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Polarography of Metal Hydroxamates. Individual and Simultaneous Determination of Tungsten and Molybdenum Using Benzo- and Cinnamohydroxamic Acids

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Methods for the determination of traces of tungsten have been developed by directly subjecting the organic extracts of its benzo- and cinnamohydroxamic acid complexes to d. c. and derivative pulse polarography. Well defined waves and peaks are obtained in a ternary solvent mixture containing the extract, methanolic lithium chloride and aqueous phase. The methods are highly selective and allow determination of the metal in the ppm range. A procedure has also been developed for the simultaneous determination of tungsten and molybdenum using their benzohydroxamates. Effects of acids and solvents on the system have been studied and the probable mechanism of reduction of the complexes has also been discussed.

Studies on the extraction-polarography of metal hydroxamates directly in the organic phase have led to the development of excellent methods for the determination of traces of molybdenum.[1-3] In this article is reported similar investigations carried out to develop methods of analysis of traces of tungsten and simultaneous determination of tungsten and molybdenum. Investigations carried out with the benzohydroxamic acid (BHA) and cinnamohydroxamic acid (CHA) complexes of tungsten reveal that the complexes after extraction into a mixture of chloroform and isobutyl alcohol or chloroform can directly be subjected to d.c. and derivative pulse polarography (D.P.P.) in a mixture of solvents containing the extract, methanolic lithium chloride and water in a definite ratio. The systems yield well defined waves or peaks which have been utilized for the determination of trace quantities of tungsten. Solvent extraction separation and direct submission of the extract to polarography have resulted in the development of highly selective and quick determination methods which are superior to those known up to date. Furthermore a quick and sensitive method for the simultaneous determination of molybdenum and tungsten, two closely related metals, have also been worked out utilizing the benzohydroxamic complexes of the elements. Highly reproducible results have been obtained with synthetic mixtures of the metals. The probable mechanism of reduction of the complexes have been discussed.

Experimental

Apparatus. A Tacussel PRG 5 Pulse polarograph was used as reported earlier.[1-3] The capillary characteristics were as follows in the different solvent extracts at the mercury height of 45 cm.

Chloroform-isobutyl alcohol extract
m=0.376 mg s^{-1} t=9.78 s.
Chloroform extract
m=0.371 mg s^{-1} t=9.90 s.

All d.c. and D.P.P. were recorded with a controlled drop time of 1 and 3 s respectively, 4 mV s^{-1} recorder speed and 50 mV pulse amplitude.

Reagents and Solutions. Standard tungsten solution was prepared from $Na_2WO_4 \cdot 2H_2O$ (analar grade) and standardized as the oxine complex.[4] Standard molybdenum solution was prepared as described earlier.[1-3]

Benzohydroxamic acid (BHA) and cinnamohydroxamic acid (CHA) were prepared as mentioned earlier.[1,3] 1.0% (w/v) ethanolic solution of BHA and 0.2% (w/v) ethanolic solution of CHA were used for the investigations.

Lithium chloride (analar, Riedel) was used as the supporting electrolyte. Methanol (G.R.S. Merck) was distilled before use. All other metal salts, solvents, acids, and chemicals used were of analytical reagent grade. Twice distilled water was used in all the studies.

Results and Discussion

Procedure for Determination of Tungsten and Simultaneous Determination of Molybdenum and Tungsten with BHA. An aliquot of standard tungsten solution or a mixture of standard molybdenum and tungsten solutions were taken in a 50 ml separatory funnel and diluted to 10 ml with water. After addition of 3 ml of BHA the acidity was adjusted to 1.5 mol dm^{-3} with 6 mol dm^{-3} hydrochloric acid and the mixture was shaken with 3 ml of 1 : 1 chloroform and isobutyl alcohol for one minute. The organic layer was drained into a 50 ml flask and aqueous layer was washed with 3 ml of the same solvent mixture. The washing was mixed with the main extract. To the combined extract was added 7 ml 1% methanolic lithium chloride, 12 ml 0.5 mol dm^{-3} perchloric acid solution and the mixture was made up to volume with methanol. Direct current and D.P.P. were recorded from −500 to −950 mV after deaeration with nitrogen for ten minutes.

Procedure for Determination of Tungsten with Cinnamohydroxamic Acid. A standard aliquot of tungsten solution taken in a 50 ml separatory funnel was diluted to 10 ml with water. The solution was treated with 5 ml of CHA solution. After adjusting acidity to 1.5 mol dm^{-3} with 6 mol dm^{-3} hydrochloric acid the mixture was extracted with 4 ml of chloroform and the organic layer was taken in a 50 ml flask. The aqueous layer was washed with 2 ml chloroform and the washing was taken with the main extract. The organic layer was made up to volume with 7 ml 1% methanolic lithium chloride, 12 ml 4 mol dm^{-3} perchloric acid and methanol. Direct current and D.P.P. were recorded from −300 to −800 mV after deaeration with nitrogen for ten minutes.

