each	a
Re^{7+}	0.05	b
Ta^{5+}	0.4	a
Ti^{4+} , Zr^{4+}	≤ 0.01 each	b
$\text{B}_4\text{O}_7^{2-}$, AsO_4^{3-} , $\text{Cr}_2\text{O}_7^{2-}$		
$\text{SbOC}_4\text{H}_4\text{O}_6^-$	20 each	*
MoO_4^{2-}	10	b
VO_3^-	2	a
WO_4^{2-}	1	b
Sulphate	20	*
Acetate	20	*
Nitrate	100	*
Perchlorate	200	*
EDTA	200	*
Citrate	100	*
Oxalate	10	a
Fluoride	1.5	a
Ascorbic acid	300	*
Tartaric acid	300	*
Phosphoric acid	200	a
Boric acid	60	*
Thiourea	200	*
Fluoroboric acid	30	a

* Not studied beyond the indicated level.

a Amount more than the tolerance limit results in negative interference.

b Amount more than the tolerance limit results in positive interference.

These results indicate that most of the common ions which are normally associated with niobium in minerals, ores, and alloys do not interfere up to 50 times to the weight of niobium by the proposed method. Since the amount of diverse ions that are associated with Nb(V) does not exceed the tolerance limits, in most cases, the proposed method for niobium can be applied to the analysis of minerals, ores and alloys.

Application. The analytical potentialities of the newly developed method have been assessed by applying the method to the determination of niobium in two Ethiopian columbite-tantalite ores which were collected from the Ethiopian Institute of Geological Surveys (EIGS). The experimental values (Table 3) are in good agreement with the certified values indicating the accuracy of the proposed method.

Table 3. Determination of niobium in Ethiopian columbite tantalite ores.

EIGS sample No.	Nb ₂ O ₅ certified (%)	Nb ₂ O ₅ *found (%)	RSD (%)
334101	31.00	30.85	1.05
334107	20.50	20.58	1.24

* Average of three determinations.

The proposed method has also been applied to the determination of niobium in several synthetic samples with compositions similar to minerals, ores and alloys containing niobium. The composition of the samples, the amount of niobium recovered and the relative standard deviation (RSD) are given in Table 4. These results indicate that the newly developed method is precise and reliable for the determination of niobium at trace levels in diverse samples.

Table 4. Determination of niobium in synthetic matrices.

Sample	Composition	Nb found* (µg)	RSD (%)
Matrix A	15 µg Nb ⁵⁺ + 15 mg Fe ³⁺ + 2 mg Cr ³⁺ + 2 mg Ni ²⁺ + 2 mg PO ₄ ³⁻ + 0.5 mg Co ²⁺ + 0.5 mg V ⁵⁺	15.01	1.21
Matrix B	20 µg Nb ⁵⁺ + 3 mg Mn ²⁺ + 3 mg Cr ³⁺ + 2 mg Ni ²⁺ + 1 mg Al ³⁺ + 2 mg PO ₄ ³⁻ + 0.4 mg Ta ⁵⁺ + 1 mg Pd ²⁺	20.00	1.27
Matrix C	25 µg Nb ⁵⁺ + 10 mg Fe ³⁺ + 3 mg Ni ²⁺ + 1 mg Cr ³⁺ + 2 mg AsO ₄ ³⁻ + 0.75 mg W ⁶⁺ + 0.25 mg Re ⁷⁺	25.02	1.04
Matrix D	30 µg Nb ⁵⁺ + 12 mg Fe ³⁺ + 2 mg Ni ²⁺ + 1 mg Al ³⁺ + 1 mg Co ²⁺ + 9.6 µg Ti ⁴⁺ + 0.4 mg Ta ⁵⁺	29.96	0.84
Matrix E	19.5 µg Nb ⁵⁺ + 5 mg Ca ²⁺ + 7.5 mg Na ⁺ + 38 µg Ta ⁵⁺ + 0.65 mg F ⁻	19.50	1.07
Matrix F	19.5 µg Nb ⁵⁺ + 5 mg Y ³⁺ + 2.5 mg Er ³⁺ + 5 mg Ce ⁴⁺ + 5 mg La ³⁺ + 8 mg U ⁶⁺ + 48 µg Ta ⁵⁺	19.46	1.18
Matrix G	24.4 µg Nb ⁵⁺ + 5 mg Y ³⁺ + 10 mg U ⁶⁺ + 15 mg Fe ³⁺ + 10 mg Th ⁴⁺ + 48 µg Ta ⁵⁺	24.38	0.78

* Average of five determinations.

Comparison with other spectrophotometric methods. A comparative study of the analytical characteristics of the proposed method and other spectrophotometric methods has been made. The data summarised in Table 5 clearly show that the proposed method is more sensitive than most of the other methods, while the stability of the complex and selectivity of the proposed method are better than the others, in particular to those which are more sensitive than the proposed method. Furthermore, the proposed method is free from the rigid control of experimental variables and can be applied to the analysis of diverse samples for niobium without using any masking reagent or prior separation of any constituent.

Table 5. Comparison of analytical characteristics of the proposed method with other methods.

No.	Reagents	λ_{\max} nm	ϵ M ⁻¹ cm ⁻¹	Acidity or pH	Interference	Stability of complex h	Ref.
1	N-Phenylbenzohydroxamic acid and thiocyanate	365	32000	9-12 M HCl	Ta(V), H ₂ O ₂ ^a	1	7
2	N-3-Tolyl-4-methoxybenzohydroxamic acid and thiocyanate	360	31200	8 M HCl	Ti(IV), Mo(VI), W(VI), V(V), Sn(II), F ⁻	30	6
3	N-4-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid	380	63000	8-10 M HCl	Ti(IV), Zr(IV) both ^b	24	23
4	Ethylene-bis-(triphenylphosphonium) ion and thiocyanate	393	31000	1-4 M HCl	Fe(III), Mo(VI), Cu(II), Zn(II), W(VI), Zr(IV), V(V) each ^c	8	25
5	Bromopyrogallol red and hexadecylpyridinium bromide	635	141000	pH 6.5-7.0	several metal ions ^b	-	29
6	Bis-(salicylohydrazone)	495	19000	conc. HCl	Ti(IV), Zr(IV), Ta(V)	24	30
7	1,2,4,6-Tetraphenylpyridinium perchlorate and thiocyanate	395	28200	4-6 M HCl	Fe(III) ^c	-	31
8	N,N'-Diphenylbenzimidine and thiocyanate	400	34000	1.5-4.0 M HCl	Co, Ti, Re, W, Mo ^c , Cu ^d	10	32
9	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	610	51000	H ₃ PO ₄	several metal ions ^b	-	33
10	N-4-Chlorophenylcinnamohydroxamic acid and thiocyanate	368	47500	3.5-6.5 M HCl	Ti(IV) and Zr(IV) each > 10 μ g	52	proposed method

^aDestroyed by heating the solution. ^bMasked with EDTA. ^cRemoved by prior extraction. ^dMasked with thiourea.

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