

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM AND IRON-APPLICATION TO CHERAT VOLCANIC ASH, N.W.F.P.

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A rapid and sensitive method for the separation and determination of titanium and iron in thiocyanate system has been developed. The extractability of Ti(II) by high molecular weight amine (HMWA) in organic solvent (CHCl₃) and its separation from Fe(III) was examined. The yellow coloured complex of Ti(II)-SCN is quantitatively extracted into the organic phase containing tribenzylamine (TBA)- a high molecular weight amine, whereas the blood red coloured complex of Fe(III)-SCN formed under the same conditions gets separated in the aqueous phase. On the basis of the selective extractability, a method has been developed for the separation as well as simultaneous determination of Ti(II) and Fe(III) in presence of many other elements. The molar extinction coefficients were found to be $1.9 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $1.11 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively for Ti(II) and Fe(III). The extractability of the complex of Ti(II)-SCN by HMWA suggests that the coloured species is anionic in nature. The method developed was successfully applied to the determination of titanium in Cherat volcanic ash.

Key words: Spectrophotometric, Cherat volcanic ash, Ti (II)-SCN.

Introduction

The use of high molecular weight amines (HMWA) as liquid anion exchanger and as extractant for the anionic complexes has been mainly confined to the separation of specific pairs of ions (Leddicottle and Moore 1952; Ellenberg *et al* 1954; Mahlman *et al* 1954 and Moore 1954). An extensive study of many metal thiocyanates in ethyl ether at various NH₄CNS concentrations has been made by (Bock 1956). More recently advantage has been taken of the use of thiocyanate complexing as a method of chemical separation (Morrison and Freiser 1966).

In addition to the thiocyanate as a complexing reagent, other complexing agents have also been used for the spectrophotometric determination of titanium (Ronald and Grilbert 1972). However these methods are cumbersome and time consuming. The present investigations were undertaken in continuation of the earlier studies on the extraction and spectrophotometric determination of traces of transition metals in thiocyanate system using high molecular weight amines (Khan *et al* 1982, 84, 90 a and b, 94).

Experimental

Erma Spectrophotometer Model LS-7 was used.

Reagents: The following reagents were prepared and used throughout the investigations. However, preparation of fresh solutions are almost preferable.

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(i) **Standard Titanium Solution:** One gram titanium metal was dissolved in a minimum volume of 1:1 HCl and diluted to 1 liter with distilled water. Further dilutions were made from this stock solution so that 1 cm³ of the standard solution corresponds to 20 µg.

(ii) **Potassium Thiocyanate Solution:** 70% (7.2 M) was prepared from potassium thiocyanate (supplied by E. Merck) by dissolving the required amount in distilled water and then diluting to the required concentration.

(iii) **Tribenzylamine (TBA) Solution:** 5% solution of tribenzylamine was prepared by dissolving the required amount in pure chloroform. All the other reagents used were of Analar grade.

Procedure: Formation of Ti(II)-SCN and Fe(III)-SCN complexes and the extraction of Ti(II)-SCN complex by tertiary amine:

The coloured complexes of Ti(II)-SCN and Fe(III)-SCN were formed by adding thiocyanate into a solution containing titanium and iron in the presence of hydrochloric acid. Tribenzylamine in chloroform (5cm³) was then added to the coloured solution in a 100cm³ separating funnel and the contents were shaken for half of a minute (30 sec). The two phases were then allowed to separate; the yellow coloured complex of Ti(II)-SCN quantitatively extracted into the organic phase was collected into 10cm³ dried flask after phasing it through a small Whatman (5.5cm) filter paper, while the blood red coloured complex of Fe(III)-SCN got separated into the aqueous phase.

The absorbances of both the coloured species were measured with respect to the respective reagent blank. The absorption maxima (λ_{\max}) for the complex of Ti(II)-SCN-TBA and Fe(III) were noted to be 500nm and 480nm respectively Fig 1.

