Monatshefte für Chemie 113, 307—311 (1982)

Monatshefte für Chemie
Chemical Monthly

Determination of Niobium(V) with 5,7-Diiodo-8-hydroxyquinoline

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(Received 19 August 1981. Accepted 29 September 1981)

The determination of niobium with the reagent 5,7-diiodo-8-hydroxyquinoline was studied spectrophotometrically in citric acid medium. The complex has absorption maximum at 435 nm ($\varepsilon = 4\,853\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) with the *pH* 6.0. The effects of heating temperature, time, *pH*, reagent concentration and other variables have been studied. The system confirms the *Beer*'s law over the concentration range investigated. The optimum condition range for the measurement in 10 mm cells is 10–12 μg of niobium(V). The metal and ligand ratio of 1:2 was confirmed by *Job*'s continuous variations and mole ratio methods.

(Keywords: Niobium, determination; Spectrophotometry)

Bestimmung von Niob(V) mit 5,7-Diiod-8-hydroxychinolin

Die Bestimmung von Niob(V) mit 5,7-Diiod-8-hydroxychinolin wurde in zitronensaurem Medium untersucht. Das Absorptionsmaximum liegt bei 425 nm ($\varepsilon = 4\,853\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) bei einem *pH* von 6,0. Der Einfluß der Erwärmungsperiode bei der Komplexbildung (Temperatur, Zeit) wurde untersucht, außerdem noch *pH*, Reagenskonzentration und weitere Variable. Das *Beer*'sche Gesetz ist über den untersuchten Bereich voll gültig. Der optimalste Bereich für eine Messung in 10 mm Küvetten liegt bei 10—12 μg Nb(V). Ein Metall: Ligand-Verhältnis von 1:2 wurde mit der *Job*-Methode und der Mol-Verhältnis-Methode überprüft.

Introduction

Niobium forms chelates with the compounds containing oxygen and nitrogen as donor atoms. Among such compounds are 8-hydroxyquinoline and its derivatives. *Alimarin*[1] and coworkers have extensively studied the extraction of niobium-8-hydroxyquinolinato complex with various polar and non polar solvents. 5,7-Diiodo-8-hydroxy-

0026-9247/82/0113/0307/$ 01.00

quinoline like its parent compound 8-hydroxyquinoline acts as a chelating agent. The complex prepared by the reaction of niobium(V) with 5,7-diiodo-8-hydroxyquinoline in the presence of some additives was studied. The present work deals with the investigations of niobium-5,7-diiodo-8-hydroxyquinoline chelate spectrophotometrically regarding its composition, sensitivity and microgram determination of niobium in stainless-steels and niobium stabilised steels.

Experimental

Standard Niobium(V) Solution (1 mg/ml)

Pure niobium pentoxide (0.1431 g) was fused with 10 g of potassium bisulphate in a silica crucible and after cooling, the melt was extracted with 10 ml of 25% citric acid solution by warming. The solution was then transferred in to a 100 ml of standard flask and made up to the volume with distilled water. The *pH* was adjusted to 4.0 with dil. ammonia[2] or dil. H_2SO_4. The solution was standardised with tannin by precipitation and weighing it as oxide[3].

Recommended Procedure

To the niobium solution (containing 25-300 μg of metal) add 4-5 ml of 0.001 *M* solution of the ligand and adjust the *pH* 6.0 by using dil. ammonia. Heat the solution for 15 min or keep aside for one h. Dilute it to 25 ml. Measure the absorbance at 435 nm against the reagent blank prepared under the identical conditions and amount of niobium determined from the calibration curve.

Results and Discussion

Spectral Characteristics

In order to observe the wavelength of maximum absorption of the complex, a solution containing a fixed amount of metal and the reagent (ligand) was prepared and the *pH* of the solution was adjusted to *pH* 6.0 making the total volume 25 ml. The absorption spectra were recorded against the corresponding reagent blank prepared as reference. The results indicate that the complex has a maximum absorbance at 435 nm. In order to observe the spectral changes on varying the *pH*, absorption curves for niobium complex were prepared in different *pH* values. The maximum absorption of niobium complex is found at 435 nm at *pH* 6.0 and shorter wavelength at lower *pH*.

Effect of Concentration of Hydrogen Ion

To study the effect of *pH* on the absorbance, a series of solutions containing a fixed amount of metal and ligand was prepared at different *pH* values making a total volume 25 ml. The absorbance was measured at 435 nm. A glance of curve was obtained by plotting the absorbance markedly with the change in *pH* of the solution. The maximum absorbance was obtained in the *pH* ranging from 5.7 to 6.3 and therefore, further studies were carried out at *pH* 6.0 and measurements were made at 435 nm.

