

# Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 18, Nos. 3-4, June-August 1975

## SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM AFTER EXTRACTION OF THE Ti(II)-SCN SYSTEM BY HIGH MOLECULAR WEIGHT AMINES

BASHIR AHMAD and M. A. KHATTAK

*PCSIR Laboratories, Peshawar*

(Received July 16, 1974; revised January 24, 1975)

**Abstract.** As investigation of the complex formed between Ti(II) and thiocyanate in sulphuric acid solutions has been carried out, and its extractability by high molecular weight (HMWA) tertiary amines in organic solvents examined. The orange yellow complex is quantitatively extractable from an aqueous phase into an organic phase containing tribenzylamine or Allamine 336. On the basis of this extractability a new method has been developed for the spectrophotometric determination of traces of titanium (0.1-1 p.p.m.) in presence of other elements. Comparison of the absorption spectra of the coloured species in the aqueous and amine phases indicate the presence of the same absorption species in each medium. The extractability of the complex by HMWA suggests that the coloured species is anionic.

The use of high molecular weight amines (HMWA) may be said to date from 1948, when Smith and Page published their work on acid bonding properties of amines. Their use as 'liquid anion exchangers' and extractant for anionic complex metal species was mainly confined to the separation of specific pairs<sup>1-5</sup> and to the extraction of uranium, thorium and plutonium.<sup>6-9</sup> In several cases the elucidation of the structure of anionic species on the basis of extraction has been possible.<sup>10-13</sup> The most popular method of extraction of metals is the halocomplexes from HCl solution into an organic phase containing the amine. The present authors after a study of the extraction of the chlor and tin chlorocomplexes of Pt(IV),<sup>14</sup> Pd(II),<sup>15</sup> and Rh(III)<sup>16</sup> used HMWA for extraction of Mo(VI)-SCN system for a spectrophotometric determination of molybdenum.<sup>17</sup>

In acid solution, thiocyanate gives an orange yellow colour with titanium, which has not been extensively investigated.<sup>18,19</sup> No attempt appears to have been made in using the coloured complex for the determination of titanium. Also the extraction of titanium into HMWA as thiocyanate complex, had not been previously employed. As the coloured species was more likely to be anionic, investigations were begun in these Laboratories with the aim of using HMWA to extract the species, and if possible, use it for the spectrophotometric determination of titanium.

### Experimental

**Apparatus.** Beckman model Du spectrophotometer.

**Reagents.** Titanium standard solution (BDH).

Titanium metal sponge was dissolved in 4N H<sub>2</sub>SO<sub>4</sub> (dil) and volume made up with the same acid. Titanium contents were determined gravimetrically and further dilutions were made from this stock solution.

**Potassium Thiocyanate.** 70% (aq) solution (w/v) (7.2M).

**Tribenzylamine.** The solution (0.2M) was prepared by dissolving the crystals in chloroform.

**Allamine 336.** The solution (5% v/v) was prepared either in chloroform or in thiophene-free benzene. All other chemicals used were of Analar grade.

**Formation of the Ti(II)-SCN Complex and Extraction by Amines.** The orange yellow complex was formed by adding thiocyanate into a solution containing titanium in presence of H<sub>2</sub>SO<sub>4</sub>. Amine solution (5 ml) in organic phase was added to the coloured solution of titanium in a separating funnel and was shaken for 1 min. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phase as no trace was ever found in the aqueous phase. The colour of the complex after extraction was the same as in the aqueous phase. The organic phase was collected in a dried flask after passing it through a small filter paper (5 cm) to remove suspended water droplets. The absorption spectrum was determined with respect to a blank containing all the reagents, but no titanium and extracted in the same way. The spectrum shows the maximum absorption at 425m $\mu$  (Fig. 1).

**Calibration, Sensitivity and Stability.** Known concentrations of titanium were extracted by the foregoing procedure and absorbance measured at 425m $\mu$ . For solution containing between 0.5-5 $\mu$ g/5 ml, i.e. 0.1-1.0 p.p.m. Beer's law was closely obeyed. The molar absorption coefficient is  $3.5 \times 10^4$ . An optical density of 0.1 corresponded to 0.6  $\mu$ g whereas the same corresponds to 347 $\mu$ g of titanium by the standard hydrogen peroxide method<sup>20</sup>; thus the present method is 578 time more sensitive and the colour is fairly stable for 2 hr. At the end of this period there is a gradual fading and lowering of the intensity of colour.



**Stability.** The stability of amine/organic solvent extract was found to be dependent on three factors : (a) KSCN and  $H_2SO_4$  concentration, (b) the type of solvent, and (c) the type of amine.

