

Chapter 9

SUBSIDIARY

9.1. Gravimetric Determination of Molybdenum(VI) with Salicylhydroxamic Acid.

Molybdenum(VI) has been precipitated and determined by precipitation with 8-hydroxyquinoline¹ and N-benzoylphenyl hydroxylamine² by weighing the complexes directly. But with the other reagents recommended, e.g., o-dianisidine³, -nitroso - naphthol⁴, cupron⁵ and purpurogallin⁶, the complexes have to be converted to molybdenum oxide for weighing. Salicylhydroxamic acid⁷ has been used by Bhaduri for the colorimetric estimation of the metal ion. In the present investigation, this reagent has been used to precipitate molybdenum(VI) ions quantitatively from acidic solutions and the metal has been determined by weighing the complex, $\text{MoO}_2(\text{C}_7\text{H}_6\text{O}_3\text{N})_2$. Separation of this metal from a good number of other ions have been effected by the adjustment of pH or using tartaric acid or ascorbic acid as masking agent for the latter ions. This method has been extended for the determination of molybdenum content of molybdenite.

EXPERIMENTAL

9.1.1. Reagents and Chemicals

Salicylhydroxamic acid solution - The reagent was prepared⁸ in the laboratory by the reaction of an alkaline solution of hydroxylamine on the sodium salt of methyl salicylate in water solution.

The reagent was recrystallised from 50% ethanol. A solution of the reagent was prepared in 2M sodium hydroxide solution.

Molybdenum(VI) solution - Molybdenum trioxide (G.R., E. Merck) was fused with potassium persulphate and the mass was taken up in 4.5M sulphuric acid. The metal content was determined with 8-hydroxyquinoline¹.

Diverse Ions - Sulphates of nickel(II), zinc(II), manganese (II), nitrates of cobalt(II), aluminium(III), iron(III), chromium(III) and uranium(VI) were dissolved in dilute acids. Sodium vanadate and tungstate were dissolved in water.

9.1.2. Apparatus

pH - Meter - A battery operated bench model Cambridge pH-meter was used for the measurements of pH.

9.1.3. Determination of Molybdenum(VI)

A known amount of the stock molybdenum(VI) solution was diluted to 60 to 70 ml and the pH was adjusted between 1.0 and 2.0 by the addition of hydrochloric acid. Salicylhydroxamic acid dissolved in minimum amount of sodium hydroxide (2M) solution was added and the mixture was allowed to stand for 10 minutes with occasional stirring. The precipitate was filtered, washed with cold dilute hydrochloric acid (pH 1.0 - 2.0) and dried at 110°C. The results given in Table 9.1 - I were calculated on the basis that the molybdenum content of the precipitate was 22.18%.

Table 9.1- I

Determination of Molybdenum(VI)

Mo taken,(mg)	Wt.of complex,(mg)	Mo found,(mg)	Rel.Error,(%)
15.76	71.6, 71.4	15.76, 15.74	nil, -0.13
25.22	113.6, 113.8	25.20, 25.24	-0.08, +0.08

9.1.4. Properties and Composition of the Complex

The yellow coloured molybdenum(VI)-salicylhydroxamic acid complex was found to be insoluble in benzene, ether and chloroform, but moderately soluble in absolute ethanol. The complex was stable upto 170^o C. The pure complex was analysed for molybdenum using 8-hydroxyquinoline and for nitrogen by Duma's method. The experimental results given in Table 9.1 - II agreed with the formula, $MoO_2(C_7H_6O_3N)_2$.

Table 9.1 - II

Element	Experimental,(%)	Calc. for $MoO_2(C_7H_6O_3N)_2$
Molybdenum	22.15, 22.16	22.21
Nitrogen	6.44, 6.46	6.48

9.1.5. Studies of Different Variables and Results

A. Effect of pH - Molybdenum(VI) solutions were adjusted to different values, and maintaining all the other conditions same, the metal

was determined with a fixed amount of the reagent (four times the amount theoretically calculated). The precipitation was found to be quantitative when the pH was in between 0.5 and 2.5. The reagent partially precipitated out below pH 0.2. The results are given in Table 9.1 -III.

