September, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2811—2813 (1983) 2811

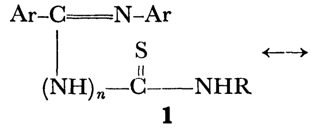
Extraction–Spectrophotometric Determination of Molybdenum(V) with Imidoyl Derivatives and Thiocyanate

Khageshwar Singh Patel*,† and Rajendra Kumar Mishra
Department of Chemistry, Ravishankar University, Raipur-496 010 M.P., India

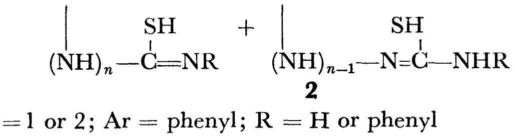
(Received January 29, 1982)

Three new organic reagents derived from *N*-phenylbenzimidoyl chloride and thiourea, phenylthiourea or thiosemicarbazide react with Mo(V) in strongly acidic media in the presence of thiocyanate ions to give rise red-orange complexes, insoluble in water but soluble in benzene. The nature of the ligands has been described to be as univalent, bidentate chelating agents which may coordinate to Mo(V) to form complexes with the composition of Mo 0.2SCN·SR (SCN denotes thiocyanate ion and SR, deprotonated form of the reagents). The molar absorptivity of the complexes was found to be in the range of $(0.8—1.4)\times10^4$ l mol^{-1} cm^{-1} at λ_{max}, 465 nm. The method is simple, rapid and highly selective for Mo. The ferroalloy elements which are associated with the metal do not interfere with the determination. The method was applied to the analysis of ore and alloy steel samples for Mo.

Many methods have been reported for the spectrophotometric determination of molybdenum in soils, ferroalloys, *etc.*[1–8] However, they suffered from many practical difficulties such as interference of cations including Mn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Nb^{5+}, Ta^{5+}, and W^{6+}; variation of color intensity of the complex with respect to amount of reagents and standing time; prolonged extraction of the metal with rigid control of some analytical variables; requirement of Fe^{2+} or Ti^{3+} for full color development.[1–2,5,8] In the present paper, a simple, convenient and highly selective extractive-spectrophotometric method is described for the determination of micro amounts of the metal with newly synthesized imidoyl derivatives, namely, (*N*-phenylbenzimidoyl)thiourea (PBTU), *N*-(*N*-phenylbenzimidoyl)-*N*-phenylthiourea (PBPTU) and 1-(*N*-phenylbenzimidoyl)thiosemicarbazide (PBTSC) in the presence of thicyanate ions. Of these, PBPTU has been preferred for detail study owing to wide acidity range for the extraction of the metal and high distribution coefficient of the reagent. They are stable towards heat, light and air, and their solutions can be stored for a long time without deterioration. Each compound may exist as the tautomers **1** and **2**, in the fashion similar to esters and amides and the species containing a SH group would react with Mb(V)–SCN$^-$ to form benzene-extractable complexes.



1



2

$n=1$ or 2; Ar = phenyl; R = H or phenyl

Experimental

Apparatus, Reagents, and Solutions. The absorbances were read with an ECIL UV-VIS spectrophotometer model GS-865 matched 1-cm cells and recorded with a Carl-Zeiss Specord UV-VIS spectrophotometer.

All chemicals and reagents used were of Analytical grade. A stock solution of molybdenum(VI) was prepared by dissolving 2.01 g of ammonium molybdate in 1 l of distilled water and standardized gravimetrically.[9]

Imidoyl derivatives were prepared by the condensation of equimolar amount of *N*-phenylbenzimidoyl chloride with the respective substances like thiourea, phenylthiourea and thiosemicarbazide at 120 °C. The products were recrystallized from ethanol and characterized in terms of melting point, elemental analysis and ultraviolet and infrared spectra.[10]

About 0.2—0.4% (W/V) solutions of the reagents in benzene, 20% (W/V) solutions of L-ascorbic acid and ammonium thiocyanate and 10 M hydrochloric acid or sulfuric acid (1 M = 1 mol dm^{-3}) were used.

All the solutions employed were presaturated with benzene.

Procedure. A sample solution containing upto 100 μg of Mo was transferred to a 100-ml separatory funnel. Into this was added 3 ml each of L-ascorbic acid and ammonium thiocyanate solution in a final volume of 25 ml at desired acidity. The solution was equilibrated with 25 ml benzene solution of the relevant reagent for 2 min. After seperation of the two phases, the organic phase was dried with 2 g of anhydrous sodium sulfate in a 50-ml beaker. The absorbance of the benzene extract was measured at λ_{max} against a suitable reference.

