

Polarographic Studies on Hydroxamic Acid Complexes—A Specific Method for Determination of Traces of Molybdenum by D.C. & Derivative Pulse Polarography

S K BHOWAL* & MITA BHATTACHARYYA

Department of Chemistry, Jadavpur University, Calcutta 700 032

Received 10 October 1983; revised 6 February 1984; accepted 1 March 1984

DC and derivative pulse polarographic methods for the determination of traces of molybdenum have been developed. The chloroform extract of the molybdenum cinnamohydroxamic acid complex has been directly subjected to polarography in a special solvent mixture comprising chloroform-water-methanol (3:6:16, v/v). Effects of acids and solvents have been studied and the nature of reduction has been discussed. The method is found to be specific for molybdenum and has been applied for the determination of molybdenum in alloy cast iron.

The introduction of the three-electrode system¹ has made it possible to develop very sensitive and selective methods for the determination of metal ions by polarographic measurement directly in the organic phase^{2,3}. Our studies on the polarographic behaviour of the molybdenum complexes of hydroxamic acids in nonaqueous medium have led to the development of a sensitive method for the determination of the element⁴, utilising benzohydroxamic acid (BHA). Further investigations show that the chloroform extract of the cinnamohydroxamic acid (CHA) complex of molybdenum when mixed with proper proportions of water and methanol furnishes well-defined waves and peaks in DC and derivative pulse polarography, respectively. The sharp derivative pulse polarograms, exhibited by Mo-CHA system in contrast to Mo-BHA system, offer a more sensitive method for the determination of molybdenum. Moreover, the greater stability of the Mo-CHA complex leads to a specific method for determination of molybdenum after extraction in the presence of suitable masking agents. The method has been successfully utilised for quick determination of molybdenum in alloy cast iron.

Materials and Methods

A Tacussel pulse polarograph was used as described in the previous work⁴. The capillary in the solvent mixture used had the following characteristics: $m = 0.372$ mg/s and $t = 10.4$ s per drop at a mercury height (h) of 45 cm. All DC-polarograms were recorded with a controlled drop time of 1s/drop and a recorder speed of 4mV/s. The derivative pulse polarograms were recorded with a controlled drop time of 5s/drop, a pulse amplitude of 50mV and a recorder speed of 2mV/s.

Standard molybdenum solution was prepared as

reported earlier⁴. Solutions of all other metal ions were prepared from their salts of analytical purity.

Cinnamohydroxamic acid was prepared according to the prescribed method⁵. A 0.2% solution in ethanol was used. LiCl (Riedel) was repeatedly crystallised from ethanol and 1% solution in methanol was used as the supporting electrolyte. Methanol (GR, S. Merck) was distilled before use. All other solvents, acids and chemicals used were of analytically pure variety. Doubly distilled water was used throughout the study.

Procedure

An aliquot of standard molybdenum solution (1 to 5 ml) was diluted to about 10 ml and the acidity of the solution adjusted to 1.5 M by the addition of requisite amount of 6 M HCl. After the addition of 0.2% CHA solution (5 ml), the mixture was extracted with chloroform (4 ml). The chloroform layer was separated and the aqueous layer washed with CHCl_3 (2 ml) and the washing combined with the main chloroform extract. The extract was treated with methanolic lithium chloride (7 ml) and 7 M perchloric acid (12 ml) or water (12 ml) and the volume made upto 50 ml with methanol. The DC polarograms were recorded with the solution containing HClO_4 and the derivative pulse polarograms were recorded with that containing water. The range of potential was from 0 to -750 mV and deaeration was done by bubbling pure nitrogen.

For the analysis of molybdenum in alloy cast iron, the alloy sample (1 g) was dissolved in a mixture of conc. HCl (15 ml) and conc. HNO_3 (5 ml). The solution was evaporated almost to dryness and the mass taken up in conc. HCl (5 ml). The acid was almost removed by evaporation and the residue dissolved in conc. HCl (6 ml) and water (15 ml). The solution was filtered from the black residue and the volume made upto 100 ml. To

an aliquot (10 ml) of this solution was added ascorbic acid (500 mg) and molybdenum extracted and determined as described above.