To prevent hydrolysis of titanium the presence of higher concentration of sulphuric acid (2-4M) is essential in stock solution, but a concentration in the range of 1.5-2.5M was found to be the most suitable for efficient extraction. Further, in this range the extract was clear and stable. Various concentrations of thiocyanate were also examined and a concentration in the range of 2.0-3.5M was found to be most suitable for maximum colour intensity and efficient extraction. Thiocyanate solutions should be freshly prepared. The effect of  $H_2SO_4$  and KSCN on the intensity of colour are shown graphically in Figs. 2 and 3 respectively.

**Solvent Effect.** When chloroform is used as the solvent, the extract is stable only for a short period of 10-15 min after extraction and slight turbidity then appears alongwith fading of colour and results are sometimes not reproducible. Pre-treatment of the chloroform amine phase with 2M  $H_2SO_4$ , however, gave better results in subsequent extraction of the system. A benzene solution of the Allamine 336 when used as extractant, a very clear solution was obtained. This was in confirmation with our earlier work in extraction of metal anionic complex species.<sup>14</sup>

#### Procedure

Take 1-3 ml titanium solution containing 0.5-5  $\mu g$  titanium in a separating funnel and add 2 ml potassium thiocyanate followed by dilution up to 5 ml with 4N  $H_2SO_4$ . Shake the contents and add 5 ml amine (Allamine 336) solution in benzene. Shake the two phases for 0.5-1 min either manually or by the aid of mechanical shaking machine and allow the phases to separate. Filter the amine layer through a small filter paper into a 5-10 ml flask to remove the suspended water droplets. Measure the absorbance at 425nm after 1 hr of extraction against a blank extracted by the foregoing procedure.

**Interferences.** In the determination of titanium by the above procedure with thiocyanate, three types of interferences are most frequently encountered: (a) Metals' ions which form an anionic complex with  $SCN^-$  will be extracted into the amine phase, e.g.  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$  and  $Nb^{3+}$ . (b) Ions which form coloured nonionic compounds with  $SCN^-$  and which extracted into neutral solvents because of its solubility in these solvent, e.g.  $Cr^{3+}$ . (c) Ions which oxidize  $SCN^-$  to a coloured soluble complex of indefinite composition.

With the exception of first type fortunately none of the remaining two types interfere in the determination of titanium by the foregoing procedure. As will be seen from the Table 1, the first type also did not interfere seriously in the determination of titanium provided these ions are present in moderate amounts. As for example,  $Co^{2+}$  which also forms an extractable anionic green complex gave the absorption maxima at 620 nm<sup>18</sup> and thus will not interfere even

in presence of three-fold excess. Similarly copper which also forms an extractable complex does not interfere even in presence of twenty-five-fold excess. Iron, if not properly masked, interferes even in traces due to the formation of coloured thiocyanate complex which is also extractable into the amine phase. (This was found during the present work and further

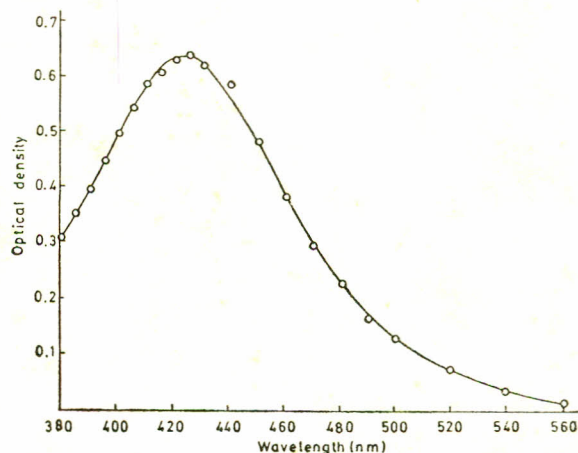


Fig. 1. Absorption spectrum of  $[Ti_x-(CNS)_y]^{y-x}$  after extraction into organic amino phase.

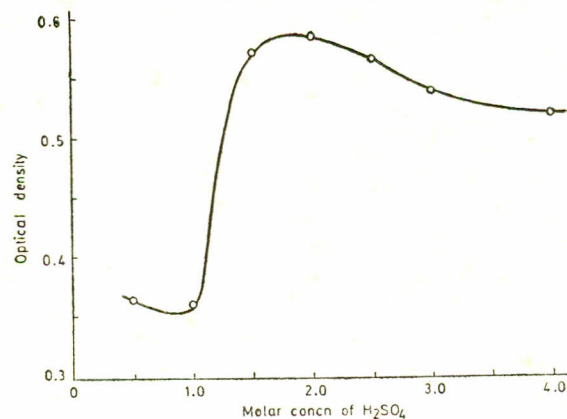


Fig. 2. Effect of sulphuric acid concentration on extraction.