Results and Discussion

Spectral Characteristics. The absorption spectra of PBPTU and its Mo(V)–SCN$^-$ complex are shown in Fig. 1. The imidoyl derivative complexes showed a sharp λ_{max} around 465 nm and its position was intact with respect to variation of the amount of reagents and the acidity of the aqueous phase. The molar absorptivity of the complex was evidently affected by the type of functional grouping or substituent, as shown in Table 1.

Choice of Solvents and Reducing Agents. The Mo(V)-complexes are extracted into many organic solvents such as benzene, toluene, chloroform, carbon tetrachloride, acetophenone and 1-pentanol. Benzene was selected as the solvent beacuse of the highest extractability as well as the highest stability of the complex. L-Ascorbic acid and tin(II) chloride were tested for the reduction of Mo(VI) to Mo(V). Variation of the amount of L-ascorbic acid was insensitive to the absorbance of the complex. Tin(II) chloride is too strong as a reducing agent for Mo(VI); it did not

---

† Present address: Department of Chemistry, K. Govt. Arts and Science College, Raigarh-496 001, M.P., India.

Table 1. Spectral data of Mo(V)–SCN^-–PBTU–PBPTU–PBTSC complexes in benzene at 2.0 M HCl

Compound	Acidity range M HCl	Molar absorptivity at λ_{max}, 465 nm $l\ mol^{-1}\ cm^{-1}$	Sandell's sensitivity $\mu g\ cm^{-2}$ of Mo
(*N*-Phenylbenzimidoyl)thiourea	1.2—2.5	8000	0.0120
N-(*N*-Phenylbenzimidoyl)-*N*-phenylthiourea	1.0—5.0	13000	0.00738
1-(*N*-Phenylbenzimidoyl)thiosemicarbazide	1.2—3.5	14000	0.00685

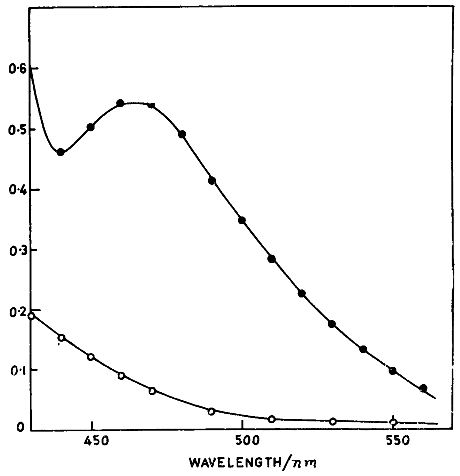


Fig. 1. Absorption spectra of PBPTU and its complex in benzene.
[HCl]: 4.0 M, [SCN]: 0.3 M, [PBPTU]: 0.006 M, [Mo]: 95 μg. —●—: Mo(V)–SCN^-–PBPTU, —○—: 0.2%, W/V (0.006 M) PBPTU.

produce color as much as L-ascorbic acid and the color intensity of the complex gradually decreased as its concentration increased. The color can also be developed in the presence of thiocyanate ions which serve not only as a weak reducing agent for Mo(VI) but also as a ligand for Mo(V). In this case, however, a prolonged time was required for the full color development. Therefore, L-ascorbic acid was preferred for the experimental work.

Effect of Acidity. The effect of acidity on the extraction of Mo(V) with imidoyl derivatives in the presence of thiocyanate ions was studied with various acids like HCl, H_2SO_4, HNO_3, and CH_3COOH. Of these, only HCl and H_2SO_4 were found to be adequate for the extraction purpose. The optimum acidity ranges for the extraction of the metal with SCN^- and PBPTU lie between 1.0—5.0 M HCl/0.8—6.0 M H_2SO_4. The optimum acidity ranges for PBTU and PBTSC were examined in a similar way and shown in Table 1. The later experimental work was performed with PBPTU at 4 M HCl.

Effect of Other Variables. At least 130-fold molar excess of PBPTU was necessary for the complete extraction of the metal. Similarly, at least 0.05—1.0 M ammonium thiocyanate was required for the full color reaction. The order of addition of reagents was not critical. Variation of temperature from 15 to 35 °C and volume of the aqueous phase from 15 to 60 ml did not affect the color intensity of the complex. A period of 2 min was sufficient for the complete extraction of the complex and more extraction up to 30 min produced no measureable change in the absorbance. The metal complex was stable for at least 10 h at room temperature. The effect of salting out agents like NaCl, KCl, or $(NH_4)_2SO_4$ was studied and no remarkable change in the extraction of the metal was noticed up to 2 M.

