

2-Benzylpyridine as a Chromogenic Reagent for the Micro Determination of Molybdenum and its Application to Steel Samples

ASLAM KHAN, ALI RUSHEED AND SUHAIL AHMED

*Nuclear Chemistry Division,
Pakistan Institute of Nuclear Science and Technology (PINSTECH),
P.O. Nilore, Islamabad, Pakistan.*

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Summary: A simple, rapid and interference free spectrophotometric method for the determination of micro amounts of molybdenum (V) is reported. The method is based on the quantitative extraction of Mo(V) by 0.05 M 2-benzylpyridine (BPy) solution in benzene from 3 M HCl solution containing 1 M thiocyanate and 0.4 M ascorbic acid. The maximum absorption of Mo(V)-SCN-BPY complex in benzene occurs at 470 nm. The Beer's law is obeyed in the concentration range 0.2-2 $\mu\text{g/g}$. The molar absorptivity and Sandell's sensitivity of the benzene extracted complex is $1.76 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $5.4 \times 10^{-4} \mu\text{g cm}^{-2}$ respectively. The effect of foreign ions has been studied. The method permits the determination of molybdenum in presence of commonly associated elements.

Introduction

2-Benzylpyridine acts as a monodentate chelating ligand and produces complex by sharing a lone pair of electron on nitrogen atom with the metal ions. This reagent has been used for selective extraction of Co(II), Hg(II) and Zn(II) [1-3]. In this communication spectrophotometric determination of Mo(V) as Mo(V)-SCN-BPy mixed ligand complex is reported subsequent to its extraction in benzene. The probable formula of the extracted complex is proposed on the basis of slope analysis of $\log D$ vs $\log [\text{reagent}]$ by curve fitting method [4]. The method can be applied for the analysis of rocks, ores, alloys, water and environmental samples.

Results and Discussion

Absorption spectrum

Absorption spectra of Mo(V)-BPy-SCN complex in benzene and reagent blank are shown in Fig. 1. The spectra of the complex shows maximum absorption at 470 nm.

Choice of solvent

Benzene, chloroform and carbon tetrachloride were tried as solvents. The complex was extractable in all these solvents. Benzene was chosen because of its easy phase separation and stability of the complex. For reduction of Mo(VI), ascorbic acid was preferred in order to avoid interference of tin.

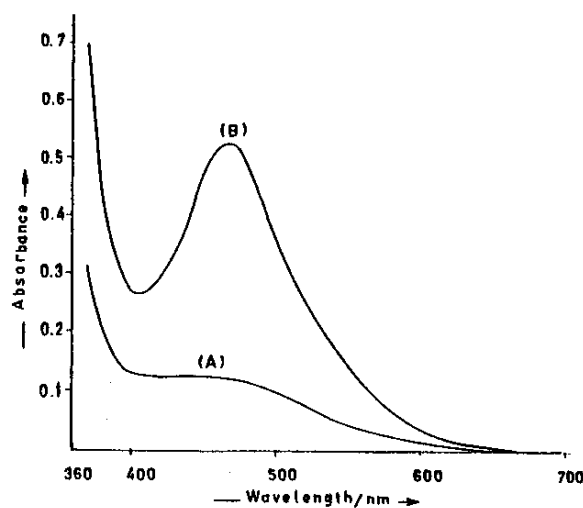


Fig. 1: Absorption spectra (A) Reagent blank. (B) Mo-BPy-SCN complex in benzene.

Effect of reagent concentration

The effect of BPy and thiocyanate on colour development was studied. The results obtained show that 10 μg of molybdenum in 3 M HCl solution required 30 mg thiocyanate and 4.23 mg BPy for colour development. The addition of excess BPy caused settling of complex. The order of reagents mixing is not critical and shaking time of 10 minutes is sufficient for full colour development.

Composition of extracted complex

The composition of the complex was determined by curve fitting method [4] based on plotting $\log D$ (distribution) vs $\log [\text{Reagents}]$, here $D = A / (A_{\text{max}} - A)$ where A is absorbance of coloured organic phase and A_{max} is the maximum absorbance of organic phase shown in Fig. 2. The slope of plot "A" is 1.9, whereas that of "B" is 2.1. Both are very close to integer 2, which shows that the ratio of Mo:SCN:BPY in the extracted complex is 1:2:2 and the probable formula of the extracted complex may be presented as $\text{Mo}(\text{BPY})_2 (\text{SCN})_2 \text{Cl}$.