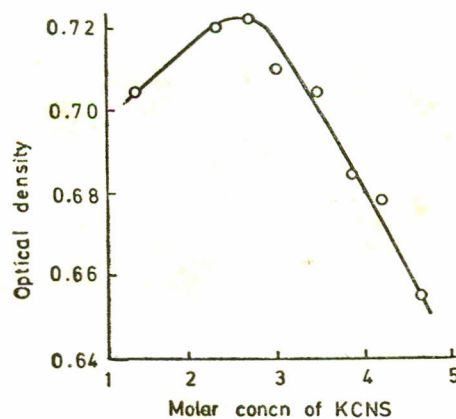


Fig. 3. Effect of KCNS concentration on extraction.



TABLE 1. EFFECT OF DIVERSE IONS.

Foreign substances added	Amount ( $\mu\text{g}$ )	Titanium present ( $\mu\text{g}$ )	Titanium found ( $\mu\text{g}$ )	Error ( $\mu\text{g}$ )
NiSO <sub>4</sub>	1000 as Ni	4	4.23	+ 0.23
Cr(NO <sub>3</sub> ) <sub>3</sub>	100 as Cr	4	3.77	- 0.23
CuSO <sub>4</sub> ·5H <sub>2</sub> O + KI + Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	100 as Cu	4	3.955	- 0.045
Fe(NO <sub>3</sub> ) <sub>3</sub> + Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	6000 as Fe	4	3.91	- 0.09
NaF	800 as NaF	4	3.3	- 0.7
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	400 as Mo	4	4.0	0.0
Al(NO <sub>3</sub> ) <sub>3</sub>	500 as Al	4	3.53	- 0.47
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	500 as S <sub>2</sub> O <sub>3</sub>	4	4.00	0.0
Tartaric acid	500	4	4.135	+ 0.135
MnCl <sub>2</sub> ·4H <sub>2</sub> O	200 as Mn	4	4.135	+ 0.135
MgCl <sub>2</sub> ·6H <sub>2</sub> O	200 as Mg	4	4.225	+ 0.225
Ca(NO <sub>3</sub> ) <sub>2</sub>	500 as Ca	4	3.7	- 0.3
NaH <sub>2</sub> PO <sub>4</sub>	250 as PO <sub>4</sub>	4	3.7	- 0.3
V <sub>2</sub> O <sub>5</sub>	600 as V <sub>2</sub> O <sub>5</sub>	4	3.9	- 0.1
Nb <sub>2</sub> O <sub>5</sub>	100 as Nb	4	Infinity	Not measurable
Ta <sub>2</sub> O <sub>5</sub>	100 as Ta	4	4.133	+ 0.133
Pb(CH <sub>3</sub> COO) <sub>2</sub>	100 as Pb	4	3.55	- 0.45
Th(NO <sub>3</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	100 as Th	4	3.35	- 0.65
ZrOCl <sub>2</sub>	100 as Zr	4	3.00	- 1.00
Na <sub>2</sub> WO <sub>4</sub>	100 as W	4	3.35	- 0.65

TABLE 2. ANALYSIS OF UNKNOWN MIXTURES.

Titanium		Error ( $\mu\text{g}$ )	Other elements ( $\mu\text{g}$ )
Present ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )		
6	5.85	-0.15	V <sub>2</sub> O <sub>5</sub> 10.0 g/ml
4	4.9	+0.9	Cu 10.0 g/ml
8	6.6	-1.4	Fe <sup>+3</sup> 10.0 g/ml
8	8.0	0.0	Mo 10.0 g/ml

investigations regarding its anionic nature, are also at hand and will be reported later.) The interference due to the iron is that the extractable species also absorb strongly in the region of 450-550nm.

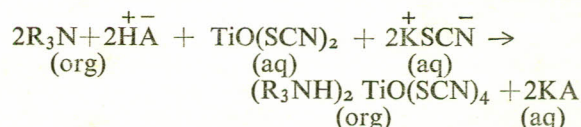
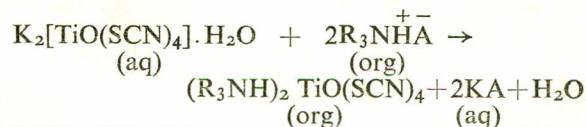
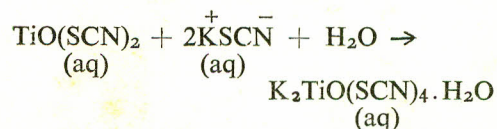
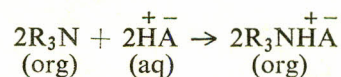
For the interferences of iron and of other two types, suitable masking agents have been suggested (Table 1).

