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Extractive Spectrophotometric Determinaton of Molybdenum(VI) with 8-Hydroxy-5-quinolinesulfonic Acid and Methyltrioctylammonium Chloride

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Synopsis. Molybdenum(VI) complex with 8-hydroxy-5-quinolinesulfonic acid (H_2qs) is reduced to the quinquevalent state by hydrazinium sulfate and extracted into chloroform as the ion-association complex with methyltrioctylammonium chloride(Q^+Cl^-). Molybdenum(VI) in the ppm range is determined spectrophotometrically. The composition of the extracted species was estimated to be $[(MoO_2qs)_2(Hqs)_3(Q)_5]$.

When molybdenum(VI) in a weakly acidic solution in the presence of 8-hydroxy-5-quinolinesulfonic acid (H_2qs) is reduced by hydrazine, a yellow molybdenum(V)–H_2qs complex is formed, which changes to a red-purple complex on heating.[1,2] The formation of the red-purple complex is the basis of spectrophotometric determination of molybdenum in water.[3] The composition of yellow complex has been ascribed[4] to two monomers, *i.e.*, $[MoO_2qs(OH)]^{2-}$ and $[MoO_2qs]^-$, and the red-purple complex to the dimer $[(MoO_2qs)_2(Hqs)_3]^{5-}$.

In the present work, spectrophotometric determination of molybdenum after extraction of the red-purple complex as an ion-association complex with a quaternary ammonium salt is described. Determination of molybdenum in the organic phase is more sensitive than in water, owing to the concentration effect, and selectivity of the method has also been improved.

Experimental

Apparatus. Spectrophotometric measurements were carried out with a Shimadzu spectrophotometer UV-240 and a 10-mm cell. A Hitachi-Horiba glass electrode pH meter F-7LC was used for pH measurements. A Yamato Shaker FA-31 was used.

Reagents. A 0.01 M (1 M = 1 mol dm^{-3}) of stock solution of molybdenum(VI) was prepared from hexaammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and standardized chelatometrically. Commercially available 8-hydroxy-5-quinolinesulfonic acid (H_2qs) was recrystallized from water. A 0.1 M stock solution of NaHqs was prepared by dissolving the weighed amount of H_2qs into the equivalent amount of sodium hydroxide solution and diluting to the volume with water. A 1.9 M hydrazine solution was prepared by dissolving 123.9 g of hydrazinium sulfate into water, neutralizing to about pH 7 with sodium hydroxide solution and diluting to 500 cm^3 with water. A 0.01 M methyltrioctylammonium chloride (Q^+Cl^-) solution was prepared by diluting 25 g of Capriquat (Dojindo Laboratories) to 500 cm^3 with chloroform. Acetate buffer solutions were prepared in the usual way. Deionized water was used. Other reagents used were of G. R. grade.

Procedure. To a sample up to 5 cm^3 containing 38—288 μg molybdenum(VI) in a 100-cm^3 Erlenmeyer flask are added 5 cm^3 of 0.1 M NaHqs solution, 5 cm^3 of 1 M acetate buffer solution (pH 4.6) and 5 cm^3 of 1.9 M hydrazine solution. The mixture is diluted to 20 cm^3 with water and heated for 20 min over a boiling water-bath. The solution at room temperature is transferred into a 100-cm^3 separatory funnel and diluted to 50 cm^3 with water. After addition of 10 cm^3 of 0.01 M QCl–chloroform solution, two phases are shaken for 5 min and allowed to stand for 5 min. The organic phase, dehydrated with anhydrous sodium sulfate, is subjected to optical measurements at 570 nm against the reagent blank obtained in the same manner.

Results and Discussion

Reduction of Mo^{VI}–H_2qs Complex. To a solution containing 96 μg molybdenum(VI) are added 5 cm^3 of 0.1 M NaHqs solution, 5 cm^3 of 1 M acetate buffer solution (pH 4.6) and different amount of 1.9 M hydrazine solution. After diluting the mixture to 20 cm^3 with water, the solution was heated for 40 min over a boiling water-bath. The solution at room temperature was transferred into a 50-cm^3 volumetric flask and diluted to the volume with water. Absorbance of the solution at 538 nm was measured against the reagent blank. It was found that the addition of more than 5 cm^3 of 1.9 M hydrazine solution is required for quantitative color development of the red molybdenum(V) complex. With 5 cm^3 of 1.9 M hydrazine solution, a maximum and constant absorbance of the molybdenum(V) complex was obtained for the heating time above 25 min. Effect of pH on the absorbance of the molyb-

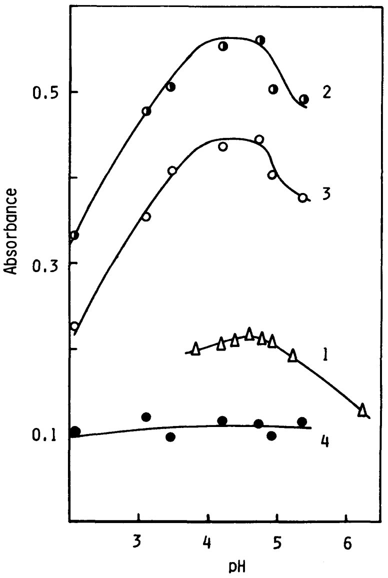

Fig. 1. Effect of pH on the absorbance of Mo^V–H_2qs complex in aqueous solution and chloroform extracts. 1: 96 μg Mo in 25-cm^3 aqueous solution, 538 nm *vs.* reagent blank, 2: 96 μg Mo in 10-cm^3 $CHCl_3$-extracts, 570 nm *vs.* $CHCl_3$, 3: 2 *vs.* reagent blank, 4: reagent blank *vs.* $CHCl_3$.