Calibration Sensitivity and Stability. Known concentration of titanium and iron were taken and the investigations were made following the foregoing procedure. The absorbances of the thiocyanate complexes were measured at 500nm and 480nm respectively. Beers law was closely obeyed for solutions containing 0.1-40 μg of titanium and iron. The molar absorptivity of the thiocyanate complexes of titanium and iron were $1.19 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $1.11 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively at 500 nm and 480nm. The yellow complex of Ti(II)-SCN-TBA extracted into the organic phase was allowed to stand overnight but no change was noted in the absorbance and colour with lapse of time. After this period there seemed a gradual change in colour intensity till reaching half its value after 48 h. However, the absorbance as well as the intensity of the colour of Fe(III)-SCN complex was not stable more than a few h.

Analysis of Volcanic Ash: 0.5g of well agated sample of volcanic ash (100 ± 120 mesh) was leached with 0.4M HCl for 2.5 h over an electric water bath at 80°C . The soluble part was then filtered through Whatman filter paper and the filtrate was diluted to 250cm^3 with distilled water adding as much HCl so that the acidity of the final solution is 0.4M HCl 5cm^3 of this solution was then transferred to a 100cm^3 separating funnel, followed by addition of KCNS solution, so that the final concentration is 1.6M KCNS.

After thorough mixing the solution was diluted to 10cm^3 with distilled water 5cm^3 tribenzylamine in chloroform was then added to this solution and the two phases were shaken for 30 sec. manually or on a mechanical shaker. The two phases were allowed to separate and after the equilibrium is attained, the organic phase was drawn into a dried flask after passing it through a small Whatman (5.5cm) filter paper. The absorbance of titanium and iron as their thiocyanate complexes were noted at 500nm and 480nm respectively against the corresponding reagent blank. The amount of titanium as well as of iron were calculated from the calibration curve and expressed as percent (%) concentration. The comparative results regarding the TiO_2 content of the volcanic ash are presented in Table 1.

Results and Discussion

Fig 1. Illustrates the absorption spectrum of Ti(ii)-SCN-TBA system after extraction into tribenzylamine (TBA).

Effect of Acid Concentration. The effect of different concentrations of HCl in the range of 0.05-2.0M was studied on the overall extraction and separation of Ti(II)-SCN and Fe(III)-SCN complexes. It was found that maximum colour intensity, efficient extraction and separation was achieved at 0.40M HCl These observations are shown in Fig 2.

Effect of Thiocyanate Concentration: The effect of various concentrations of KSCN (0.10-4.0M) was also in-

Table 1

Comparative analysis report of cherat volcanic ash
N.W.F.P (titanium determined as TiO_2)

S. No.	Hydrogen peroxide method ^a	British standard method ^b	Present method
1.	1.39	1.40	1.45
2.	1.00	0.90	0.90
3.	0.65	0.60	0.59
4.	1.00	1.01	1.00
5.	1.22	1.02	1.03
6.	1.04	1.03	1.01
7.	1.01	0.90	1.00
8.	1.03	1.02	1.04

a. E. B. Sandell "Colorimetric Determination of traces of Metals" 3rd Ed. Wiley interscience, New York, p-870, 1959; b. British Standards Specification No. 1975 (1958).

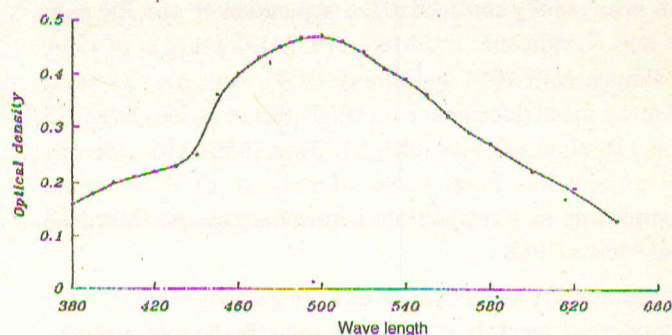


Fig 1. Absorption spectrum of Ti(II)-SCN after extraction into organic amino phase.