As a final check one of us (B. A.) analysed the following unknown solutions. The results are shown in Table 2.

### Discussion

As indicated above, the orange yellow coloured complex formed between Ti(IV) and SCN<sup>-</sup> in presence of H<sub>2</sub>SO<sub>4</sub> (dil) is readily extracted into tribenzylamine and Allamine 336 in chloroform or benzene solution. The ready extraction of the coloured complex indicates that the complex is

anionic in nature like other metal thiocyanate complexes and liquid anion exchange occurred between the charged complex and the high molecular weight amines. The overall reaction for this type might be represented as follows:



Rosenheim and Colm<sup>19</sup> reported the formation of oxythiocyanate type of complex with pyridine and quinoline which is anionic in nature where H<sup>+</sup> + A<sup>-</sup> (aq) in the present case represent, H<sub>2</sub>SO<sub>4</sub> and Ti(II) and SCN<sup>-</sup> in aqueous solution. The conclusion that the complex is anionic in nature needs to be further investigated and its structure to be established.

The fact that the absorption spectra of the complex species is the same with all the amines in organic phase would indicate that the absorbing species is the same in each case. The fading of colour of the complex in aqueous phase indicates the instability of the complex which when bonded with a high molecular weight amine is sufficiently stable to make use of it as a very sensitive spectrophotometric method. The sensitivity of the absorbing species and the high molar absorption coefficient also indicate that the peak being used at 425nm is the only peak in the spectrum. This is also indicated by the size of the molar extinction coefficient.

Fe<sup>3+</sup> also forms various kinds of complexes with thiocyanate, and under optimal conditions they are also extractable in a similar way which are being looked into regarding their extractability by HMWA and will be reported later.

**Acknowledgement.** The authors wish to express their thanks to Professors Kai Grjotheim and Dosent Gunnar Thorseen, Technical University, Trondheim (Norway), for free supply of Allamine 336 which made this work a success.

#### References

1. E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.*, **67**, 48 (1948).
2. F. L. Moore, *Anal. Chem.*, **27**, 70 (1955).
3. H. A. Mahlman, G. W. Leddicotte and F. L. Moore, *ibid*, **26**, 1939 (1954).
4. J. Y. Ellenberg, G. W. Leddicotte and F. L. Moore, *ibid*, **26**, 1045 (1954).
5. G. W. Leddicotte and F. L. Moore, *J. Am. Chem. Soc.*, **74**, 1618 (1952).
6. C. F. Soleman, K. B. Brown, J. G. Moore and D. G. Crouse, *Ind. Eng. Chem.*, **50**, 1956 (1958).
7. K. B. Brown, C. F. Coleman, D. J. Course, C.A. Blake and A.D. Ryon, Second International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, paper 509.
8. J. B. Rosenbaum, S. R. Borrowman and J. B. Clemmer *ibid*, paper 501.
9. F. L. Moore, paper 85, presented to the Analytical Chemistry Division at 136th National Meeting of the American Chemical Society, Atlantic City, September, 1959.
10. K. A. Allen, *J. Am. Chem. Soc.*, **80**, 4133 (1958).
11. *idem*, *J. Phys. Chem.*, **60**, 239 (1956).
12. C. F. Baes, Jr. ORNL-1930, August, 1955.
13. C. F. Coleman, C. A. Blake Jr. and K. B. Brown, *Talanta*, **9**, 297 (1962).
14. M. A. Khattak and R. J. Magee, *Talanta*, **12**, 733 (1965).
15. M. Akram Khattak and R. J. Magee, *Anal. Chem. Acta*, **17**, 35 (1966).
16. M. A. Khattak and R. J. Magee, *ibid*, **45**, 297 (1969).
17. M. A. Khattak, *Pakistan J. Sci. Ind. Res.*, **14**, 43 (1971).
18. H. E. Affsprung, N. A. Barnes and H. A. Potratz, *Anal. Chem.*, **23**, 11 (1951).
19. C. A. Jacobson, *Encyclopaedia of Chemical Reaction*, (Reinhold, New York, 1958) vol. VII, p. 411.
20. E. B. Sandell, *Colorimetric Metal Analysis* (Interscience, New York), third edition, p. 873.