Polarographic Determination of Molybdenum in Rocks and Ores

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Several methods for colorimetric determination of molybdenum in rocks and ores by means of thiocyanate have been published¹⁻⁵. In our experiments, we found it difficult to obtain a stable colour; the extinction tended to grow with the time. The method of Winterstein⁵ has been tried here, but very often an extremely stable emulsion was formed during the extraction with *n*-butyl acetate, preventing the completion of the analysis.

Therefore, an investigation was carried out to find a polarographic method for the determination. According to Kanevskii and Shvartsburd⁶, the sample is fused with potassium hydroxide and sodium peroxide, and leached with hot water. To an aliquot of the filtrate a large amount of phosphoric acid is added, and the polarogram is recorded and measured. Meites⁷ has described a method for polarographic determination of molybdenum in sodium tungstate. The supporting electrolyte is a neutral solution of sodium citrate, and a rather broad single wave is obtained with half-wave potential of -1.111 V and -0.927 V *vs.* S.C.E. in 0.1 M, and 1 M sodium citrate, respectively.

The investigation showed that it is possible to determine molybdenum in rocks and ores using a modification of the polarographic method of Meites⁷. The modification consists in a fusion with peroxide and hydroxide; indifferent salts coming from the sample or introduced for the fusion remain in the solution. The range of molybdenum content covered by the method is 0.01% to several per cent. No interfering elements are found.

Experimental

Apparatus. The polarograms were obtained with a Polariter, type PO4, from Radiometer, Copenhagen. Diffusion currents were measured, using the extrapolation method, described by Meites⁸.

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Measuring of pH and automatic titrations were performed with a titrator, type TTTL, from Radiometer, Copenhagen.

Reagents. All reagents were analytical grade and were used without further purification.

Standard solutions of molybdenum containing 1 mg/ml or 0.2 mg/ml were prepared as follows. A weighed amount of molybdenum trioxide was dissolved in the minimum amount of 1 N sodium hydroxide, and neutralised with 1 N perchloric acid to pH $6-7$; the volume was adjusted to make the content 1.0 mg/ml, and then this solution was further diluted with water to make 0.2 mg/ml.

Sodium citrate (50%) was prepared by dissolving 500 g of trisodium citrate in water and diluting to 1 liter.

Procedure. Grind the sample to pass mesh 100 (to the inch) and mix well. Weigh 1 g in a nickel crucible and mix with 4 g of sodium peroxide and 1 g of sodium hydroxide. Place the crucible in an oven and heat to 500°C for 30 min. After cooling dissolve in water and adjust the volume to 50 ml in a volumetric flask. Filter the solution through a dry paper, the first 5 ml of filtrate being discarded. Boil an aliquot of 10 ml for 15 min to destroy peroxide. After cooling add 20 ml of 50% sodium citrate and titrate the mixture potentiometrically with 4 N perchloric acid, added slowly to pH $= 6.0$. Transfer the resulting solution to a volumetric flask and adjust the volume to 50 ml with water. If a copious amount of silica-gel is formed, allow the solution to stand overnight to complete the coagulation, and filter through a dry paper, the first 5 ml of filtrate being discarded.

The solution is now ready for recording the polarogram. Each 10 ml corresponds to $\frac{10}{50} \cdot \frac{10}{50} = \frac{1}{25}$ of the original sample weight. No addition of maximum depressant agent is needed.

Place 10 ml solution in the cell, deaerate with nitrogen (freed from oxygen), and record the polarogram. The molybdenum wave appears at $E_{1/2} = -1.0$ V. The diffusion current is about $6 \mu\text{A}/\text{mg Mo}/10$ ml. Assess the content of molybdenum according to this; add a corresponding amount of standard solution of molybdenum, and record the new polarogram.

Measure the two diffusion currents using the geometric extrapolation⁸ shown in Fig. 1. The length of the line MN at $E_{1/2}$ is a measure for the diffusion current. Calculate the content of molybdenum:

$$\% \text{ Mo} = 2500s[i_1/(i_2(1 + v/10) - i_1)]/W$$

Table 1. Molybdenum content in ore samples.

No.	Mo	Mo
	polarographic determination %	colorimetric determination %
8	0.18	0.17
9	0.16	0.16
32	0.16	0.15—0.16
42	0.14	0.125—0.14
44	0.11	0.115—0.13
standard ore	0.30	0.31

Colorimetric determinations of samples Nos. 32, 42 and 44 by Nordisk Mineselskab, performed according to the method of Winterstein⁵. Samples Nos. 8 and 9 were analysed simultaneously by Dr. Christoph Winterstein, Staats-hüttenlaboratorium, Hamburg, and here, whereupon the results were exchanged. Standard ore prepared by American Metal Climax Inc.

where W is the sample weight, s and v the molybdenum content and volume of the standard solution, i_1 and i_2 the diffusion currents of the original solution and of the solution after the standard addition.