N-Phenylbenzimidoyl Derivatives as Analytical Reagents. All the derivatives react with Mo(V) in hydrochloric acid solution in the presence of thiocyanate ions to give benzene-extractable red-orange complexes, the optimum acidity ranges being tabulated in Table 1. The colored systems obeyed Beer's law. When PBPTU was used as the reagent, Beer's law is obeyed over the range 0.5—7.0 ppm of Mo, the optimum concentration range for the determination being 0.8—6.5 ppm. The precision of the method was evaluated by determining 75 μg of Mo/25 ml and the relative standard deviation was found to be ±0.81% for 10 measurements. As shown in Table 1, the phenyl substitution on the thioureido group of PBTU improved the molar absorptivity of the complex and the optimum acidity for the extraction of the metal to a considerable extent. The high extractability of the complex may be attributed to the highly organophilic nature of PBPTU molecule. At least 2—3 times molar excess of PBTU and PBTSC to PBPTU was required for the complete extraction of Mo. Therefore, PBPTU was found to be the most convenient reagent for the spectrophotometric determination of Mo(V) in the present investigation.

Composition of the Complex. The composition of the complex was determined by curve-fitting method[11] using the relationship between log *D* (distribution ratio of the metal) and log [Reagent concentration]. The results obtained indicates the formation of a 1 : 2 : 1 (Mo : SCN^- : RS^-) red-orange ternary complex in benzene. The overall reaction can be expressed as follows:

$$MoO^{3+} + 2\,SCN^- + HSR_o \rightleftharpoons Mo\,0.2\,SCN\cdot SR_o + H^+.$$

Where, subscript o denotes organic phase.

Effect of Diverse Ions. The effect of diverse ions in the solvent-extraction and subsequent spectrophotometric determination of 3 ppm of Mo at 4 M HCl with

Table 2. Determination of molybdenum in ore and alloy steels with PBPTU

Sample	Mo found[a] (%)	Mo certified (%)	Relative standard deviation ±%
Ore[b]	2.086	2.091	0.62
BCS 64	4.092	4.11	0.78
BCS 219/3	0.595	0.60	0.86
BCS 225/2	0.340	0.34	0.84

a) Average of six determinations. b) Obtained from Indian Bureau of Mines, Nagpur, India. BCS, British Chemical Standard.

thiocyanate ions (0.3 M) and PBPTU (0.006 M) in benzene was examined. The following metal ions did not interfere up to 2 M Cl^-, Br^-, SO_4^{2-}, or alkali metals; up to 1 M Mn^{2+}, Ni^{2+}, Cr^{3+}, or U^{6+}; up to 0.5 M alkaline earth elements, lanthanoid, Zn^{2+}, Cd^{2+}, Fe^{2+}, Al^{3+}, $C_2O_4^{2-}$, citrate, tartrate, or phosphate. The tolerated amounts of other ions (in ppm) causing an error $<2\%$ are shown in parentheses: Fe^{3+}, Bi^{3+}, Sb^{3+}, Tl^{3+}, Th^{4+} (1500); Hg^{2+}, F^-, $S_2O_3^{2-}$ (1000); Pb^{2+}, Zr^{4+} (2000); I^-, AsO_4^{3-} (3000); Co^{2+}, Pd^{2+}, V^{5+}, Ta^{5+} (400); Nb^{5+}, or W^{6+} (200).

Application of the Method. The method was satisfactory applied to the determination of Mo in ore and some alloy steels, the results being tabulated in Table 2. A weighed sample containing about 2 mg of Mo was decomposed first with aqua regia (10 ml), and then with concentrated H_2SO_4 (3 ml). The sulfuric acid solution was heated to fumes of SO_2, cooled, dissolved with 0.5 M HCl and made up with water to a desired volume. The metal content of the solution was determined as described in the recommended procedure using a suitable reference.

References

1) Z. Marczenko, "Spectrophotometric Determination of Elements," Horwood, Chichester (1976), p. 361.

2) C. P. Savariar, M. K. Arunachalam, and T. R. Hariharan, *Anal. Chim. Acta*, **69**, 305 (1974).

3) D. A. Willian, I. J. Holomb, and D. F. Boltz, *Anal. Chem.*, **47**, 2025 (1975).

4) B. Tamhina, M. J. Herak, and V. Jagodic, *Anal. Chim. Acta*, **76**, 417 (1975).

5) A. G. Fogg, J. L. Kumar, and D. T. Burns, *Analyst*, **100**, 311 (1975).

6) M. Mitra and B. K. Mitra, *Talanta*, **24**, 698 (1977).

7) H. P. Tarasiewicz, A. Grudniewska, and M. Tarasiewicz, *Anal. Chim. Acta*, **94**, 435 (1977).

8) T. J. Koralewski and G. A. Parker, *Anal. Chim. Acta*, **113**, 389 (1980).

9) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," 3rd ed, Longmans Green and Co. Ltd., London (1961), p. 508.

10) K. S. Patel and R. K. Mishra, to be communicated.

11) L. G. Sillen, *Acta Chem. Scand.*, **10**, 185 (1956).