

## SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AFTER EXTRACTION OF THE Mo(VI)-Sn(II)-CNS SYSTEM BY A HIGH MOLECULAR WEIGHT AMINE

MOHAMMAD AKRAM KHATTAK

*PCSIR Laboratories, Peshawar*

(Received January 20, 1970)

An investigation of the complex formed between molybdenum(VI) and thiocyanate in presence of Sn(II) in hydrochloric acid solutions has been carried out, and its extractability by a high molecular weight amine (HMWA) in organic solvent examined. The orange coloured Mo(VI)-Sn(II)-CNS-complex is quantitatively extractable from an aqueous phase into an organic phase containing tribenzylamine. On the basis of this extractability a method has been developed for the spectrophotometric determination of molybdenum in presence of many 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 a HMWA suggests that the coloured species is anionic.

The use of high molecular weight amine (HMWA) as "liquid anion exchangers" and extractant for anionic complex metal ions has been mainly confined to the separation of specific pairs of ions<sup>1-4</sup> and to the extraction of uranium, thorium and plutonium.<sup>5-8</sup> In several cases, the elucidation of the structure of anionic species on the basis of extraction has been possible.<sup>9-12</sup> The most popular method of extraction of metals is as the halocomplexes from hydrochloric acid solution into an organic phase containing the amine. The present author studied the extraction of tin chlorocomplexes of Pt(IV),<sup>13</sup> Pd(II)<sup>14</sup> and Rh(III)<sup>15</sup> for the first time by HMWA.

In acid solution, thiocyanate gives an amber to orange red colour with molybdenum in presence of stannous chloride. Isoamyl alcohol and isopropyl ether are used as extractants for increasing the stability. The latter has the advantage of lower solubility in water as compared to isoamyl alcohol and therefore a mixture of isoamyl alcohol and carbon tetrachloride have been recommended.<sup>16</sup>

It has been observed that the colour on extraction and even before extraction develops a red colour on shaking with amyl alcohol, probably due to atmospheric oxidation of iron(III) thiocyanate which is an undesirable feature.

In a study on the nature of the Mo(VI)-CNS complex system, Babko<sup>17</sup> indicated the formation of red colour to be due to the presence of Mo(CNS)<sub>5</sub> in which molybdenum exists in quintuplicate form. In the belief that the species was more likely to be anionic than a neutral complex, investigations were begun in this laboratory with the aim of using tribenzylamine to extract the species and, if possible, use it for the spectrophotometric determination of molybdenum. The investigations were carried out to this end, and the results obtained are reported below.

### Experimental

#### Apparatus

Beckman Model Du spectrophotometer.

#### Reagents

*Molybdenum Standard Solution.*—1.5 g pure MoO<sub>3</sub> was dissolved in a few ml of dil sodium hydroxide, diluted with water, made slightly acidic with hydrochloric acid, and made upto 1 l. The solution was further diluted to 0.001% in 0.1N hydrochloric acid 1 ml=10 µg.

*Tin Chloride.*—10 g of the dihydrate in 100 ml of 1N hydrochloric acid.

*Ferrous Ammonium Sulphate.*—1 g in 100 ml of 0.2N sulphuric acid.

*Potassium Thiocyanate.*—10% aq solution.

*Tribenzylamine.*—A 0.2M solution was prepared by dissolving the crystals in chloroform. All other chemicals used were of AnalaR Grade.

*Formation of the Mo(VI)-CNS Complex and Extraction by Tribenzylamine.*—The orange coloured complex was formed by adding thiocyanate into a solution containing molybdenum in presence of hydrochloric acid and iron. The colour due to iron thiocyanate was readily discharged by the addition of stannous chloride and the orange colour of molybdenum thiocyanate was shaken with 5 ml of tribenzylamine in chloroform for 1-2 min. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phase. The colour of the complex after extraction was the same as in the aqueous phase. After filtering through filter paper to remove suspended water droplets, the solution was made upto volume in 10 ml flask with chloroform and the absorption spectrum determined with respect to a blank containing all the reagents, but no molybdenum, and extracted in the same way. The spectrum obtained is shown in Fig. 2. In Fig. 1 the absorption spectrum for the Mo(VI)-



CNS system extracted with amyl alcohol by the standard procedure, is shown for comparison. From these two figures it will be seen that the curves are identical, showing maximum absorption at 475 and 480  $m\mu$  in Figs. 1 and 2 respectively.