Extraction and Polarographic Behavior of W-BHA and W-CHA Complexes. The colorless complex of tungsten with BHA is found to be sparingly soluble in common extracting solvents like chloroform, benzene, methyl isobutyl ketone, and 3-methyl-1-butanol. However, the complex can be easily extracted into a 1 : 1 mixture of chloroform and isobutyl alcohol from 1.0 to 6.0 mol dm^{-3} hydrochloric acid solutions. The extract when mixed with methanolic lithium chloride and an aqueous phase containing 0.5 mol dm^{-3} perchloric acid in the ratio 3:16:6 furnishes excellent polarograms with d.c. and D.P.P. techniques. The pulse polarogram yields a sharp peak at −800 mV and d.c. polarogram shows a single wave with $E_{1/2}$ value at −780 mV (Fig. 1). Inspite of the fact that tungsten benzohydroxamate produces a single reduction wave like molybdenum,[1)] the nature of reduction happens to be quite different. The value of the slope obtained from the log plot of the d.c. wave (50.8 mV) is nearly compatible with a one electron reduction step which is not totally reversible. The transfer coefficient, α, 1.16, being close to unity points towards a quasireversible reduction. The peak half width (123 mV) of the D.P.P. at 50 mV amplitude is, however, indicative of a reversible one electron process. Thus it may be concluded that the d.c. wave and pulse peak indicate the reduction of W(VI) to W(V) species. Like molybdenum, reduction of tungstate ion in aqueous medium observed by other workers[5)] show two reduction waves W(VI) to W(V) and W(V) to W(III) where the first wave appears at a potential of zero volt. So in the present case the reduction of tungsten appears to happen in the complexed form as the $E_{1/2}$ of the first wave is shifted to negative direction and that of second one cannot be obtained due to the same reason. The linear relationship of current with square root of mercury height indicates that the reduction is diffusion controlled.

The W-CHA complex is freely soluble in chloroform due to presence of a conjugation in the reagent molecule. The complex is completely extracted into the said solvent from 0.5 to 2.5 mol dm^{-3} hydrochloric acid solution. The organic phase can be mixed with aqueous phase and methanol in the ratio 3 : 6 : 16 to give a homogeneous phase whose D.P.P. produce a sharp peak at −620 mV. $E_{1/2}$ of the d.c. polarogram lies at −625 mV (Fig. 2). The average slope (50.2 mV) obtained from the log plot of the d.c. wave and transfer coefficient, 1.17 suggest the reduction to be a one electron quasireversible one. The peak half width 115 mV is also indicative of the same. That the wave appears due to reduction of complex rather than the uncomplexed oxo ion, WO_2^{2+}, is evidenced by the fact that free tungstate ion under the same conditions does not show any wave or peak. The linear relationship of current with square root of mercury height indicates the reduction is diffusion controlled.

We have previously reported[1)] the determination of traces of molybdenum after extraction of its benzohydroxamate in chloroform and subjecting the extract to polarography in a solvent mixture containing chloroform, methanol, and an aqueous phase in a definite ratio. It has now been observed that molybdenum benzohydroxamate can be extracted into a chloroform isobutyl alcohol mixture like that of the tungsten complex. The extract when subjected to polarography in the same solvent mixture as used in the case of tungsten, furnishes well defined peak in D.P.P. with an E_p of −330 mV. Simultaneous determination of

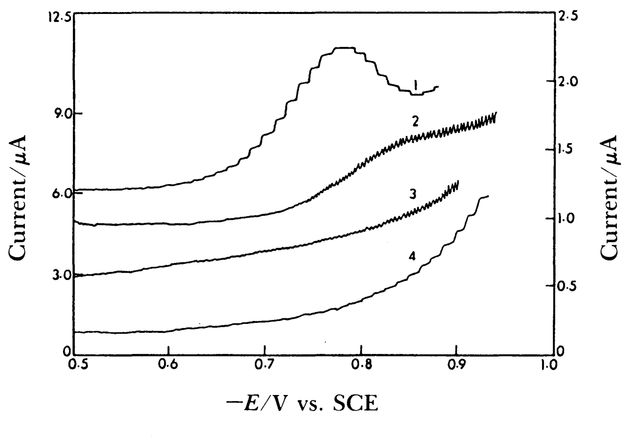

Fig. 1. Polarograms of W-benzohydroxamic acid complex; concentration of W=8×10^{-5} mol dm^{-3}; Curve 1-pulse polarogram; Curve 2-d.c. polarogram; Curve 3-d.c. polarogram of reagent blank; Curve 4-pulse polarogram of reagent blank; Curves 3 and 4 right hand side scale.

