Concentration and Spectrophotometric Determination of Molybdenum with Thiocyanate and Rhodamine 6G

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A method is described for the determination of molybdenum based on reaction with potassium thiocyanate and Rhodamine 6G in 0.55—0.8 mol dm^{-3} hydrochloric acid medium. The method is sensitive ($\varepsilon=2.63\times10^5$ l mol^{-1} cm^{-1}) and obeys Beer's law over the range 0.04—0.24 ppm of molybdenum. Selectivity can be considerably improved by collecting molybdenum on iron(III) hydroxide. In conjunction with the collection procedure, the method is useful to determine as low as 5 ppb of molybdenum present in 100 cm^3 of aqueous samples.

A number of ternary systems have been proposed for the spectrophotometric determination of molybdenum[1–5] and, amongst these, the method based on its reaction with thiocyanate and Rhodamine B in the presence of copper–thiourea complex[3] is attractive as it possesses high sensitivity ($\varepsilon=1.10\times10^5$ l mol^{-1} cm^{-1}), selectivity and, in addition, allows the determination to be completed directly in aqueous medium. Our investigation on these lines revealed that the use of Rhodamine 6G instead of Rhodamine B is advantageous, as the reaction proceeds in dilute hydrochloric acid medium without the addition of copper–thiourea complex and providing much superior sensitivity ($\varepsilon=2.63\times10^5$ l mol^{-1} cm^{-1}). Furthermore, Rhodamine 6G is less susceptible to colour changes due to slight changes in the acidity of the medium. Detailed study on this colour system showed that the few ions that interfere in the determination can be conveniently overcome by selectively collecting molybdenum(VI) on iron(III) hydroxide precipitate. In conjunction with the collection procedure, the method was found useful to determine as low as 5 ppb of molybdenum present in aqueous samples.

Experimental

Reagents. *Molybdenum(VI) Solution*: Dissolve 0.115 g of ammonium molybdate in water and dilute to 250 cm^3. Dilute appropriate volumes of this stock solution (250 ppm) with water to provide a 1.0 ppm solution.

Potassium Thiocyanate Solution (3%): Dissolve 3 g of potassium thiocyanate in water and dilute to 100 cm^3.

Rhodamine 6G Solution (0.01%): Dissolve 0.1 g of reagent (chrom a Gesellschaft, Schmid and Co., Stuttgart) in water and dilute to 1 dm^3.

Gelatin Solution (1%): Dissolve 1 g of gelatin in boiling water and dilute to 100 cm^3.

Apparatus: A Carl Zeiss PMQ-II spectrophotometer with 10 mm quartz cells and a Knick pH-meter with an Ingold combined glass-calomel electrode were used.

Recommended Procedure. *Determination*: Transfer a suitable aliquot (upto 10 cm^3) of the sample solution containing not more than 6 μg of molybdenum to a 25 cm^3 volumetric flask. Adjust the acidity to 0.55—0.8 mol dm^{-3} with hydrochloric acid and add with mixing 5 cm^3 each of potassium thiocyanate and Rhodamine 6G solution. Allow the reaction to proceed for 1 h and then add 1 cm^3 of 1% gelatin. Dilute the solution to mark with distilled water and measure the absorbance in 10 mm cells at 570 nm against a reagent blank. Prepare a calibration graph for 1—6 μg of molybdenum by the above procedure.

Concentration and Separation: To a suitable aliquot (upto 100 cm^3) of the sample add 2 mg iron(III) and adjust the pH to 4.0 under a pH-meter. Add 5 cm^3 of acetone, stir well and centrifuge the suspension. Discard the centrifugate and wash the suspension twice with 5 cm^3 of a 2% solution of ammonium chloride. Dissolve the precipitate by digesting with 5 cm^3 of 0.2 mol dm^{-3} hydrochloric acid and then treat with 2.5 cm^3 of 0.5 mol dm^{-3} sodium hydroxide to reprecipitate the iron. Centrifuge, wash the precipitate twice with 5 cm^3 of water and combine the centrifugate and washings. If the molybdenum content is large, make up the solution to a known volume and subject an aliquot to molybdenum determination. Otherwise, evaporate the solution to a small volume and complete the determination as given under "Procedure."

Results and Discussion

Preliminary Studies. Initial experiments indicated that after the addition of thiocyanate and Rhodamine 6G to molybdenum solution in 0.6 mol dm^{-3} hydrochloric acid, if the solutions were immediately diluted to 25 cm^3 with water, the colour development was quite incomplete. Omission of dilution with water caused both test and blank solution to acquire an intense pink colour but on standing, the colour of the blank slowly changed to orange red. However, later dilution with water as above to 25 cm^3 caused the pink colour of the test solution also to fade off gradually. Systematic investigation revealed that the colour system is colloidal in nature and stabilization can be achieved by the addition of small amounts of gelatin prior to dilution with water. In preliminary experiments, therefore, after the addition of reagent solutions, the reaction was allowed to proceed for 60 min to facilitate complete disappearence of the pink colour of the blank, and then treated with 1 cm^3 of 1% solution of gelatin and sufficient water to 25 cm^3.

