

Extraction and Spectrophotometric Determination of Trace Amounts of Molybdenum Present in Rocks and Minerals

CHANCHAL KUMAR PAL and AMIYA KUMAR CHAKRABURTTY

Department of Chemistry, Jadavpur University, Calcutta-32

Manuscript received 25 June 1974; revised 6 September 1974; accepted 12 September 1974

Molybdenum (VI) forms a yellow coloured chelate with salicylhydroxamic acid at pH 2.5-3.0, which is extractable with isoamyl alcohol. The coloured extract can be directly measured spectrophotometrically at 345 nm or at 360 nm. The system follows Beer's law at these wavelengths over the concentration range 0.10 p.p.m. to 10.0 p.p.m. Mo. The coloured species with a sensitivity, $0.010 \mu\text{g Mo cm}^{-2}$ ($\epsilon = 9020$) at 345 nm and $0.014 \mu\text{g Mo cm}^{-2}$ ($\epsilon = 6730$) at 360 nm, can be suitably used for determination of molybdenum present in geological specimens.

OF the yellow molybdenum (VI)-chelate compounds formed with different hydroxamic acids¹⁻⁶, the one obtained with salicylhydroxamic acid has been found to be easily extractable in isoamyl alcohol in acid medium giving rise to an intense yellow solution. On this basis a simple and sensitive method for the extraction and spectrophotometric determination of trace amounts of the metal has been formulated.

Experimental

Apparatus and reagents

A Beckman D.B. automatic recording spectrophotometer was used for the absorbance measurements and all pH-measurements were made with a Beckman pH-meter (Model H-2).

The reagent salicylhydroxamic acid was used after crystallization of the ordinary product for several times, (m.p. 167° - 168°). All the reagents including isoamyl alcohol were of analytical grade. Potassium hydrogen phthalate-hydrochloric acid buffer (pH 3) was prepared in the usual way⁶.

Stock solutions of molybdenum were prepared by dissolving ammonium molybdate (A.R.) in water and the molybdenum contents estimated by the oxine method⁶. A 0.01M salicylhydroxamic acid was prepared in isoamyl alcohol (0.153%). Solutions of other diverse ions were prepared by dissolving analytical grade reagents.

Absorbance curves

The absorption spectra of the yellow molybdenum (VI)-salicylhydroxamic acid chelate extracted in isoamyl alcohol at pH 2.5-3.0, was taken against reagent blank (Fig. 1). The absorbance was maximum at 345 nm. The maximum absorbance of the reagent was in the region lower than 340 nm and it has practically very little absorption above 360 nm.

For the absorbance measurement of the yellow molybdenum(VI)-salicylhydroxamic acid chelate extract, the wavelengths 345 nm or 360 nm were found

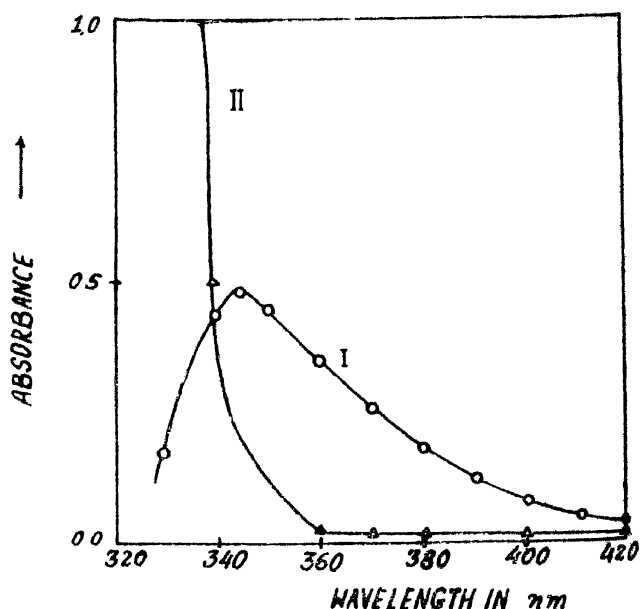


Fig. 1.

- (I) Absorption spectra of Mo(VI)-Salicylhydroxamic acid chelate extracted in isoamyl alcohol at pH 3.0 against reagent blank [Mo(VI) 5 p.p.m.]
(II) Absorption spectra of reagent blank at pH 3.0.

to be workable, where all the measurements were made.

Results and Discussion

Effect of pH

The formation of molybdenum(VI)-salicylhydroxamic acid chelate at different pH values (0-6) were studied after extraction in isoamyl alcohol. The maximum colour intensity of the isoamyl alcohol extract was obtained between pH 2.5-3.0.

The percentage extraction of molybdenum(VI)-salicylhydroxamic acid chelate at different pH-values were determined and are shown in Fig. 2.

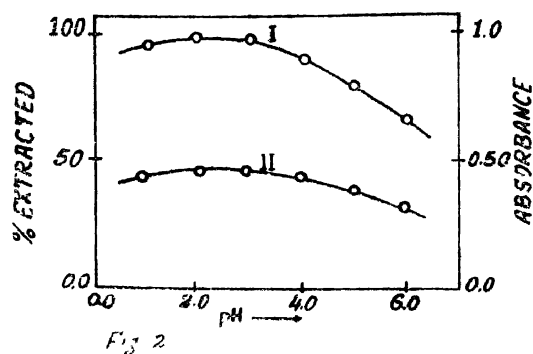


Fig. 2.

- (I) Extraction of Mo(VI)-Salicylhydroxamate chelate as a function of pH [Mo(VI) 5.0 p.p.m.]
 (II) Absorbance of Mo(VI)-Salicylhydroxamate chelate extract as a function of pH [Mo(VI) 5.0 p.p.m.]