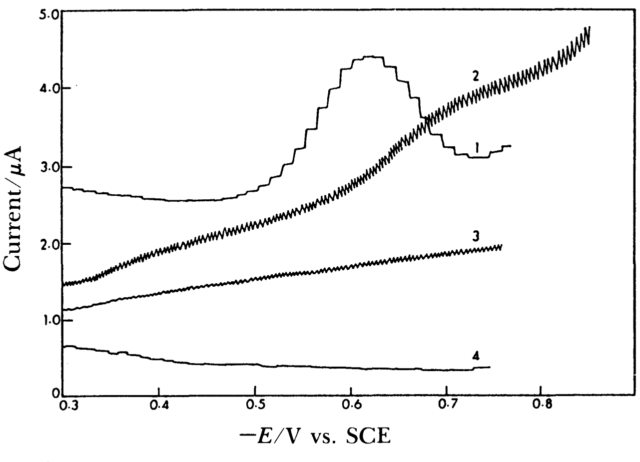

Fig. 2. Polarograms of W-cinnamohydroxamic acid complex; concentration of W=8×10^{-5} mol dm^{-3}; Curve 1-pulse polarogram; Curve 2-d.c. polarogram; Curve 3-d.c. polarogram of reagent blank; Curve 4-pulse polarogram of reagent blank.

Table 1. Simultaneous Determination of Molybdenum and Tungsten in a Mixture

Ratio W : Mo	Concn of metals taken mol dm^{-3}	Current μA	Concn of metals found mol dm^{-3}
1 : 1	2.0×10^{-5} W	0.82	1.84×10^{-5} W
	2.0×10^{-5} Mo	0.46	2.30×10^{-5} Mo
1 : 3	2.0×10^{-5} W	0.84	1.90×10^{-5} W
	6.0×10^{-5} Mo	1.20	6.0×10^{-5} Mo
3 : 1	3.0×10^{-5} W	1.28	2.90×10^{-5} W
	1.0×10^{-5} Mo	0.26	1.10×10^{-5} Mo
1 : 5	2.0×10^{-5} W	0.82	1.84×10^{-5} W
	1.0×10^{-4} Mo	2.0	1.01×10^{-4} Mo
5 : 1	5.0×10^{-5} W	2.10	4.80×10^{-5} W
	1.0×10^{-5} Mo	0.24	1.09×10^{-5} Mo

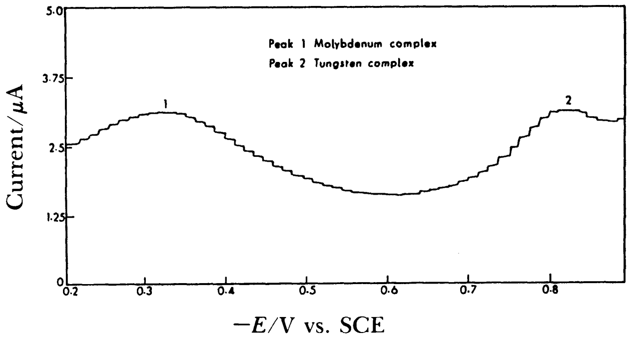

Fig. 3. Pulse polarogram of mixture of molybdenum and tungsten-benzohydroxamic acid complexes. Concentration of Mo=4×10^{-5} mol dm^{-3}; concentration of W=2×10^{-5} mol dm^{-3}.

trace quantities of the said metals has become possible in a ratio of 1 : 5 and vice versa (Fig. 3). The results are given in Table 1. Attempts have been made to develop a method for the simultaneous determination of molybdenum and tungsten after extraction of their cinnamohydroxamates in chloroform. But the method could not be worked out as the peaks of the two metals happened to be overlapping with each other.