The spectra of gelatin-stabilized solutions in 10 mm cells against distilled water is shown in Fig. 1. It is evident that the reagent blank absorbs maximally at 530 nm. In the presence of molybdenum, there is, in addition to this maximum, a new shoulder at 570 to 575 nm. The difference between the spectra of the complex and the reagent blank showed that 570 nm is the optimum wavelength for measurement.

Considerable enhancement in the absorbance of the sample at 570 nm was noticed when Rhodamine 6G concentration was increased to 5 cm^3 of 0.01%. This is

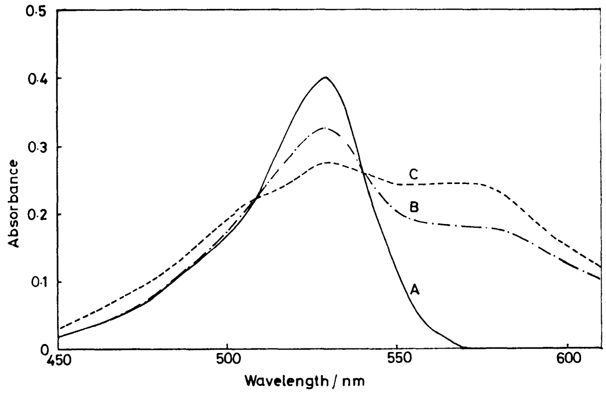

Fig. 1. Absorption spectra of molybdenum–thiocyanate–Rhodamine 6G system (0.6 mol dm^{-3} in HCl; total volume 25 cm^3; 10 mm cells).
A: 1.0 cm^3 of 2.1×10^{-4} mol dm^{-3} (0.01%) Rhodamine 6G, 1 cm^3 of 10% potassium thiocyanate and 1 cm^3 of 1% gelatin, reference: water, B,C: as in A, with 0.5 and 1 cm^3 of 1.05×10^{-4} mol dm^{-3} molybdenum, reference: water.

apparently due to increased association of the complex. Under these conditions, the blank showed an absorbance of 0.06 at 570 nm as against 0.28 and 0.61 obtained with solutions containing 0.2 and 0.5 cm^3 of 1.05×10^{-4} mol dm^{-3} of molybdenum present in 25 cm^3 respectively when measured in 10 mm cells.

Optimization of Experimental Conditions. Maximum absorbance was obtained when the acidity of the reaction medium, containing 3 μg of molybdenum, 5 cm^3 each of 3% potassium thiocyanate and 0.01%. Rhodamine 6G, was maintained from 0.55 to 0.8 mol dm^{-3} in hydrochloric acid. Similar studies at 0.6 mol dm^{-3} acidity on the variation of potassium thiocyanate and Rhodamine 6G concentration showed that the addition of 2 cm^3 of 5% potassium thiocyanate and 4 cm^3 of 0.01% solution of Rhodamine 6G was sufficient to provide maximum absorbance. Though 1 cm^3 of 0.75% solution of gelatin was found to be sufficient to stabilize the colour system, further addition did not affect the absorbance. When the recommended concentration of reagent solutions were added, maximum colour was produced after a standing time of 45 min, which after dilution remained stable for 90 min and the addition of as high as 5 cm^3 of saturated sodium chloride solution did not affect the absorbance. Under these conditions, the calibration graph was a straight line for 1—6 μg of molybdenum and passed through the origin. The molar absorptivity and Sandell sensitivity were established to be 2.63×10^5 dm^3 mol^{-1} cm^{-1} and 0.36 ng cm^{-2} respectively for the colour system at 570 nm.

Ten replicate determination of standard solutions containing 3.0 μg of molybdenum(VI) gave an average recovery of 102.5% with a relative standard deviation of 2.5%.

Effect of Diverse Ions. The effect of 40 diverse ions on the determination of 3.0 μg of molybdenum was examined. A few ions that interfered were overcome by adding thiourea, ascorbic acid or tartrate. The results obtained are summarized in Table 1. The interference due to zinc and cobalt(II) could not be masked.