Results and Discussion

Extraction behaviour and polarographic behaviour of Mo-CHA complex

The Mo-CHA complex is freely extracted in chloroform from 2.5 M HCl solutions upto a pH of 4.5. Amongst the organic solvents used methyl isobutyl ketone behaves like chloroform.

The chloroform extract of the Mo-CHA complex when mixed with requisite quantity of aqueous perchloric acid and methanolic lithium chloride furnishes a perfectly homogeneous solution. The DC polarogram of this solution shows two well-defined reduction waves indicating a two-step reduction of the molybdenum (VI) species present in solution. The $E_{1/2}$ values of these waves occur at -120 mV and -510 mV, respectively. The log plot of the first wave exhibits a slope of 72.7 mV and that of the second wave a slope of 89.3 mV. The first wave may be assigned to the reduction of Mo(VI) to Mo(V) and the second to that of Mo(V) to Mo(III), an observation which is compatible with the reduction waves obtained for aqueous solutions of Mo(VI) containing H_2SO_4 or HCl ⁶. The slopes of the log plots obtained with the first and second waves of Mo-CHA system do not fall in the range of reversible reactions involving one-electron and two-electron reduction steps, respectively. Considering irreversible character of both the waves, the transfer coefficients, α , are found to be 0.81 and 0.33, respectively, for the first and second waves. As the value of α for the first wave is quite close to unity the reduction step may be designated as a quasireversible one. However, the low value of α for the second wave indicates considerable irreversible character of the reduction step. The linear relation of \sqrt{h} versus i_d shows that both the DC waves are diffusion-controlled. The polarogram recorded with uncomplexed molybdate in the solvent mixture mentioned above also exhibits two reduction waves with almost the same $E_{1/2}$ values as observed with the Mo-CHA complex. So it may be concluded that in 7M $HClO_4$ solutions the Mo-CHA complex breaks down and the solvated Mo(VI) species is reduced in two consecutive steps.

The methyl isobutyl ketone extract of Mo-CHA shows two waves having $E_{1/2}$ values of $+45$ mV and -150 mV but the waves are not so well-developed and well-separated as found in the case of the chloroform extract.

The derivative pulse polarogram of the Mo-CHA system in 7M $HClO_4$ shows a well-defined peak with

the peak potential of -75 mV and a broad hump corresponding to the second wave of the DC polarogram, the peak potential of which could not be accurately ascertained. When the aqueous perchloric acid phase is replaced by the same volume of water keeping the ratio of the other solvents constant, the first peak of the Mo-CHA system becomes sharper and more well-defined. The first peak is shifted to more negative potential (-110 mV) and the second peak, however, remains broad. Trace amount of molybdenum has been determined by utilising this peak. The DC waves in the said medium have not been found to be better than those obtained in the presence of perchloric acid. The analysis of the nature of the pulse polarograms⁷ corroborates the findings obtained from the analysis of the corresponding DC waves.

Effects of using different solvents, supporting electrolytes and acids

It is observed that the most well-defined polarograms are obtained in the solvent mixture having the composition, chloroform-water-methanol as 3:6:16 (v/v). Methanolic lithium chloride is the best supporting electrolyte. Ethanolic lithium chloride or lithium perchlorate is unsatisfactory.

The presence of different acids in the aqueous phase plays an important role in the reduction of the Mo-CHA complex. The waves obtained with the aqueous phase containing acetic, hydrochloric, sulphuric or phosphoric acid are not well-defined and suitable for analytical purposes. The most well-defined DC waves are obtained with aqueous perchloric acid and the current is found to remain constant when 12 ml of 6.5M to 7.5M $HClO_4$ is used as the aqueous phase, the $E_{1/2}$ values of the waves being -120 mV and -510 mV. All the measurements, therefore, have been performed in 7M $HClO_4$. Addition of NH_3 in the aqueous phase furnishes distorted waves. When the aqueous acidic phase is replaced by simple water the first peak of the pulse polarogram becomes very well-defined and sharp and this peak has been utilised for the determination of molybdenum. Slight variation of the peak potential with the concentration of molybdenum is observed in this case and on the average the value is -110 mV.