Extracting Solvents, Supporting Electrolyte, Composition of Solvent Mixture and Current-Concentration Relationship. Chloroform-isobutyl alcohol mixture in a ratio of 1 : 1 was found to be the best extractant for the W-BHA complex. A homogeneous solution was obtained by mixing 6 ml of the extract, 7 ml 1% methanolic lithium chloride, 12 ml of aqueous phase and 25 ml of methanol in a total volume of 50 ml. Acids like HCl, H_2SO_4, CH_3COOH, H_3PO_4, and also NH_3 in the aqueous phase did not furnish well defined waves or peaks. Most well defined and reproducible polarograms were produced only when the aqueous phase contained 0.25 to 1.0 mol dm^{-3} $HClO_4$. For the tungsten-CHA complex chloroform alone was found to be the best extractant. A mixture of the chloroform extract, methanolic lithium chloride, and aqueous phase containing 3 mol dm^{-3} to 5 mol dm^{-3} $HClO_4$ in the ratio 3 : 16 : 6 produced the best polarogram in this case. Acids such as HCl, H_2SO_4, H_3PO_4, CH_3COOH were not found suitable as an aqueous phase. Methanolic solution of LiCl was used as the supporting electrolyte in all the cases. For both W-BHA and W-CHA complexes the diffusion current is found to vary linearly with concentration of the metal and the said ranges applicable for d.c. and D.P.P. techniques are shown in Figs. 4 and 5.

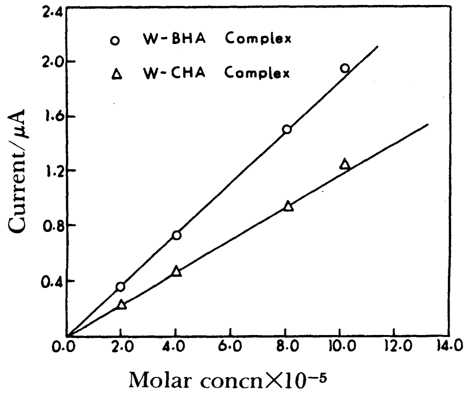

Fig. 4. Current-concentration relationship of benzo- and cinnamohydroxamates of W. (d.c. polarography).

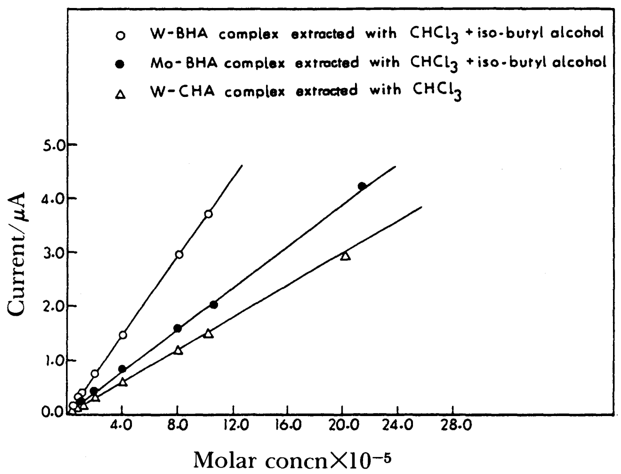

Fig. 5. Current-concentration relationship of benzo- and cinnamohydroxamates of W and Mo (D.P.P.).

Effect of Diverse Ions. The effects of diverse ions and complexing agents are given in Table 2. It is observed W-CHA system can tolerate larger concentration of metals like iron(III) and cerium(IV) and complexing agents like ascorbic acid, tartaric acid, oxalic acid, and fluoride. This behavior may be attributed to the greater stability of the W-CHA complex in comparison to W-BHA complex. However, benzo and cinnamohydroxamates of tungsten cannot be extracted in presence of metals like copper(II), cobalt(II), manganese(II), chromium(III), cadmium(II), mercury(II), titanium(IV), tin(IV). Molybdenum(VI) is found to interfere with determination of tungsten with CHA.

Table 2. Tolerance Limits of Diverse Ions and Complexing Agents
Concentration of W=2.0×10^{-5} mol dm^{-3}

Metal ion or complexing agent	Tolerance ratio of the metal ion or complexing agent to complexes of W with		Remarks
	BHA	CHA	
Fe(III)	10	70	Extracted in presence of ascorbic acid
Pb(II)	100	100	Extracted from 1.5 mol dm^{-3} perchloric acid solution
Ni(II)		2	
Re(VII)	100	100	
Ce(IV)	10	100	Extracted in presence of ascorbic acid
V(V)	10	100	Extracted in presence of ascorbic acid
Zr(IV)	10	50	Extracted in presence of fluoride
U(VI)	50	50	
Mo(VI)	5		
Ascorbic acid	20	500	
Tartaric acid	200	500	
Citric acid	500	500	
Oxalic acid	40	70	
Fluoride	40	100	
EDTA	500	500	

Statistical Errors in the Determination of Tungsten. The relative standard deviation values for the pulse polarographic determination of tungsten with benzo- and cinnamohydroxamic acids have been calculated from a set of ten determinations in each case. The said values are ±6.37% for the W-BHA and ±2.78% for W-CHA complexes.

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