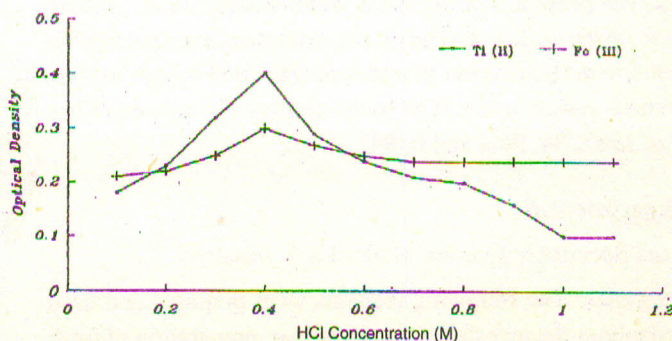


Fig 2. Effect of HCl concentration on extraction & separation of Ti(II) & Fe(III).

investigated to find out the optimum concentration for maximum colour intensity and separation of titanium and iron. Thiocyanate concentration of 1.60M was found to be the optimum concentration. These results are illustrated in Fig 3.

Effect of Shaking Time: Having studied the effect of HCl and thiocyanate concentration on the overall extraction, the effect of shaking time for equilibration of the two phases was also observed, and 30 sec. were found to be the optimum time. The observations are presented in Fig 4.

Effect of Phase-Volume Ratio: Keeping the acid, thiocyanate concentrations and volume of the organic phase (Vorg) as constant the extraction as well as separation of both the complexes were studied by varying the volume of the aqueous phase (Vaq). It was noted that the ratio 1:2 (Vorg: Vaq) is the optimum ratio for maximum separation and quantitative extraction.

Effect of the Diverse Ions: During investigations it was found out that usually three types of interferences are almost

repeatedly encountered (i) metal ions which form anionic complexes with SCN^- e.g. Cu(II), Co(II), Mo(V), W(VI), Mn(II), V(V) (ii) those ions which form coloured anionic species with SCN^- and are extracted into neutral solvents because of their solubility in these solvents, (iii) ions which oxidize SCN^- to a coloured soluble complex of indefinite composition.

As can be seen from Table 2, even the first type of ions do not interfere seriously, provided these ions are present in moderate amounts. Co(II) and Mn(II) present in 50 fold excess and giving coloured complexes with SCN^- ion do not interfere seriously, but Sb(III), Ni(II), Pb(II), W(VI), Ba(II) and Cr(III) interfere seriously. However, the interference of anions e.g. SO_4^{-2} , Cl^- , CO_3^{-2} , HCO_3^- , PO_4^{-3} do not encounter seriously.

To check up the validity of the method developed, a number of synthetic mixtures were also prepared and then analyzed the results are shown in Table 3.

Table 2
Determination of titanium and iron in the presence of diverse ions (titanium and iron taken 29 μg each)

S. No.	Diverse Ions	Amount added(μg)	Titanium		Iron (μg)	
			Found	Error	Found	Error
1.	Ba ⁺²	1000	19.89	-0.11	19.79	-0.21
2.	Cr ⁺³	1000	19.99	-0.01	19.88	-0.12
3.	Mg ⁺²	2000	20.00	0.00	20.00	0.00
4.	Ca ⁺²	2000	19.99	-0.01	19.97	-0.03
5.	Pb ⁺²	1000	19.88	-0.12	19.89	-0.1
6.	Al ⁺³	2000	20.00	0.00	20.00	0.00
7.	Na ⁺	2000	20.01	+0.01	20.00	0.00
8.	K ⁺	1000	20.01	+0.01	20.00	0.00
9.	Co ⁺²	1000	19.99	-0.01	20.00	0.00
10.	Mn ⁺²	1000	20.30	+0.30	20.05	+0.50
11.	Zn ⁺²	2000	20.02	+0.02	19.98	-0.02
12.	U ⁺⁶	2000	20.30	+0.30	19.90	-0.10
13.	W ⁺⁶	1000	20.20	+0.20	19.80	-0.20
14.	Ni ⁺²	2000	20.05	+0.05	19.89	-0.11
15.	Sb ⁺³	1000	19.97	-0.03	19.59	0.41
16.	Si ⁺⁴	1000	20.02	+0.02	20.00	0.00
17.	F ⁻	1000	20.10	+0.10	19.99	-0.01
18.	PO ₄ ⁻³	2000	19.98	-0.02	20.00	0.00
19.	I ⁻	1000	20.20	+0.20	19.88	-0.21
20.	Tartaric Acid	2000	20.00	0.00	19.98	-0.02
21.	CO ₃ ⁻²	2000	20.00	0.00	20.00	0.00
22.	HCO ₃ ⁻	2000	20.00	0.00	20.00	0.00
23.	Cl ⁻	2000	20.00	0.00	20.00	0.00
24.	SO ₄ ⁻²	2000	20.00	0.00	20.00	0.00