Table 1. Effect of diverse ions

Foreign ion	Added as	Added (μg)	Mo found (μg)	Error %
Ca^{II}	Sulfate	10000	94.9	−1.1
Mg^{II}	Sulfate	9700	96.4	+0.4
Zn^{II}	Chloride	1000	99.6	+3.7
Al^{III}	Chloride	200	98.9	+3.0
W^{VI}	Sodium salt	200	98.9	+3.0
V^{IV}	Sulfate	50	99.6	+3.7
Ni^{II}	Sulfate	20	99.5	+3.6
Cr^{III}	Chloride	20	96.7	+0.7
Cu^{II}	Sulfate	20	90.7	−5.5
Mn^{II}	Sulfate	20	94.1	−2.0
Co^{II}	Chloride	12	97.8	+1.9
Fe^{III}	Mohr's salt	10	159.1	+65.7
Fe^{III}	Mohr's salt	$10^{a)}$	102.4	+6.4

Mo^{VI} taken: 96.0 μg. a) Backwashed with 0.2 M sodium oxalate solution (pH 4).

denum(V) complex is shown in Fig. 1. The absorbance of the complex is constant in the pH range from 4.5 to 4.8.

Extraction of Mo^V–H_2qs Complex. The molybdenum(V) complex extracted according to the above procedure shows absorption maxima at 372 and 570 nm. The complex is quantitatively extracted in the pH range from 4.0 to 4.7, as shown in Fig. 1. A maximum and stable absorbance of the extracts at 570 nm was obtained for the addition of more than 4 cm^3 of 0.1 M NaHqs solution and for QCl concentration above 40 mM. The molybdenum(V) complex is quantitatively extracted for shaking time of 1—10 min at an aqueous-to-organic volume ratio of 5 : 1. Absorbance of the extracts remains constant at least for 30 min.

Calibration Curve. The calibration curve does not pass through the origin, but it is linear in the concentration range of molybdenum(V) from 38 to 288 μg in 10-cm^3 extracts. The results of regression analysis for the linear calibration range gave $Y=-(61\pm6.7)\times10^{-3}+(51\pm0.47)\times10^{-3}X$ at a significance level of $\alpha=0.05$, where Y is absorbance of the extracts at 570 nm and X is the concentration of molybdenum(V) in μg/cm^3-extracts.

Effect of Diverse Ions. Effect of foreign metal ions on the determination of molybdenum is given in Table 1. Interference by vanadium(IV) and iron(III) was significantly diminished as compared with the method of Busev and Fan.[3]

Composition of the Extracted Species. When the molybdenum(V)–H_2qs complex having the absorption maximum at 570 nm is predominantly extracted, the equilibrium is given by

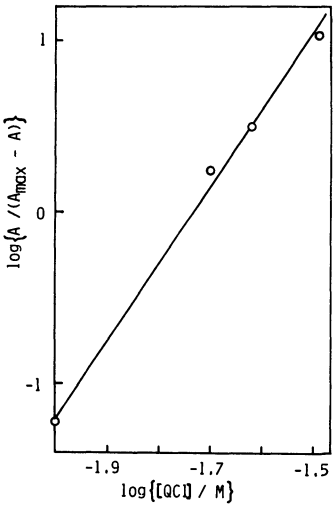

Fig. 2. A plot of log D *vs.* log[QCl] at pH 4.6.
Aqueous layer: [Mo]=96 μg, [NaHqs]=0.01 M, [Hydrazine]=0.19 M, [NaCl]=0.1 M.
The plot has a slope of 4.7 as evaluated by the method of least squares.

$$M^{m-} + m\,QCl_o \rightleftharpoons MQ_{m,o} + m\,Cl^- \quad (1)$$

where M^{m-} indicates the anionic Mo^V–H_2qs complex and subscript o the organic phase. The distribution ratio D of molybdenum(V) complex is given by

$$D=\frac{A}{A_{max}-A} \quad (2)$$

where A is the absorbance of the extracts at 570 nm and A_{max} that of the extracts where molybdenum(V) is quantitatively extracted. Thus, a plot of log D *vs.* log $[QCl]_o$ should give a straight line with a slope of m. As shown in Fig. 2, the plot has a slope of $m=4.7$, suggesting the composition of $[(MoO_2qs)_2(Hqs)_3(Q)_5]_o$.

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