Current-concentration relationship

Both the DC waves of the Mo-CHA system exhibit linear current-concentration relationship over a wide range of concentration and both the waves can be utilised for the determination of molybdenum. In both the DC waves the current varies linearly with molybdenum concentration in the range 2×10^{-5} to 4.26×10^{-4} M (2-42.6 ppm). The height of pulse polarogram with the peak potential of -110 mV also

Table 1—Tolerance Limits of Diverse Ions and Complexing Agents

[Conc. of molybdenum = $1.06 \times 10^{-4} M$]		
Metal ion or complexing agent	Tolerance ratio*	Remarks
Cu(II)	100	
Co(II)	100	
Ni(II)	100	
Mn(II)	100	
Fe(III)	250	Extracted in presence of ascorbic acid
Cd(II)	100	
Hg(II)	100	
Pb(II)	100	Extracted from 1.5M HClO ₄ solution
Re(VII)	100	
Ce(IV)	100	Extracted in presence of ascorbic acid
Zr(IV)	50	Extracted in presence of fluoride
V(V)	100	Extracted in presence of ascorbic acid
Cr(III)	100	
U(VI)	100	
W(VI)	50	Extracted in presence of tartaric acid
Ti(IV)	70	Extracted in presence of fluoride
Sn(IV)	50	-Do-
Ascorbic acid	10000	
Tartaric acid	500	
Citric acid	500	
Oxalic acid	500	
Fluoride	400	

*Metal ion or complexing agent to molybdenum.

varies linearly with molybdenum concentration in the range of 8×10^{-6} to $1.06 \times 10^{-4} M$, corresponding to 0.8 to 10.6 ppm of the metal.

Effect of diverse ions

The tolerance limits of various foreign ions and complexing agents are given in Table 1. Extraction of

lead is performed in 1.5M HClO₄ solution to avoid precipitation of lead chloride. Extraction of iron is completely suppressed by ascorbic acid. The Mo-CHA system can tolerate higher concentrations of tungsten and vanadium, than the Mo-BHA⁴ system. Moreover, Mo-CHA system is free from interference from tin, titanium, fluoride, tartrate, citrate and oxalate. This is a definite advantage of the present method over that reported earlier using the Mo-BHA system⁴.

A sample of alloy cast iron (Bureau of Analysed Sample, London) containing 0.4% molybdenum has been analysed. The concentration of molybdenum is found to be 0.39% utilising DC technique, the value being almost the same (0.392%) as that obtained by the pulse method. The relative standard deviation is calculated to be $\pm 2.2\%$. The present method is rapid and specific and is much superior to the laborious and time-consuming procedure of Von Stackelberg and coworkers⁸, where prior separation of molybdenum from steel is mandatory in order to get rid of the interference from iron.

Acknowledgement

The authors express their gratitude to the authorities of Alexander von Humboldt-Stiftung, West Germany for the donation of the pulse polarograph. One of the authors (MB) wishes to thank the UGC, New Delhi for the award of a research fellowship.

References

- 1 Flato J B, *Analyt Chem*, **44** (1972) 75A.
- 2 Bhowal S K & Umland F, *Z anal Chem*, **282** (1976) 197.
- 3 Bhowal S K & Umland F, *Z anal Chem*, **285** (1977) 226.
- 4 Bhowal S K & Bhattacharyya Mita, *Z anal Chem*, **310** (1982) 124.
- 5 Thiele J & Pickard R H, *Anal Chemie*, **309** (1899) 194.
- 6 Heyrovsky J & Kuta J, *Principles of polarography* (Academic Press, New York) 1966, 540.
- 7 Parry E P & Osteryoung R A, *Analyt Chem*, **37** (1965) 1634.
- 8 Kolthoff I M & Lingane J J, *Polarography*, Vol II, 1955, 613.