Table 3
Analysis of synthetic mixtures

S. No.	Titanium (μg)			Iron (μg)		
	Present	Found	Error	Present	Found	Error
1.	3.00	2.90	-0.10	4.00	3.90	-0.10
2.	6.00	6.10	+0.10	8.00	7.88	+0.12
3.	12.00	11.99	-0.01	12.00	12.10	+0.10
4.	15.00	14.90	-0.10	16.00	16.07	+0.02
5.	18.00	18.20	+0.20	20.00	19.90	-0.10
6.	21.00	21.00	0.00	24.00	24.10	+0.10
7.	24.00	24.05	+0.05	28.00	28.15	+0.15
8.	27.00	27.10	+0.10	34.00	33.99	-0.10
9.	30.00	30.00	0.00	38.00	38.20	+0.20
10.	33.00	33.02	+0.02	44.00	44.20	+0.20
11.	36.00	35.80	-0.20	48.00	48.00	+0.10
12.	39.00	39.01	+0.01	52.00	51.90	-0.10
13.	41.00	41.20	+0.20	56.00	56.20	+0.20
14.	43.00	43.10	+0.10	60.00	59.99	-0.01
15.	50.00	50.05	+0.05	100.00	99.67	-0.33

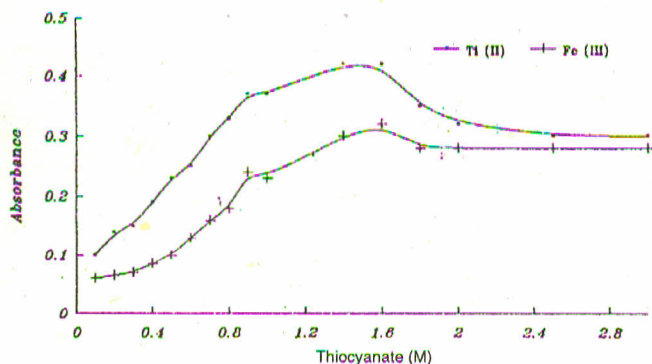


Fig 3. Effect of thiocyanate on the extraction & separation of Ti(II) & Fe(III).

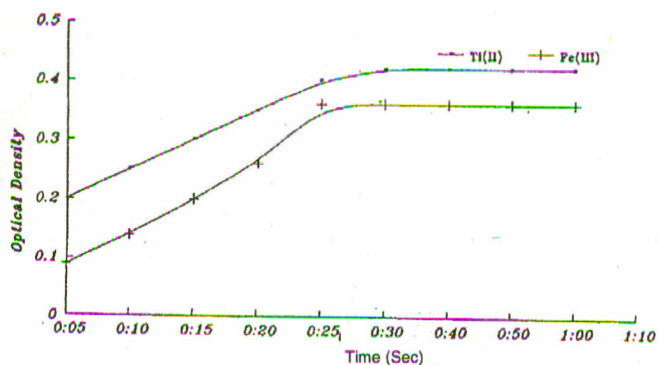


Fig 4. Effect of time on the extraction & separation of Ti(II) & Fe(III).

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