CROATICA CHEMICA ACTA CCACAA **49** (3) 533—537 (1977)

YU ISSN 0011-1643

CCA-1027 544.6:541.821

Original Scientific Paper

Spectrophotometric Determination of Titanium as a Mixed Thiocyanate-1-phenyl-2-methyl-3-hydroxy-4-pyridone Complex

B. Tamhina, V. Vojković and M. J. Herak

Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

Received November 22, 1976

The extn. of titanium(IV) thiocyanate complex by 1-phenyl-2-methyl-3-hydroxy-4-pyridone(HX) dissolved in chloroform has been investigated from hydrochloric and sulphuric acid solns. The extd. complex has the ratio Ti : SCN : HX 1 : 2 : 2. Chloroform solns. follow Beer's law and are stable for at least 24 h. A sensitive and reproducible spectrophotometric detn. of titanium is possible. The molar absorptivity of the method is 26 500 l mol^{-1} cm^{-1} at 365 nm. Few metals interfere, and their sepn. is discussed.

INTRODUCTION

Titanium(IV) forms with thiocyanate in the presence of acetone an intensively coloured yellow complex. The intensity of the colour depends on the kind of acid used, temperature, and on the sequence in which the reagents are added[1-4]. After the addition of various organic ligands, titanium thiocyanate forms mixed complexes which are soluble in organic solvents and can be applied for the spectrophotometric determination of titanium[5-7]. In the present paper, a sensitive, selective and reproducible extraction-spectrophotometric method is described. It is based on the extraction of titanium as a mixed thiocyanate-1-phenyl-2-methyl-3-hydroxy-4-pyridone complex, which is determined spectrophotometrically in the organic phase.

Apart from the higher selectivity and sensitivity of the proposed method in comparison with other described thiocyanate methods for titanium, an advantage of the method described here is that quantitative extraction of titanium is carried out at lower acidity. Therefore, the solutions of the titanium complex, as well as the reagent blank solutions, are without the polymerization of thiocyanate and are more stable so that there is no need to filter the organic phase before the measurement.

Titanium(IV) can be extracted with 1-phenyl-2-methyl-3-hydroxy-4-pyridone from an aqueous solution. The organic phase thus obtained can be applied to the spectrophotometric determination of titanium[8]. However, the method described here is more sensitive than the previous one[8].

EXPERIMENTAL

Reagents and Apparatus

For the standard titanium solution (0.01 *M*), fuse 0.8 g of titanium dioxide with potassium hydrogensulphate in a platinum crucible. Extract the melt with dilute sulphuric acid (1 + 9), filter and dilute with the same acid to 1 l. Standardize the solution by the cupferron method[9]. 1-Phenyl-2-methyl-3-hydroxy-4-pyridone (HX) was synthesized as described previously[10]. Its solution in chloroform served as the organic phase. A Perkin-Elmer Coleman 124 spectrophotometer with 1-cm quartz cells was used.

Procedure

Place a solution containing 1—20 μg of titanium into an erlenmeyer flask, and add 1 ml of 10 M hydrochloric acid or 0.5 ml of 10 M sulphuric acid, 1.5 ml of 50% (*w*/*v*) potassium thiocyanate solution and water to bring the total volume to about 5 ml. Add 5.0 ml of 0.003 M HX in chloroform and shake for 15 min using a mechanical shaker. After the phases separate, measure the absorbance of the organic phase at 365 nm against a reagent blank.

RESULTS AND DISCUSSION

Optimal Conditions for Extraction

The titanium(IV) complex formed with thiocyanate in hydrochloric or sulphuric acid solution can be extracted with 1-phenyl-2-methyl-3-hydroxy-4--pyridone (HX) in chloroform as a yellow mixed complex which has a maximum absorbance at 365 nm. The influence of the concentration of mineral acids, potassium thiocyanate and HX were studied and the results obtained are showed in Figure 1. Optimal concentrations are found to be 2 M hydrochloric acid or 1 M sulphuric acid, 15% (*w*/*v*) potassium thiocyanate and 0.003 M HX