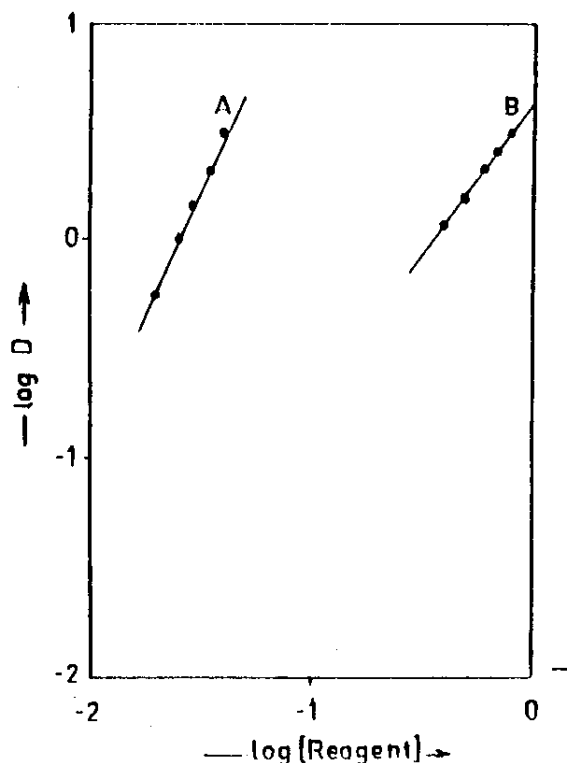


Fig. 2: Determination of the composition of complex Mo-BPY-SCN in benzene by curve fitting method. $[\text{HCl}]$, 3 M; [Ascorbic acid], 0.25 M. (A) Dependence of $\log D$ vs $\log [\text{BPY}]$ at constant $[\text{SCN}]$. (B) Dependence of $\log D$ vs $\log [\text{SCN}]$ at constant $[\text{BPY}]$.

Calibration, sensitivity and stability

Known concentrations of molybdenum were complexed by the foregoing procedure and their absorbance was measured at 470 nm. For solutions

containing 0.2 - 1.0 $\mu\text{g/g}$ molybdenum, Beer's law was obeyed. The molar absorptivity is $1.76 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity is $5.43 \times 10^{-4} \mu\text{g cm}^{-2}$. The colour of the complex is stable at least for three days when kept in dark.

Effect of diverse ions

The results obtained from the effect of different ions on the determination of 10 μg are presented in Table-1. These results show that most of associated ions do not interfere, and the interference of $\text{Cu}(\text{II})$ and $\text{Fe}(\text{III})$ ions can be easily masked with sodium thiosulphate.

Table-1: Effect of different ions on the determination of 10 μg Mo(V) at 3 M HCl.

Ion	Amount Added (mg)	Mo Found (μg)	% Error
Zn(II)	1	10.10	1.0
Al(III)	4	9.75	2.5
Sb(III)	1	9.80	2.0
Th(IV)	1	10.00	0.0
Zr(IV)	3	9.9	1.0
Fe(II)	6	10.1	1.0
Ni(II)	8	10.2	2.0
Cd(II)	4	9.85	1.5
Hg(II)	2	10.2	2.0
Pb(II)	1	9.9	1.0
Ce(II)	10	10.0	0.0
Eu(III)	10	10.0	0.0
Cr(III)	10	10.2	2.0

The mean error is less than $\pm 2\%$.

Application

The usefulness of the proposed method was tested by analyzing different synthetic mixtures and steel alloys and the results are given in Table-2 and 3 respectively, which show that the amount of molybdenum found in each mixture was in good

Table-2: Determination of Molybdenum in various synthetic mixtures

Mixture No.	Composition	Mo found (μg)	Relative standard deviation \pm (%)
1.	40 μg Mo(VI)+ 10mg Mg(II) + 10mg Bi(III)+ 20mg Zr(IV)	39.8	0.20
2.	40 μg Mo(VI)+ 10mg Cd(II) + 5mg Mn(II)+ 10mg Zn(II)	38.9	0.18
3.	40 μg Mo(VI)+ 2mg W(VI) + 5mg Cd(II)+ 5mg Th(IV)	40.2	0.22
4.	40 μg Mo(VI)+ 5mg Mn(II) + 1mg Zr(IV)+ 10mg Pb(II)	39.8	0.21
5.	40 μg Mo(VI)+ 2mg Cr(III) + 2mg Eu(III)+ 10mg Fe(II)	40.1	0.19

*Average of five determinations.