*Calibration, Sensitivity and Stability.*—Known concentrations of molybdenum were extracted by the foregoing procedure and absorbance measured at 480  $m\mu$ . For solutions containing between 1–60  $\mu\text{g}/10$  ml (0.1–6 ppm) Beer's law was closely obeyed. The results are shown graphically in Fig. 3. The sensitivity in tribenzylamine is the same as in amyl alcohol extract. The stability is greatly increased. The coloured solutions of molybdenum extracted by tribenzylamine were kept in the room in diffuse sunlight for a period of 15–30 days. The absorbancies were measured at regular intervals. At the end of the period there was no appreciable change in the measured readings.

*The Effect of Iron.*—A number of workers have observed that the presence of small amounts of iron increases the colour sensitivity in the stannous chloride–thiocyanate method.<sup>18</sup> In the present work, it was noted that while the presence of iron is essential, yet it affords a number of drawbacks from the practical standpoint, particularly when the coloured complex is extracted by isoamyl alcohol. Even in small amounts there is a tendency for the appearance of coloration of ferric thiocyanate in the organic phase. It has been reported that this can be prevented by shaking the extract with an equal volume of 1% stannous chloride.<sup>18</sup> Re-shaking of the extract was found to remove the colour in the blank, but at the same time there was a tendency of fading of colour very rapidly. The colour of ferric thiocyanate in most cases was found to be more pronounced in the blank and

on addition of even a few crystals of stannous chloride on the filter paper before filtration did not remove the colour as given in the recommended procedure.

Using tribenzylamine as extractant instead of isoamyl alcohol, the blank was found to be completely free from colour and reproducible results were achieved. The presence of iron was found to be essential for the development of maximum colour intensity but its presence did not give an additional colour of ferric thiocyanate.

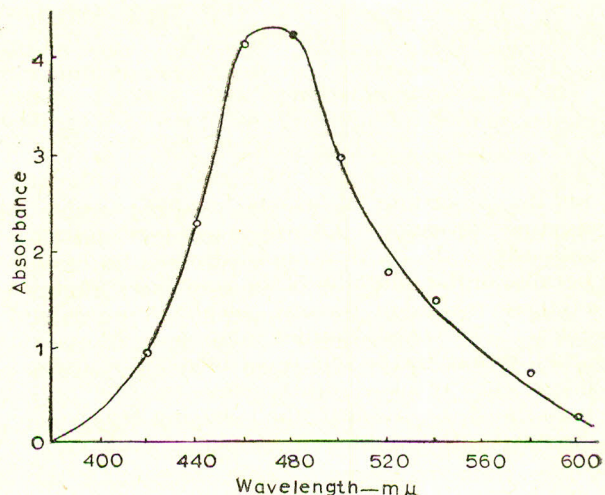


Fig. 2.—Absorption spectrum of Mo(VI)–CNS–Sn(II) system after extraction in 0.2 M tribenzylamine in chloroform.

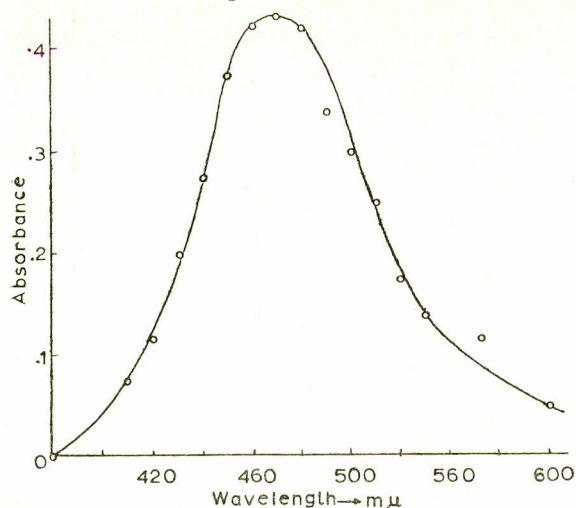


Fig. 1.—Absorption spectrum of Mo(IV)–CNS–Sn(II) system after extraction with isoamyl alcohol.