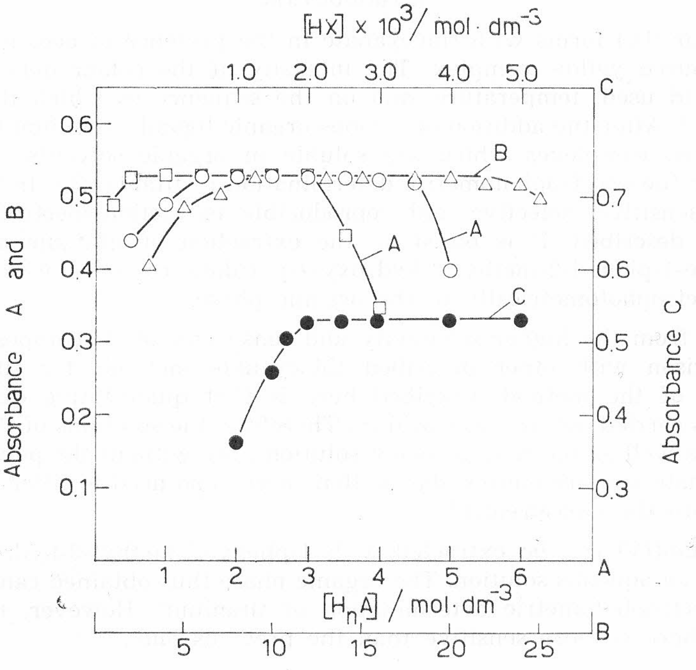

Figure 1. Dependence of Ti(IV)-thiocyanate-HX complex formation on various parameters. (Curve and scales indicated by the same letters). Titanium conc. 2×10^{-5} M.
A — (○) M HCl and (□) M H_2SO_4;
B — (△) % KSCN; C — (●) M HX.

dissolved in chloroform. Under these conditions, it is possible to determine 0.1—2 μg Ti ml^{-1}. The absorbance of the complex at 365 nm obeys Beer's law over this range. The respective molar absorptivity is 26 500 l mol^{-1} cm^{-1}. The Sandell[11] photometric sensitivity is 0.0019 μg Ti cm^{-2}. The reproducibility, of the measurements, expressed as standard deviations, is 0.2—2% depending on the titanium concentration. The colour of the complex is stable for more than 24 h.

Influence of Diverse Ions

The influence of various cations and anions was studied on the determination of titanium from hydrochloric and sulphuric acid solutions. It was found that chloride, sulphate, bromide, phosphate, cyanide and perchlorate do not interfere in a 5000-fold amount from sulphuric acid solutions and in a 2000-fold amount from hydrochloric acid solutions. Iodide, acetate, tartrate, nitrate and oxalate do not interfere in a 4000-fold amount from sulphuric acid and in a 2000-fold amount from hydrochloric acid solutions. Fluoride and citrate can be tolerated in 1000-fold amounts from sulphuric acid and in a 500-fold amount from hydrochloric acid solutions. Ammonium, potassium, sodium, magnesium, calcium, barium, zinc, cadmium, aluminum, chromium(III), manganese(II), nickel, lead, cobalt, gallium, strontium, mercury and antimony are tolerated in 1000-fold amounts, and vanadium, uranyl, thorium, ruthenium and palladium in 100-fold amounts from sulphuric and hydrochloric acid solutions. The interfering cations are listed in Table I. Niobium and tantalum

TABLE I

Interfering Cations (2×10^{-5} M *Titanium(IV), 0.003* M *HX, 15% KSCN and 2* M *HCl or 1* M H_2SO_4)

Cation	Cation : Ti molar ratio	absorbance from HCl solution	absorbance from H_2SO_4 solution
—	—	0.530	0.530
Niobium(V)	10	> 2	> 2
Tantalum(V)	10	> 2	> 2
Iron(III)	1000	0.760	0.770
	100	0.692	0.665
	10	0.531	0.530
	100	0.530[a]	0.530[a]
	1000	0.529[a]	0.531[a]
Copper(II)	1000	0.850	0.855
	100	0.660	0.650
	10	0.532	0.531
	100	0.530[a]	0.531[a]
	1000	0.531[a]	0.530[a]
Molybdenum(VI)	10	> 2	> 2
	10	0.529[b]	0.531[b]
	50	0.530[b]	0.530[b]
Tungsten(VI)	10	> 2	> 2
	10	0.530[b]	0.529[b]
	50	0.521[b]	0.530[b]

[a] 0.1 *M* ascorbic acid present.

[b] 20% thioglycolic acid present.

should be removed prior to titanium determination. Interference of iron(III) and copper(II) can be eliminated by their reduction with ascorbic acid while the interference of molybdenum(VI) and tungsten(VI) can be eliminated by addition of thioglycolic acid. The absorbance is independent of the purity of chloroform; commercial chloroform containing 1% of ethanol or chloroform freed from ethanol can be used.

Composition of the Complex

The ratio of titanium to the thiocyanate and HX ligand was determined by Job's method of continuous variations. The composition of the complex was studied by the extraction of titanium from 2 M hydrochloric acid and from 1 M sulphuric acid media. Since three components are involved in the formation of the extractable complexes, two series of experiments were carried out at each acidity. The results obtained (Figure 2) show that the molar ratio of Ti : SCN : HX is 1 : 2 : 2. The ratio is independent on the kind of mineral acid used in the aqueous phase. This indicates that most probably $TiO(SCN)_2 \cdot 2\,HX$ is formed and transferred into the organic phase.