Table-3: Determination of Molybdenum in steel alloys

*Sample	Mo found by ICP	**Mo found by proposed method	Relative standard deviation \pm (%)
Steel I	0.171	0.173	+1.17
Steel II	2.900	2.875	-0.86
Steel III	0.749	0.741	-1.07
Steel IV	2.799	2.778	-0.75

*Steel purchased from market.

**Mean triplicate analysis.

agreement with that added in the mixture. The relative standard deviation is, $\leq 0.22\%$ ($n=5$). Similarly the results of steel alloys show % error ≤ 1.0 .

Comparison with other spectrophotometric methods

Table-4 presents the comparison of the prescribed method with some other spectrophotometric methods for the determination of molybdenum. It is

evident that the sensitivity of this method is higher than the sensitivity of the methods [15-21] and is more sensitive than procedures reported [5-14].

Experimental

Hitachi-557 UV-Visible double beam spectrophotometer with matched 1 cm quartz cells was employed to measure the absorbance.

Reagents

The standard solution of Mo(VI) was prepared by dissolving sodium hepta-molybdate tetrahydrate in doubly distilled water. 2-benzylpyridine (BPy) was obtained from Fluka, A.G., and was used as such. All other chemicals used in this work were of analytical grade supplied by Merck. 5 M potassium thiocyanate solution, 8 % ascorbic acid and 5 M HCl were used for extraction. A 0.05 M solution of 2-benzylpyridine was prepared in benzene.

Table-4: Comparison of spectrophotometric methods for determination of molybdenum.

Method	Extinction coefficient ($e^{m\mu}$) $M^{-1} cm^{-1}$	Interferences	Ref.
2-Benzylpyridine + thiocyanate (proposed method)	$e^{470}, 1.76 \times 10^4$	The interference of Fe and Cu may be masked with $Na_2S_2O_3$	
Triethyl amine	$e^{460}, 2.4 \times 10^4$	Cu, Ta, Ti, Nb, W	5
Quinoline	$e^{470}, 1.8 \times 10^4$	Cu, Co, Fe, Ti, W,	6
Tetrabutyl ammonium ion	$e^{465}, 2.7 \times 10^4$	V, Co, Cr, Fe, Cu	7
Antipyrine	$e^{440}, 1.9 \times 10^4$	Fe, Cu, Nb, Ta, Bi	8
Chloropromazine hydrochloride	$e^{465}, 1.6 \times 10^4$	Co, Cu, Fe, Bi, Ti, W, UO	9
e-Capro lactum	$e^{475}, 2.0 \times 10^4$	Mg, Al, Ca, Ba, Mn, As, Ag, Cu, Pb, Sn, V, Zn, Co, Cr, Fe, Ni, Zr	10
Hexamethyl phosphoramide	$e^{460}, 1.76 \times 10^4$	Re, Nb, Ta, Cu, Fe and W	11
Nitron	$e^{465}, 1.5 \times 10^4$	Mn(VIII), Ti(IV), and peroxide interfere at all concentration	12
Methotrimeprazine	$e^{465}, 1.6 \times 10^4$	Fe, V, Mn, Cu.	13
Octyl (a-anilino benzyl) phosphate	$e^{470}, 5.8 \times 10^3$	Cu, Ti, Zr, Th, Fe, U.	14
N-(4-chlorophenyl)-N-hydroxy-N-(2,3-xylyl) p-(toluamidine)-hydrochloride	$e^{470}, 4.0 \times 10^3$	Most of the cations and anions associated with Mo may be tolerated	15
Dialkyl anilinium perchlorate	$e^{470}, 1.5 \times 10^4$	Fe	16
Perazinedimalonate {10-[3-(4-methyl 1-peparizinyl) propyl]p-henothiazine diamalonate}	$e^{460}, 1.06 \times 10^4$	V, Ca, Cr, Fe	17
N-(4-chlorophenyl)-N-(4-chloro-ions o-tolyl)-N-hydroxy-benzamidine hydrochloride	$e^{470}, 4.5 \times 10^3$	No interference from most of the metal ions	18
Thiocyanate-hydroxy amidine [N-hydroxy-N-p-tolyl-N-3,4-xylyl-benzamidine	$e^{470}, 3.8 \times 10^3$	No interference from Ni, Co and Mn.	19
2-Chloro-N,N-bis(4-chlorophenyl)-N-hydroxybenzamide	$e^{470}, 3.3 \times 10^3$	Most of cations and anions within studied limits do not interfere	20
Butyl triphenyl phosphonium bromide	$e^{470}, 1.2 \times 10^4$	Ni, Zn, Co, Mn, V, Fe, W	21