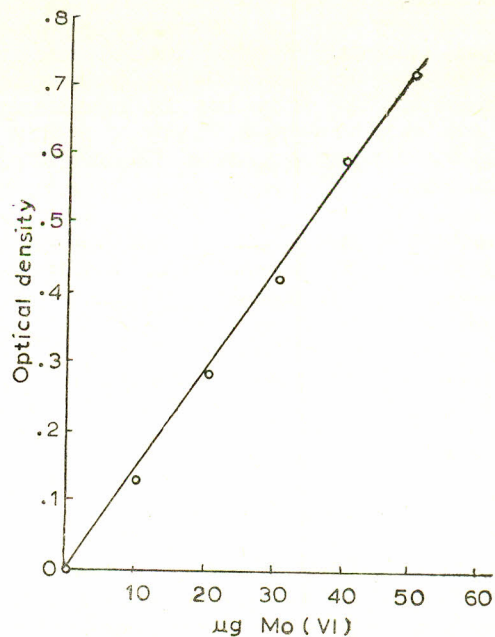


Fig. 3.—Std graph of Mo(VI) at 480 $m\mu$  extracted by 0.2 M TBA in chloroform.



*Interferences.*—Three types of interferences in the determination of molybdenum by the above procedure are most frequently encountered.

1. Ions which form an anionic complex with thiocyanate or tin(II) chloride will be extracted into the amine phase e.g. Pt(IV), Pd(II) and Rh(III).

2. Ions which form coloured non-ionic compounds with CNS and which are extracted into neutral solvents like isoamyl alcohol because of its solubility in these solvents e.g. Cr<sub>3</sub>.

3. Ions which oxidize CNS to a coloured, alcohol-soluble complex of indefinite composition.

With the exception of first type, fortunately none of the remaining two types interfere in the determination of molybdenum by the foregoing procedure. As will be seen the first type which interferes in the above procedure also interferes by the procedure in which isoamyl alcohol is used as extractant. The other two types interfere seriously in the amyl alcohol extraction procedure because of the solubility of the coloured complexes of these metals in isoamyl alcohol but are not extracted by tribenzylamine solution in chloroform and therefore the present procedure can be applied in presence of many other elements.

As shown in Table 1, the following results were obtained with the different elements examined.

TABLE 1.—DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF DIVERSE IONS.  
(Molybdenum taken, 40 µg)

Diverse ion	Amount µg	Molybdenum µg	
		Found	Error
Iron	1000	40.5	+0.5
Cobalt	2000	40.0	0
Nickel	2000	39.0	+1.0
Chromium	5000	39.5	-0.5
Copper	5000	40.3	+0.3
Lead	5000	40.0	0.0
Titanium	5000	40.0	0.0
Vanadium	3000	40.0	+0.4
Tungsten	5000	40.5	+0.5
Uranium	5000	41.0	+1.0
Sulphate	1 g	40.0	0.0
Nitrate		40.0	0.0
Phosphate		40.5	+0.5

### Discussion

As indicated above, the complex formed between Mo(VI) and CNS<sup>-</sup> in presence of tin(II) chloride is readily extracted into tribenzylamine in chloroform solution. The HMWA such as TBA in water-immiscible organic solvents behaves as "liquid anion exchangers" and it is assumed that

the coloured complex is anionic in nature and that 'liquid anion exchanges' occurs between the charged complex and the high molecular weight amine.