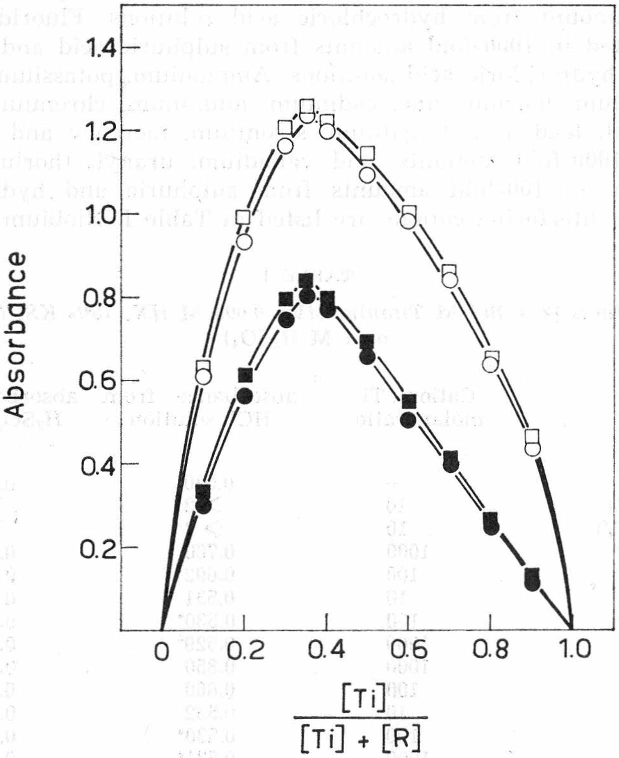

Figure 2. Determination of complex composition by Job's method. R = KSCN (○ □), conc. HX 1×10^{-2} M, [Ti] + [SCN] = 2×10^{-3} M, (○) 2 *M* HCl and (□) 1 *M* H_2SO_4; R = HX (● ■), conc KSCN 20%, [Ti] + [HX] = 5×10^{-4} M, (●) 2 M HCl and (■) 1 M H_2SO_4.

Acknowledgement. The authors are grateful to Mrs. V. Koban for technical assistance.

REFERENCES

1. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyze,* Springer Verlag, Berlin, 1964, p. 939.
2. C. E. Crouthamel and C. E. Johnson, *Anal. Chem.* **24** (1952) 1780.
3. C. E. Crouthamel and C. E. Johnson, *Anal. Chem.* **26** (1954) 1284.
4. C. E. Crouthamel, B. E. Hjelte and C. E. Johnson, *Anal. Chem.* **27** (1955) 507.
5. A. T. Pilipenko and V. G. Safronova, *Ukr. Khim. Zh.* **40** (1974) 755.
6. J. P. Young and J. C. White, *Anal. Chem.* **31** (1959) 394.
7. B. Tamhina, M. J. Herak, and V. Jagodić, *Anal. Chim. Acta* **86** (1976) 223.
8. V. Vojković, B. Tamhina, and M. J. Herak, *Z. Anal. Chem.* in press.
9. A. I. Vogel, *A text-Book of Quantitative Inorganic Analysis,* 3rd edn., Longmans and Green, London, 1961, p. 544.
10. B. Tamhina, K. Jakopčić, F. Zorko, and M. J. Herak, *J. Inorg. Nucl. Chem.* **36** (1974) 1855.
11. E. B. Sandell, *Colorimetric Determination of Traces of Metals,* 3rd edn., Interscience, New York, 1959.

SAŽETAK

Spektrofotometrijsko određivanje titana u obliku mješovitog tiocijanato-1-fenil-2-metil-3-hidroksi-4-piridono-kompleksa

B. Tamhina, V. Vojković i M. J. Herak

Opisana je ekstrakcija titan(IV) tiocijanat kompleksa iz klorovodično i sumporno kiselih otopina 1-fenil-2-metil-3-hidroksi-4-piridonom (HX) otopljenim u kloroformu. U ekstrahiranom kompleksu molni omjer Ti : SCN : HX iznosi 1 : 2 : 2. Kloroformne otopine kompleksa slijede Beerov zakon, stabilne su najmanje 24 sata i pogodne su za osjetljivo i reproducibilno spektrofotometrijsko određivanje titana. Molarni koeficijent apsorpcije iznosi 26 500 l mol^{-1} cm^{-1} kod 365 nm. Nekoliko metalnih iona interferira te je opisano uklanjanje smetnji od tih iona.

ZAVOD ZA ANALITIČKU KEMIJU
PRIRODOSLOVNO MATEMATIČKI FAKULTET,
41001 ZAGREB

Prispjelo 22. studenog 1976.