Procedure

A mixture of solutions containing 2-10 µg Mo(VI), 0.5 ml of ascorbic acid, 1 ml of thiocyanate solution and 3 ml of HCl, was diluted to 5 ml with distilled water and mixed thoroughly with 5 ml BPY in benzene in a separating funnel. After ten minutes the organic layer was separated dried over anhydrous sodium sulphate and its absorbance was measured at 470 nm against reagent blank.

Conclusion

The present method is simple sensitive, rapid and does not need prior separation for the determination of molybdenum. The colour of the complex is stable and the order of mixing of reagents is not critical. The method can be applied for the analysis of molybdenum steel.

References

1. S. Zuha, A. Rusheed, *J. Radioanal. Nucl. Chem.*, **133**, 241 (1989).
2. A. Rusheed, S. Ahmed, *J. Radioanal. Nucl. Chem. Articles*, **159**, 13 (1992).
3. A. Rusheed, S. Zuha (unpublished results).
4. *Acta. Chem. Scad.*, **10**, 185 (1956).
5. N.A. Verdizade and S.R. Melikov, *Azerb. Khim. Zh.*, 1136 (1973).
6. V.P. Rao, Y. Anjeneyulu and A.S.R. Krishnamurthy, *Mikrochim. Acta*, **1**, 265 (1975).
7. Yu. G. Eremin, E.F. Kolpikova and T.V. Radionova, *Zh. Anal. Khim.*, **31**, 732 (1976).
8. N.A. Verdizade and S.R. Melikov, *Uchebu. Zap. Azerb. Gas. Univ. Ser. Khim. Nauk*, (1973).
9. H. Puzanowska-Tarasiewicz, A. Grundnieweska and M. Tarasiewicz, *Anal. Chim. Acta*, **101**, 9 (1979).
10. Yu. G. Eremin, T. V. Radionova and E.F. Kolpikova, *Zh. Anal. Khim.*, **34**, 491 (1979).
11. M. Mitra and B.K. Mitra, *Talanta*, **24**, 698 (1977).
12. T.J. Koralewski and G.A. Parker, *Anal. Chim. Acta*, **113**, 389 (1980).
13. B. Keshvan, P. Nagaraja, *Analyst*, **111**, 1397 (1986).
14. B. Tamhina, M.J. Herak, *Anal. Chim. Acta*, **76**, 417 (1975).
15. H. Snake Gowda, *Indian J. Chem. Sect. A*, **18**, 276 (1979).
16. L.A. Mineeva, A.S. Babenko and K.I. Godovskaya, *Izv. Vyssh. Khim. Tekhnol.*, **19**, 1671 (1976).
17. B. Keshavan and P. Nagaraja, *Mikrochim. Acta*, **II**, 379 (1985).
18. R.S. Kharsan, K.S. Patel, K.K. Dev and R.K. Mishra, *Fr. Zr. Anal. Chem.*, **295**, 415 (1979).
19. R.S. Kharsan and R.K. Mishra, *Bull. Chem. Soc. Jpn*, **53**, 1736 (1980).
20. L.P. Chandrakar, R. Singh and R. Mishra, *Analyst*, **112**, 1511 (1987).
21. D.T. Burns and N. Tungkananuruk, *Anal. Chim. Acta*, **219**, 323 (1989).