Table 1. Effects of diverse ions[a]

Ion	Amount Added (mg)	Molybdenum Found (μg)	Ion	Amount Added (mg)	Molybdenum Found (μg)
Li^+	1	3.0	W(VI)	0.1[d]	3.0
Na^+	5	3.0	UO_2^{2+}	0.1[c]	3.1
Be^{2+}	1	3.2	Mn^{2+}	1	3.0
Mg^{2+}	1	3.0	Fe^{3+}	0.5[c]	3.0
Ca^{2+}	1	3.1	Co^{2+}	—	—
Sr^{2+}	1	3.0	Te^{4+}	1	3.1
Al^{3+}	1	3.3	Ni^{2+}	1[b]	3.1
Pb^{2+}	1[b]	3.0	Pd^{2+}	1[b]	3.0
Bi^{3+}	1[b]	3.1	Pt^{4+}	1[b]	2.9
Sb(V)	1	2.9	F^-	1	3.0
Cu^{2+}	1[b]	3.0	PO_4^{3-}	1	2.9
Zn^{2+}	—	—	SO_4^{2-}	5	3.0
Cd^{2+}	1[b]	3.2	Br^-	5	3.0
Hg^{2+}	1[b]	3.1	ClO_4^-	1	3.2
La^{3+}	1	3.0	NO_3^-	5	3.1
Ce^{4+}	1	3.0	Citrate	5	3.0
Th^{4+}	1	3.1	Oxalate	5	2.9
V(V)	0.1[c]	3.2	Tartrate	5	3.1
Cr(VI)	1[b]	3.0	Arsenate	1	3.1
Ba^{2+}	1	3.1	Arsenite	1	3.2

a) Molybdenum taken was 3.0 μg. b) 1 cm^3 of 5% thiourea. c) 1 cm^3 of 2% ascorbic acid. d) 1 cm^3 of 10% tartrate.

Composition of the Complex. The ratio of molybdenum to Rhodamine 6G was determined by both mole ratio and Job's continuous variation methods. The results obtained (Figs. 2 and 3) showed that the molar ratio of molybdenum to Rhodamine 6G is 1 : 2. The molar ratio of molybdenum to thiocyanate could not be established, as no colour developed upon treating with Rhodamine 6G, evidently due to instability of the molybdenum–thiocyanate binary complex.

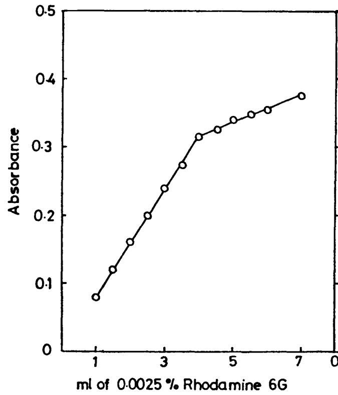

Fig. 2. Mole-ratio method (0.6 mol dm^{-3} in HCl, total volume 25 cm^3; 10 mm cells; 570 nm).
[Mo] = 1 cm^3 of 1.05×10^{-4} mol dm^{-3}, [Rh6G] = 1 to 7 cm^3 of 5.25×10^{-5} mol dm^{-3}.

Fig. 3. Continuous variation method (0.6 mol dm^{-3} in HCl; total volume 25 cm^3; 10 mm cells; 570 nm).
$[Mo+Rh6G]_{total} = 2.1 \times 10^{-5}$ mol dm^{-3}.

With Rhodamine B colour system,[3] it has been indicated that Mo(VI) is reduced to Mo(V) by copper–thiourea complex in sulfuric acid medium to form $[MoO(SCN)_5]^{2-}$ to facilitate association with 2 molecules of Rhodamine B cation. However, with the Rhodamine 6G colour system, as the presence of copper–thiourea did not affect the sensitivity, it appeared reasonable to conclude that the reduction of molybdenum(VI) proceeds smoothly in dilute hydrochloric acid medium in the presence of thiocyanate to form $[MoO(SCN)_5]^{2-}$ which then associates with 2 molecules of Rhodamine 6G cation to produce the observed spectral shift.

Evaluation of Iron(III) Hydroxide Collection. Though solvent extraction and ion-exchange find common use to separate interferents from the desired constituent, collection of molybdenum on a sparingly soluble metal hydroxide was considered for its separation from interfering elements. Earlier studies have shown that for the collection of molybdenum from weakly acidic solutions, thorium hydroxide (99.5% collected in 30 min)[6] is much superior to iron(III) hydroxide (96.5% in 2h),[7] aluminium hydroxide (7.8% in 2 h)[6] or manganese dioxide (100% in 24 h).[8] Iron(III) hydroxide collection, however, was chosen in the present study. Detailed investigations revealed that the addition of miscible organic solvents such as acetone, methanol, ethanol, 2-propanol, 4-hydroxy-4-methyl-2-pentanone, acetonitrile, 1,4-dioxane, and *N*,*N*-dimethylformamide to weakly acidic solution of molybdenum promoted rapid and quantitative collection on ferric hydroxide. Addition of acetone was chosen for further investigations. Later studies revealed that the molybdenum collected on iron(III) hydroxide was quantitatively released by dissolving the precipitate in dilute hydrochloric acid and reprecipitating it with alkali.