Table 9.1 - III

Effect of pH

Mo taken : 15.76 mg

pH	Wt.of complex,(mg)	Mo found,(mg)	Rel.Error (%)
0.2	73.4	16.17	+2.60
0.5	71.6	15.76	nil
0.9	71.4	15.74	-0.13
1.5	71.7	15.80	+0.25
2.2	71.4	15.74	-0.13
2.5	71.6	15.76	nil
3.0	46.0	12.76	-19.03

B. Effect of the Concentration of the Reagent

Molybdenum(VI) was precipitated with salicylhydroxamic acid from solutions maintained at pH 1.5 using different amounts of the reagent. All other conditions were the same. It was observed that three fold excess of the calculated amount of the reagent was

necessary for the quantitative precipitation. The experimental results are in Table 9.1 - IV.

Table 9.1 - IV

Effect of the Concentration of the Reagent
Mo taken : 15.76 mg

Reagent (g)	Wt.of the complex,(mg)	Mo found,(mg)	Rel.Error,(%)
0.18	68.7	15.14	-3.93
0.19	69.5	15.31	-2.85
0.20	71.6	15.76	nil
0.21	73.0	16.08	+2.03

C. Effect of Sequestering Agents - Tartaric, citric and ascorbic acids were found not to interfere with the determination of molybdenum(VI), but fluoride prevented the precipitation. Disodium-EDTA could not be used at this pH region as the free acid is separated. The experimental results are given in Table 9.1 - V.

Table 9.1 - V

Effect of the Sequestering Agents

Mo taken : 15.76 mg

Sequestering agent	Wt.of complex, (mg)	Mo found,(mg)	Rel. Error,(%)
Citric acid, 0.5g	71.7, 71.4	15.80, 15.74	+0.25, -0.13
Tartaric acid,0.5g	71.4, 71.6	15.74, 15.76	-0.13, nil
Ascorbic acid,0.5g	71.4, 71.6	15.74, 15.76	-0.13, nil

D. Effect of Diverse Ions - A known amount of molybdenum(VI) solution was mixed with desired amounts of foreign ion solution. The determination of molybdenum was carried out following the procedure described in Section 9.1.3. Thus, molybdenum(VI) could be separated from Co^{2+} , Ni^{2+} , Mn^{2+} , Al^{3+} or UO_2^{2+} at pH 1.0 - 2.0.

However, 0.5 g of tartaric acid was added before the addition of the reagent when molybdenum(VI) was determined in the presence of Zn^{2+} , Cr^{3+} , VO_3^- and WO_4^{2-} . In effecting separation of this metal ion from Fe^{3+} , the latter was masked with 0.5 g of ascorbic acid. In all these separations, the primary wash solution contained the appropriate masking agent. The final washing was, however, done with dilute hydrochloric acid (pH 1.0 - 2.0). The results of these separations are given in Table 9.1 - VI.

Table 9.1 - VI

Separation of Molybdenum(VI) from Diverse Ions

Mo taken : 15.76 mg

Diverse ion,(mg)	Masking agent	Wt.of complex,(mg)	Mo found,(mg)	Rel.Error,(%)
Ni ²⁺ , 20,40	-	71.7, 71.7	15.80, 15.80	+0.25, +0.25
Co ²⁺ , 20,40	-	71.6, 71.6	15.76, 15.76	nil, nil
Mn ²⁺ , 20,40	-	71.4, 71.4	15.74, 15.74	-0.13, -0.13
Zn ²⁺ , 20,40	a	71.4, 71.7	15.74, 15.80	-0.13, +0.25
Al ³⁺ , 20,40	-	71.4, 71.4	15.74, 15.74	-0.13, -0.13
Cr ³⁺ , 20,40	a	71.4, 71.4	15.74, 15.74	-0.13, -0.13
Fe ³⁺ , 20,40	b	71.4, 71.4	15.74, 15.74	-0.13, -0.13
VO ₃ ⁻ , 20,40	a	71.4, 71.4	15.74, 15.74	-0.13, -0.13
UO ₂ ²⁺ , 20,40	-	71.4, 71.4	15.74, 15.74	-0.13, -0.13
WO ₄ ²⁻ , 20,40	a	71.4, 71.4	15.74, 15.74	-0.13, -0.13

