1736 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 1736—1738 (1980) [Vol. 53, No. 6

Hydroxyamidine as a Highly Selective Extractant for Spectrophotometric Determination of Molybdenum with Thiocyanate

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(Received April 16, 1979)

A highly selective method for the extractive-spectrophotometric determination of molybdenum is described. Molybdenum is reduced with ascorbic acid in strongly acidic media (2.0—4.5 mol dm^{-3} HCl), and complexed with N^1-hydroxy-N^1-*p*-tolyl-N^2-(3,4-dimethylphenyl)benzamidine in the presence of thiocyanate. The stoichiometry of mixed complex is found to be 1:2:2 (metal:reagent:thiocyanate). The red-orange molybdenum complex shows a sharp maximum at 470 nm having molar absorptivity 3800 dm^3 mol^{-1} cm^{-1}. All the metal ions associated with a matrix of molybdenum such as Ni(II), Co(II), Cu(II), Mn(II), Ti(IV), Zr(IV), V(V), Nb(V), Ta(V), and W(VI) do not interfere. The applicability of the method has been tested with an ore and various alloys.

A number of reagents such as thiocyanate–tin(II) chloride,[1] thiocyanate–copper(I) chloride,[1] toluene-3,4-dithiol,[1] phenylhydrazine,[1] chloranilic acid,[1] mercaptoacetic acid,[1,2] dithiooxamide,[3] 4-methyl-2-pentanol,[4] 2-mercapto-4*H*-1-benzothiopyran-4-one,[5] potassium ethylxanthate,[6] monooctyl α-anilinobenzylphosphonate thiocyanate,[7] and salicylhydroxamic acid[8] have been reported for extraction photometric determination of molybdenum. N^1-hydroxy-N^1,N^2-diarylbenzamidines, monobasic and bidentate chelating agents have been used for gravimetric determination[9—11] of nickel, copper, and molybdenum and colorimetric determination[12—14] of manganese, iron, and vanadium. N^1-Hydroxy-N^1-*p*-tolyl-N^2-(3,4-dimethylphenyl)benzamidine (abbreviated as Hhtdb), a newly synthesized monobasic and bidentate chelating agent is found to be a selective chromogenic reagent for extractive-photometric determination of molybdenum(V)–thiocyanate complex into benzene (using ascorbic acid as a reducing agent).

The present method is compared with the other methods mentioned above. All the methods except for those using thiocyanate–tin(II) chloride and thiocyanate–copper(I) chloride suffer either from interference of one or more elements such as iron, copper, nickel, cobalt, tin, titanium, zirconium, niobium, chromium, and tungsten, or absorbance due to reagent at wavelength of maximum absorption. The thiocyanate–tin(II) chloride is commonly used for extractive-photometric determination of molybdenum. However, a serious drawback of this method is that the colour intensity produced by a constant quantity of molybdenum depends upon a number of factors such as volume of the aqueous phase, coefficient of expansion of isopentyl alcohol, concentration of iron, and tin(II). The thiocyanate–copper(I) chloride method also has a number of drawbacks from a practical standpoint. The original volume of the sample solution should not exceed a few millilitres and iron should not be present in more than minute amounts. The disadvantages are overcome successfully in the present *N*-hydroxyamidine thiocyanate method. The *N*-hydroxyamidine thiocyanate method is simple, rapid and highly selective. Moreover, it is free from volume ratio of aqeuous phase, concentration of reagents, order of addition of reagents, temperature, standing time and correlation of colour intensity with iron concentration.

The present paper reports the solvent extraction and photometric determination of molybdenum(V)–thiocyanate complex with htdb, various optimization constants and nature of complex separation from various diverse ions and its application to the analysis of ore and alloys.

Experimental

Apparatus. Absorbance measurements were made with an ECIL UV-VIS spectrophotometer model-865 matched with 1-cm silica and quartz cuvettes. All pH measurements were made with a Systronic pH meter type-322.

Standard Molybdenum Solution. A 1000-ppm molybdenum solution was prepared by dissolving 1.8401 g of A. R. ammonium molybdate tetrahydrate in glass distilled water and diluting to 1 dm^3. The metal content of the solution was determined with use of 8-quinolinol.[15] The stock solution was diluted to desired concentration.

Preparation of Reagent. The reagent was prepared by condensation of equimolar ratio of *N*-(3,4-dimethylphenyl)-benzimidoyl chloride and *N*-*p*-tolylhydroxylamine in ether medium.[13,16] The resulting hydrochloride was treated with dilute ammonia to liberate the corresponding free base. The free base was crystallized from benzene:petroleum ether (2:1). Mp 154 °C; yield 68%. Found: C, 79.64; H, 6.42; N, 8.22%. Calcd for $C_{22}H_{22}N_2O$: C, 80.00; H, 6.66; N, 8.48%.

A 0.1% w/v solution of reagent in benzene was used. A 10 and 5% w/v aqueous solution of ascorbic acid and potassium thiocyanate respectively, were used throughout the experiment.