Systematic study of collection of molybdenum was made by adding 2 mg of iron(III) to 20 cm^3 aliquots of solution and using dilute sodium hydroxide to precipitate iron(III) hydroxide. The suspensions obtained were centrifuged and the supernatant liquid was rejected. In each instance the precipitate, after washing twice with 5 cm^3 of 2% ammonium chloride, was dissolved by digesting with hydrochloric acid ($\approx$5 cm^3 of 0.2 mol dm^{-3}) and then the pH was raised to $>$10.0 using sodium hydroxide ($\approx$2.5 cm^3 of 0.5 mol dm^{-3}) to reprecipitate the iron. The suspension was centrifuged and washed twice with 3 cm^3 portions of water. The centrifugate and washings were combined and evaporated to about 5 cm^3. Molybdenum content was then established by the procedure described under "Experimental."

Figure 4 shows the effect of variation of pH of the medium containing 5 cm^3 of acetone on the collection of 3 μg of molybdenum by iron(III) hydroxide. It is evident that the recovery is quantitative over the pH range 4.0 to 4.5 and that iron(III) hydroxide is ineffective at pH's greater than 9.0. Subsequent studies at pH 4.0 using 2 mg of iron(III) revealed that the addition of 5 cm^3 of acetone was sufficient to recover quantitatively 0.5 μg to 1 mg of molybdenum present in 100 cm^3 of sample. Collection of molybdenum was unaffected by the presence of 5 g of sodium chloride present in 100 cm^3 of sample.

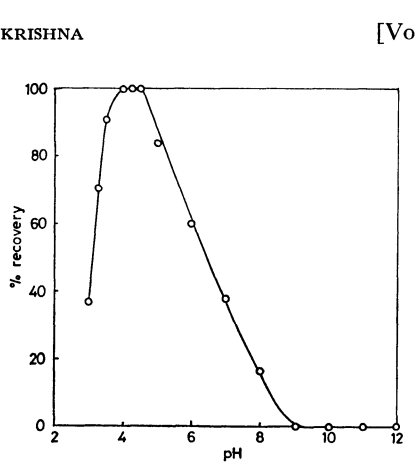

Fig. 4. Effect of pH on the collection of molybdenum on iron(III) hydroxide; 3 μg of molybdenum in 100 cm^3, 2 mg of iron(III) and 5 cm^3 of acetone.

Synthetic sample solutions containing 1—6 μg of molybdenum(VI) present in 100 cm^3 were taken through the collection and determination procedure and a calibration graph was prepared. A linear relationship was obtained over the whole range and the slope was identical to that obtained from aliquots of the standard molybdenum solution analysed without the collection step. The absorbance of blanks prepared with and without the collection step were also found to be comparable.

The ions that were found to interfere in the determination of molybdenum in the absence of masking agents were re-examined in conjunction with the collection procedure. Excepting tungsten, none of the ions at 1 mg level interfered in the determination of 3 μg of molybdenum. Small quantity of tungsten was found to accompany molybdenum as was evident from the enhancement in the absorbance value (0.33 to 0.90). Addition of tartrate, as described earlier, eliminated the interference due to tungsten.

Recovery Studies. As no standard samples were available for testing the collection and determination procedure developed, it was decided to examine the recovery of molybdenum added to soil and sea water samples collected at random. 5 g of finely ground soil samples dried at 110 °C were treated with 0, 5, and 10 μg of molybdenum(VI). Each sample was heated in a platinum crucible at 400—450 °C for 3 h to decompose any organic matter present. Then 10 cm^3 of water, 2 cm^3 of concentrated sulphuric acid and 10 cm^3 of concentrated hydrofluoric acid were added and heated gently until most of the liquid was evaporated. The crucible was then heated strongly to expel the residual sulphuric acid. The residue was dissolved in 6 mol dm^{-3} hydrochloric acid, rinsed into a beaker, and heated nearly to boiling, to bring all soluble material into solution.[9] The solution was filtered through Whatman No. 42 filter paper, washed with dilute hydrochloric acid collecting the filtrate and washings in a 100 cm^3-flask. The volume was then made up with water.

Aliquots of soil solution and sea water samples were

Table 2. Recovery of molybdenum added to soil and sea water samples

Sample	Aliquot taken (cm^3)	Mo added (μg/100 cm^3)	Mo Found (μg)	Recovery (%)
Soil extract	25	—	—	—
	25	5	1.3	104
	25	10	2.4	96
Sea water	50	—	—	—
	100	—	—	—
	50	10	5.1	102
	100	10	10.0	100
	100	1	1.05	105
	100	5	4.90	98

subjected to collection and determination procedure as described under "Experimental." The results are summarised in Table 2 which clearly indicate satisfactory recovery of molybdenum from both soil and sea water samples.

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