Effect of Temperature and Time

For metal:ligand ratio at the room temperature 27 °C, about 60-70 min are required for full colour development. When a prepared sample is heated on water bath at 40-50 °C the reaction is greatly accelerated and the maximum colour development is obtained in 15 min. The additional heating of 10 min did not cause any further change. A standard development time of 15 min was required to ensure the full colour development of all samples. The absorbance is stable for at least 24 h.

Citric Acid Concentration

Citric acid is added to prevent the hydrolysis of niobium salt. The tests showed that the minimum amount of citric acid necessary to prevent the hydrolysis completely is about 5 g, a reasonable safety margin is provided in the presence of 10 ml of 25% solution of citric acid. Increase in the amount of citric acid > 10 g caused a decrease in the absorbance.

Calibration Range, Sensitivity and Precision

The yellowish—orange coloured complex of niobium(V)—5,7-diiodo-8-hydroxyquinoline has maximum absorption at 435 nm and *pH* 6.0 with molar absorptivity $4\,853 \cdot 10^3\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. The sensitivity of the complex is 0.042 μg niobium(V) $\mathrm{cm^{-2}}$. *Beer*'s law is valid over the concentration range of 1.0-12.0 μg of niobium (V) $\mathrm{ml^{-1}}$. The precision of the method was evaluated by preparing and measuring 10 identical samples, containing 5 μg of niobium(V). The absorbance averaged with standard deviation of 0.002.

Interference of Ions

The solutions containing 20 μg of niobium and varying amounts of foreign ions were prepared at *pH* 6.0. The following ions with their amounts given in parenthasis did not cause more than ± 3% in absorbance.

$C_2O_4^{2-}$ (1 500 μg), NO_3^- (1 000 μg), Cl^-, Br^-, I^-, (500 μg); Al^{2+} (480 μg), Zn^{2+} (520 μg), Mn^{2+} (620 μg), Co^{2+} (340 μg), Ba^{2+} (450 μg), Ca^{2+} (400 μg), Pb^{2+} (180 μg), Fe^{3+} (310 μg), PO_4^{3-} (280 μg), Cr^{3+} (270 μg), Ti(IV) (320 μg), V(V) (290 μg), Ta(V) (250 μg), Mo(VI) (380 μg) and W(VI) (370 μg).

Stoechiometry of the Complex

Some studies on the stoechiometry of the complex have been performed. The molar ratio of niobium(V): 5,7-diiodo-8-hydroxyquinoline (*DIHQ*) was shown to be 1:2 (ML_2) by *Job*'s method of continuation variations[4], and mole ratio method[5]. Niobium is reported to exist as NbO^{+3} in acid media and the composition of the complex is $NbO(DIHQ)_2$. The apparent stability constant of the complex evaluated by mole ratio method was $\log K = 8.6 \pm 0.1$ at 27 °C.

Table 1

Samples	Niobium% certified	niobium% found
1. NBS-123 a	0.80	0.78
2. BCS-261	0.71	0.70
3. NBS-363	0.04	0.03
4. NBS-361	0.021	0.020

Determination of Niobium in Steels

A sample of 100 mg, containing 0.02-1.50% of niobium was dissolved in 50% sulphuric acid. After cooling, dil. hydrochloric acid was added and the silica was filtered off, washed and ignited in platinum. This impure silica was dissolved in a few drops of hydrochloric acid and hydrofluoric acid and added it to the original solution. 10 ml of the reagent 5,7-diiodo-8-hydroxyquinoline solution was added, then 2.5% solution of tannin was added drop by drop with stirring until the precipitation of niobium was complete. The precipitate was filtered off and then washed with 1% tannin solution. The precipitate was ignited in a silica crucible and the residue was fused with potassium pyrosulphate. The cooled cake was dissolved in 10 ml of 25% by weight citric acid solution. This was then diluted with distilled water up to the volume of 100 ml, 5 ml of this solution was placed into a 25 ml of standard flask, 10 ml of the reagent 5,7-diiodo-8-hydroxyquinoline solution was added and the *pH* adjusted to 6.0 with dil. ammonia and the solution was diluted 25 ml with distilled water. After 1 h the absorbance at 435 nm was measured.

Application

Results of niobium in niobium stabilised steels are given in Table 1. Determinations of niobium in these samples gave recoveries of 99%.

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