Procedure. Place an aliquot of solution containing 200 μg of molybdenum on a 100-cm^3 separatory funnel. To this add 5 cm^3 of ascorbic acid followed by 5 cm^3 of potassium thiocyanate in final dilution of 25 cm^3 aqueous volume with subsequent adjustment of the acidity to 3.5 mol dm^{-3} HCl. Add 25 cm^3 benzene solution of reagent and equilibrate for 3 min. Allow the phases to separate and transfer the benzene layer to a 50-cm^3 beaker containing 2 g of anhydrous sodium sulfate. Measure the absorbance at 470 nm against a reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of reagent and mixed complex are shown in Fig. 1. The reagent shows a negligible absorption in the region 450—700 nm. In the presence of thiocyanate a stable orange-red Mo(V)–htdb–SCN mixed complex is formed into benzene, showing a molar absorptivity of 3800 dm^3 mol^{-1} cm^{-1} at 470 nm.

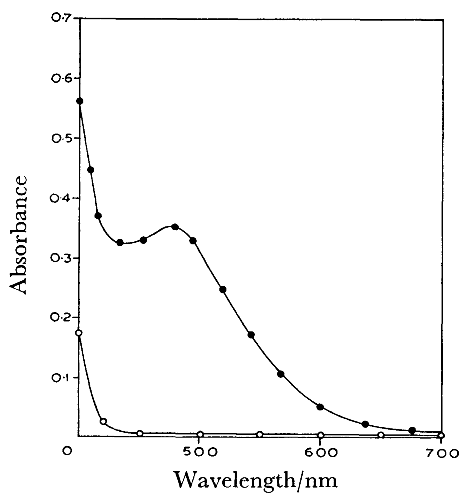

Fig. 1. Absorption spectra.
●: Mo(V)-htdb-SCN (8.33 10^{-5} M C_{Mo}), ○: 0.1% (w/v) Hhtdb in benzene.

Effect of Experimental Variables. Various water immiscible organic solvents such as benzene, toluene, carbon tetrachloride, and chloroform were examined for extracting the molybdenum mixed complex. Benzene was found to be the best solvent because of high extractability of mixed complex of molybdenum into it.

The acidity of aqueous phase was maintained with hydrochloric acid. Other mineral acids are unsuitable for extraction. If the concentration of hydrochloric acid in aqueous phase lies between 0.5—8.0 mol dm^{-3} the position of the absorption band of benzene extract remains intact but the absorbance value is affected. The optimum acidity range was found to be 2.0—4.5 mol dm^{-3} HCl.

A 30 and 300 fold molar excess of Hhtdb and thiocyanate were necessary for quantitative extraction of molybdenum. Addition of more reagents (100 and 2000 fold molar excess of Hhtdb and thiocyanate, respectively) has no adverse effect on the absorption and maximum wavelength of the coloured complex.

The period of equilibration was varied from 3 to 30 min. Extraction being quantitative after 3 min, it is recommended that the mixture be shaken for at least 3 min.

Variation in volume of aqueous phase in the range 10—60 cm^3 and temperature range 20—35 °C caused no measurable change in the absorbance of the molybdenum mixed complex. The benzene extract was stable for at least 20 h at 27±2 °C.

Beer's Law, Optimum Concentration Range and Precision. The molybdenum concentration range which follows Beer's law was found to be 3—20 ppm of metal. The optimum concentration range evaluated on the basis of the Ringbom plot[17] was 5—18 ppm of molybdenum. The precision of the system was checked by measuring the absorbance values of 10 samples, each containing 200 μg molybdenum/25 cm^{-3}. The relative standard deviation of the method was found to be 0.98%.

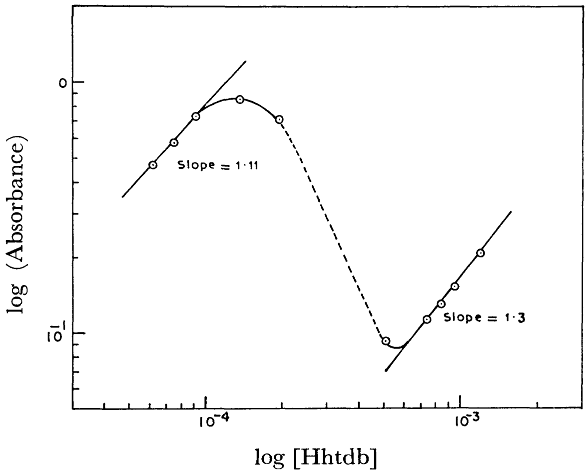

Fig. 2. Curve fitting method to determine the ratio of Mo(V) to $HOC_{22}H_{21}N_2$ in Mo(V)-$OC_{22}H_{21}N_2$-SCN complex.
0.1 mol dm^{-3} SCN, 3.0 mol dm^{-3} HCl.