Dick and Bingley postulated the formation of the complex Mo<sub>2</sub><sup>III</sup> [Mo<sup>V</sup>O(CNS)<sub>5</sub>] in the absence of iron and of Fe<sup>II</sup> [Mo<sup>V</sup>O(CNS)<sub>5</sub>] in its presence, the part of the molecule within the brackets being the chromogenic portion. This formulation is based on the observation that when iron is absent, the molybdenum colour intensity is about 65 per cent of that obtained when an adequate amount of iron is present. Kolling<sup>19</sup> found that the addition of tetraphenylarsonium chloride forms tetraphenylarsoniummolybdenum (V) thiocyanate which is chloroform extractable. This would indicate that the complex need not be of the structure Mo<sub>2</sub><sup>III</sup>(Mo<sup>V</sup>(CNS)<sub>5</sub>) postulated by Dick and Bingley. The conclusion drawn from the present work that the complex is anionic in nature (on the basis of its extractability in HMWA) confirms the contention of Kolling. Further, from the fact that the absorption spectra of the complex species in amyl alcohol and organic amine phase is the same and would indicate that the absorbing species is the same in each case.

**Acknowledgement.**—The author wishes to express his thanks to Dr. S.A. Warsi, the then Director, PCSIR Laboratories, Peshawar for his keen interest shown in this work and also to Dr. M.L. Smith, Cento Scientific Secretary, Tehran, Iran, for supply of tribenzylamine through Cento, and to Mr. S. R. Saedi for his technical assistance.

### References

1. F.L. Moore, *Anal. Chem.*, **27**, 70 (1955).
2. H.A. Mahlman, G.W. Leddicotte and F.L. Moore, *Anal. Chem.*, **26**, 1939 (1954).
3. J.Y. Ellenberg, G.W. Leddicotte and F.L. Moore, *Anal. Chem.*, **26**, 1045 (1954).
4. G.W. Leddicotte and F.L. Moore, *J. Am. Chem. Soc.*, **74**, 1618 (1952).
5. C.F. Coleman, K.B. Brown, J.G. Moore and D. J. Crouse, *Ind. Eng. Chem.*, **50**, 1756 (1958).
6. K.B. Brown, C.F. Coleman, D.J. Crouse, G.A. Blake and A. Yon, Paper 509, Presented at the 2nd U.N. Intern. Conf. Peaceful Uses of Atomic Energy, Geneva (1958).
7. J.B. Rosenbaum, S.R. Borrowman and J.B. Clemner, Paper 501 Presented at the 2nd U.N. Intern. Conf. Peaceful Uses of Atomic Energy, Geneva (1958).
8. F.L. Moore, Paper 85, Presented to the Analytical Division, 136th Nat. Meet. Am. Chem. Soc., Atlantic City, N. J., (September 1959.)



9. M.L. Good and S.E. Bryan, J. Am. Chem. Soc., **82**, 5636 (1960); J. Inorg. Nucl. Chem., **20**, 140 (1961); **21**, 339 (1961).
10. M.L. Good, S.C. Srivastava and F.F. Holland, J. Anal. Chim. Acta., **31**, 534 (1964).
11. S.E. Bryan, M.L. Good and F. Juge, J. Inorg. Chem., **2**, 963 (1963).
12. M.L. Good and F.F. Holland, Jr., J. Inorg. Nucl. Chem., **26**, 321 (1964).
13. M.A. Khattak and R. J. Magee, Talanta, **12**, 733 (1965).
14. M. Akram Khattak and R. J. Magee, Anal. Chim. Acta., **35**, 17 (1966).
15. M.A. Khattak and R. J. Magee, *ibid.*, **45**, 297 (1969).
16. A.T. Dick and J.B. Bingley, Australian J. Expt. Bio. Med. Sci., **29**, 459 (1951).
17. A.K. Babko, J. Gen. Chem. (USSR), **17**, 642 (1947).
18. E.B. Sandell, *Colorimetric Metal Analysis* (Interscience, New York, 1959), 3rd edn., p. 645.
19. O.W. Kolling, Trans. Kansas Acad. Sci., **58**, 430 (1955).