Reagent concentration

Salicylhydroxamic acid is highly soluble in methanol, ethanol, acetone, etc., but comparatively less soluble in higher alcohols like isopropanol, isobutanol, isoamyl alcohol and hexanol. 0.01M concentration of salicylhydroxamic acid in isoamyl alcohol was found to be most suitable for extraction of molybdenum. With lower reagent concentrations, insufficient extraction of molybdenum resulted which however could be remedied by further extractions.

Beer's law and Standard curves

The absorbance of different amounts of molybdenum-salicylhydroxamic acid chelate extracted at pH 3 by the above procedure, was measured at 420 nm to 330 nm wavelengths against reagent blank. In each case extraction was carried out exhaustively till the aqueous phase was free from molybdenum. The result shows that molybdenum(VI)-salicylhydroxamic acid chelate system follows Beer's law at 345 nm and 360 nm over the concentration range of 0.10 ppm to 10.0 ppm. The sensitivities ($\log I_0/I - 0.001$) calculated, as described by Sandell, are 0.10 $\mu\text{g Mo cm}^{-2}$ ($\epsilon = 9020$) at 345 nm and 0.014 $\mu\text{g Mo cm}^{-2}$ ($\epsilon = 6730$) at 360 nm.

Period of extraction

The period of extraction was varied from 1 to 10 mins. keeping other variables constant. 5 mins was found to be optimum.

Effect of diverse ions

In the presence of the following ions at pH 3, 5 ppm of molybdenum was determined after extraction with salicylhydroxamic acid in isoamyl alcohol. Al^{3+} (100 ppm), Cu^{2+} (50 ppm), Co^{2+} (50 ppm), Cd^{2+} (100 ppm), Hg^{2+} (100 ppm), Pb^{2+} (50 ppm), Be^{2+} (100 ppm), Mg^{2+} (200 ppm), Ca^{2+} (200 ppm), Ni^{2+} (100 ppm), Zn^{2+} (100 ppm), $\text{W}_6\text{O}_{21}^{4-}$ (40 ppm), Sn^{2+} (50 ppm), UO_2^{2+} (30 ppm), Cr^{3+} (50 ppm), Mn^{2+} (50 ppm), Pd^{2+} (10 ppm), fluoride (10 ppm),

oxalate (20 ppm), tartarate (20 ppm), phosphate (50 ppm), citrate (20 ppm), borate (20 ppm).

The interference due to Cr^{3+} , Fe^{3+} , V^{5+} can be prevented by masking with EDTA in presence of which the tolerance limits of some of the ions mentioned are increased appreciably.

General procedure

2 ml of molybdenum solution containing 100 ppm and 8 ml of potassium hydrogen phthalate—hydrochloric acid buffer solution (pH 3) were taken in a 50 ml separatory funnel. After adding 10 ml of 0.01M salicylhydroxamic acid solution in isoamyl alcohol the mixture was shaken for 5 min and allowed to stand till the organic and the aqueous phases separated. The aqueous phase was collected separately and pH of the solution was checked. The organic phase was collected after treatment with anhydrous sodium sulphate in a 10 ml volumetric flask and made upto the required volume with 0.01M salicylhydroxamic acid in isoamyl alcohol and the absorbance was measured at 345 nm or 360 nm against reagent blank. The technique developed has been successfully applied for the determination of trace amounts of molybdenum present in the silicate rocks. For the treatment of the rock samples the procedure adopted by Sandell in the determination of molybdenum by stannous chloride-thiocyanate method in silicate minerals was adopted⁸. After collecting the filtrate and washings in a 100 ml volumetric flask, molybdenum was extracted from suitable aliquots, in presence of 5 ml of 5 percent EDTA solution, and determined spectrophotometrically according to the procedure already described. The results obtained were found to be quite satisfactory as is evident from the following table.

TABLE		
Rock samples	Molybdenum present in ppm (determined by this method)	Molybdenum found by thiocyanate ^{8,9} method in ppm
S ₁	68	65
S ₂	125	121
S ₃	150	143
S ₄	275	271

Acknowledgement

The authors' grateful thanks are due to Professor Dr. A. K. Majumdar for his kind and constant encouragement. One of the authors (C.K.P.) is grateful to the Council of Scientific & Industrial Research (New Delhi) for the award of a fellowship.

References

1. A. K. CHAKRABURTTY, Symposium on the Chemistry of Coordination Compounds, Agra (India), Part III, 1959, p. 235.
2. C. K. PAL, Ph.D. Thesis 1969, Jadavpur University, Calcutta-32, India.
3. N. K. CHOUDHURI, A. K. SARKAR and J. DAS, *Z. analyt. Chem.*, 1971, 254, Heft 5, p. 365.

4. S. K. SINHA and S. C. SHOME, *Anal. Chim. Acta.*, 1961, 24, 33.
5. C. K. PAL and A. K. CHAKRABURTTY, Proc. 60th Indian Science Congress, Part III, 1972.
6. N. P. BORZENKOVA, *Vestn. Mosk. Univ., Khim.*, 1968, 23, 84; *Chem. Abs.*, 69, 90380a.
7. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis, Longmans, London, 3rd ed., 1962.
8. E. B. SANDELL, "Colorometric Determination of Traces of Metals", Interscience Publishers Inc., New York, 3rd ed., 1959.
9. E. B. SANDELL, *Ind. Eng. Chem. Anal., Ed.*, 1936, 8, 336