Results. The method was used to determine the molybdenum content of 54 samples containing molybdenite (MoS_2). The molybdenum content ranged from 0 to 0.8 %. Five analysed samples from the Mestersvig area, Greenland, and a stan-

Fig. 1. Typical polarogram, obtained with the standard ore from American Metal Climax Inc.; Mo content: 0.31 %. The geometric extrapolation used to measure diffusion currents is shown; the length MN at $E_{1/2}$ gives the diffusion current.

dard ore prepared by American Metal Climax Inc. were placed at our disposal by Nordisk Mineselskab. The molybdenum content of these samples are found in Table 1, which shows the close agreement between the polarographic and the colori-

Table 2. Polarographic waves in citrate electrolyte.

Element	$E_{1/2}$	Notes	Effect of fusion.
CuII	-0.17 V.	W.-d.	Wave disappears
ZnII	-1.3 V.	Ill.-d. ^b	
CdII	-0.68 V.	W.-d.	Wave diminished
TlIII	-0.48 V.	Small wave	Wave disappears
ZrIV	ca. -0.7 V.	Ill.-d. ^c	Wave disappears
PbII	-0.51 V.	W.-d.	Wave diminished
VV	>0 V.	W.-d.	
BiIII	-0.33 V.	W.-d.	Wave disappears
CrVI	>0 V.	W.-d. ^d	
MoVI	-1.00 V.	W.-d.	
WVI	-1.5 V. ^a	Ill.-d. ^b	
UVI	ca. -0.7 V.	Ill.-d. ^e	Wave diminished

W.-d. = Well-determined plateau of the wave.

Ill.-d. = Ill-determined wave.

a: Meites⁷.

b: Interfering with the final reduction of the electrolyte.

c: Very broad wave, extending from -0.5 to -0.9 V.

d: Large maximum, eliminated on fusion.

e: Very broad, apparently composed wave, extending from -0.5 to -0.9 V.

metric methods. Molybdenum contents down to 0.01 % can be determined. This corresponds to about 0.004 mg of molybdenum in 10 ml of the final solution or to a diffusion current of 0.02–0.03 μ A. The error of the analysis is assessed at about ± 5 % (rel.), or ± 0.01 % (abs.), whichever is the larger.

A typical polarogram is shown in Fig. 1. The molybdenum wave is found at -1.00 or -1.01 V; Meites⁷ found $E_{1/2} -1.111$ V or -0.927 V, depending on the concentration of the electrolyte. Most of the samples produced a wave with $E_{1/2}$ about -0.3 V. It has not been possible to identify the substance producing this wave; it is not bismuth.

Interferences. With the purpose of finding any interfering substances, and of identifying, if possible, the substance producing the wave at -0.3 V, a series of metals were examined. Cerium IV, titanium IV, thorium VI, tin IV, niobium V, tantalum V, arsenic V, antimony V, cobalt II, and nickel II did not produce any wave. Solutions of copper II, thallium III, zirconium IV, bismuth III, and uranium VI, in the electrolyte were reduced, but these metals were eliminated by the fusion. Zinc II, cadmium II, lead II, vanadium V, chromium IV and tungsten VI produced polarographic waves, persisting after fusion, but none of these waves interfered with the molybdenum wave. The values of $E_{1/2}$ are shown in Table 2.

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The Structure of Cedrollic Acid

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Recently a saturated, tricyclic hydroxy acid, $C_{15}H_{24}O_3$, was isolated from the heartwood of the American desert juniper, *Juniperus utahensis* Lemm.¹ The name cedrollic acid and the structure 2 are proposed for this compound, which appears to be the first naturally occurring sesquiterpene hydroxy acid described. Small amounts of three other compounds of the same class have since been isolated from heartwood of *Juniperus* species^{2,3}.

Cedrollic acid melts over a wide range (m.p. 181–187°). The sharp-melting methylester (3, m.p. 98.0–98.5°) was reduced to a diol¹ (4, m.p. 130–131°). This diol has now been oxidised with chromic acid in pyridine to the hydroxy aldehyde 5, which on reduction by the Huang-Minlon procedure gave cedrol (6) in good yield.

Of the possible structures 1, 2 and 7 for cedrollic acid, 1 can be eliminated because the acid formed on dehydration from cedrollic acid is not α,β -unsaturated¹. Evidence against 7 is obtained from the infrared spectra of cedrollic acid, its methylester, the diol 4 and the hydroxy aldehyde 5. These spectra have only a single peak in the 1375 cm^{-1} region, indicating the absence of a *gem*-dimethyl group in the above compounds.