(a) tartaric acid (b) ascorbic acid

9.1.6. Determination of Molybdenum in Molybdenite

About 0.5g of finely powdered molybdenite was weighed and heated to fumes with 11 M perchloric acid. The mass was then treated

with 12M hydrochloric acid and evaporated almost to dryness. Finally, the mass was dissolved in 9 M sulphuric acid, diluted and filtered into a 100 ml measuring flask. The volume was made up.

The molybdenum content of the solution was determined in an aliquot (25 ml). Using ascorbic acid and tartaric acid (each, 0.5g) as masking agents. The results are given in Table 9.1 - VII.

Table 9.1 - VII.

Determination of Molybdenum in Molybdenite

Ore taken, (g)	Wt. of complex, (mg)	Mo found, (%)		Rel. Error, (%)
		Standard method	Given method	
0.4064	94.8	20.52	20.69	+0.83
0.4302	99.8	20.52	20.58	+0.29

9.1.7 Standard Deviation

The relative standard deviation in 32 determinations of molybdenum was $\pm 0.13\%$.

9.1.8 Discussion

The main advantage of this method is the rapid determination of small quantities of molybdenum (16 to 25 mg) with good accuracy. Separation from allied ions like vanadate, tungstate, as well as, Zn^{2+} , Cr^{3+} and Fe^{3+} is possible using tartaric or ascorbic acid, while Ni^{2+} , Co^{2+} , Mn^{2+} , Al^{3+} and UO_2^{2+} do not interfere at the pH range 1.0 to 2.0. The method described for the determination of molybdenum in molybdenite is also very simple.

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Summary

Molybdenum(VI) (16 to 25 mg) has been determined gravimetrically using salicylhydroxamic acid. The yellow complex, $\text{MoO}_2(\text{C}_7\text{H}_6\text{O}_3\text{N})_2$, containing 22.18 % of the metal is quantitatively precipitated in the pH range, 0.5 to 2.5 and weighed after drying at 110°C . The determination can be effected in the presence of Ni^{2+} , Co^{2+} , Mn^{2+} , Al^{3+} and UO_2^{2+} . Separation from Zn^{2+} , Cr^{3+} , VO_3^- and WO_4^{2-} are carried out by masking these ions with tartaric acid. Ascorbic acid is used to mask Fe^{3+} . A simple method for the determination of molybdenum content of molybdenite has been developed.

REFERENCES

1. Welcher, F. J. "Organic Analytical Reagents," Vol.II, D. Van Nostrand Inc., New Jersey (1959), p.300.
2. Sinha, S. K. and Shome, S. C. Anal. Chim. Acta, 24, 33 (1961).
3. Kodama, K. "Methods of Quantitative Inorganic Analysis", Interscience, New York (1963), p.217.
4. Patil, S. V. Indian J.Chem., 2, 317 (1964).
5. Welcher, F. J. "Organic Analytical Reagents," Vol. III, D. Van Nostrand, New Jersey(1959), p.246.
6. Dutt, Y. and Singh, R. P. Current Sci. (India), 35, 122(1966); Chem. Abstr., 64, 18398 (1966).
7. Bolomey, R.A. and Wish, L. J. Amer. Chem. Soc., 72, 4483(1950).
8. Merck Index 7th Ed., Merck & Co (U.S.A.) (1960), p.917.