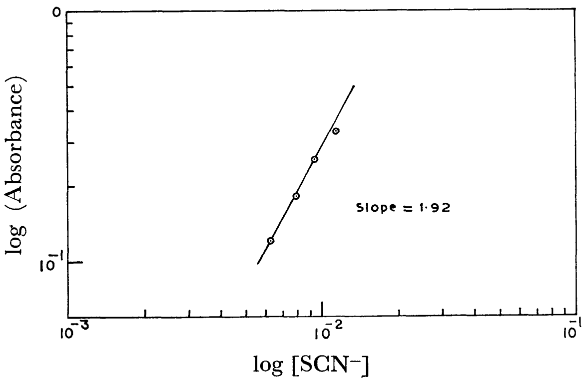

Fig. 3. Curve fitting to determine the ratio of Mo(V) to SCN^- in Mo(V)-$OC_{22}H_{21}N_2$-SCN complex.
0.003 mol dm^{-3} $HOC_{22}H_{21}N_2$, 3.0 mol dm^{-3} HCl.

Composition. In molybdenum–thiocyanate–htdb mixed complex the ratio of molybdenum to reagent and thiocyanate was determined by the curve fitting method[18] (log absorbance *vs.* log [M] of reagent/thiocyanate). The results showed the formation of a 1:2:2 (metal:reagent:thiocyanate) mixed complex in benzene (Figs. 2 and 3).

The absorbance of Mo(V)–htdb–SCN mixed complex varies with the amount of reagent. Absorbance increases up to 2 fold molar excess of reagent, then a sudden decrease in absorbance is observed in 3—6 fold molar excess and beyond 6 fold molar excess the absorbance gradually increases. The results indicate that 1:1:2 and 1:2:2 (metal:htdb:SCN) stable complexes are formed (Fig. 2). However, if the reagent is added in excess only a 1:2:2 mixed complex is formed.

The overall extraction equilibrium may be expressed as follows:[19)

$$MoO^{3+} + 2SCN^- + 2Hhtdb_o \rightleftharpoons MoO(SCN)_2OC_{22}H_{21}N_2(HOC_{22}H_{21}N_2)_o + H^+,$$

where $HOC_{22}H_{21}N_2$ denotes hydroxyamidine and subscript o, the organic phase.

Effect of Foreign Ions. In order to study the effect of diverse ions on the determination, an aliquot of molybdenum solution containing 200 μg of the metal was transferred to a 100-cm^3 separatory funnel and to this was added a solution containing a known amount of diverse ions. The acidity was adjusted to 3.5 mol dm^{-3} with hydrochloric acid and the total volume to about 25 cm^{3}, molybdenum being extracted with the reagent as described above. Chloride, bromide, nitrate, sulfate, urea, thiourea, tin(II), triethanolamine, borate, phthalate, selenate, alkali, and alkaline earth elements and lanthanoid elements have no interfering effect up to 3000 ppm. The tolerance limits for other ions are given in Table 1.

Application of the Method. In order to test the validity of method, two alloy steels obtained from Bureau of Analysed Sample Ltd., Newham Hall, Middlesbrough, Yorks, and an ore from Indian Bureau of mines, Nagpur, India, have been employed. The results are given in Table 2.

Dissolve an appropriate weight of the sample (1 g for 0.5% of molybdenum, 0.1—0.3 g for 5% of molybdenum) in 50 cm^{3} sulfuric acid, and oxidize with concentrated nitric acid. The solution is evaporated almost to dryness 3—4 times and diluted with water. Undissolved silica and inorganic matter are filtered off and the solution is diluted to a definite volume in a calibrated flask. Take an aliquot of this solution, add 5 cm^{3} of ascorbic acid solution and determine the molybdenum content by the procedure given above.

TABLE 1. TOLERANCE LIMIT FOR DIVERSE IONS

Ions added	Tolerated amount[a) ppm	Ions added	Tolerated amount[a) ppm
Fe(III)	1500	Ce(IV)	500
Ti(IV)	120	V(V)	120
Zr(IV)	700	Nb(V)	200
W(VI)	70	Ta(V)	250
Pd(II)	900	U(VI)	1600
Zn(II)	2200	Al(III)	2200
Ni(II)	2000	Co(II)	2000
Mn(II)	1600	Th(IV)	1500
Cr(III)	1600	Cu(II)	1200
Oxalate	800	Citrate	800
Tartrate	800	Phosphate	1500
Fluoride	900	Iodide	1000
Thiosulfate	700	EDTA	1000

a) Less than 2% error.

TABLE 2. DETERMINATION OF MOLYBDENUM IN ORE AND ALLOY STEELS

Sample	Certified value %	Found,a) %	Standard deviation
Oreb)	2.9	2.89	±0.0328
Steel, BCSc) No. 64a	4.11	4.08	±0.0469
Steel, BCSc) No. 241/1	0.52	0.495	±0.0636

a) An average of 6 determinations. b) Obtained from Indian Bureau of Mines, Nagpur. c) British Chemical Standard.

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