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Gravimetric Determination of Molybdenum(VI) Employing *N*-Hydroxy-*N*-*p*-Chlorophenyl-*N*'-(2-Methyl-4-Chlorophenyl) Benzamidine Hydrochloride

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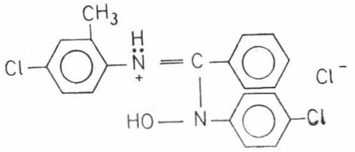
The use of *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-(2-methyl-4-chlorophenyl)benzamidine hydrochloride abbreviated as HCPMCPBH as a highly selective chelating agent for molybdenum has been investigated. The dioxomolybdenum complex $MoO_2(C_{20}H_{15}N_2OCl_2)_2$ is quantitatively precipitated at pH = 2.8—6.6. As the complex can not be washed free of excess reagent, the dried complex is ignited at 500—550 °C to MoO_3 for final determination. Most of the usual ions do not interfere. The method has also been applied for the determination of molybdenum in ferro-molybdenum and molybdenum ores.

The methods commonly used for the gravimetric determination of molybdenum are based on the formation of either insoluble molybdates[1] or on the precipitation with other chelating agents such as α-benzoin oxime[2], 8-quinolinol[3], *N*-benzoyl-*N*-phenylhydroxylamine (BPHA)[4] and its analogous[5]. However, most of these methods suffer from serious interferences due to lack of selectivity. The lead molybdate method shows interferences due to iron, vanadium, tungsten, titanium, arsenic, antimony, phosphate and chromium. In the α-benzoin oxime method the complex is ignited to MoO_3 for final weighing and is seriously interfered by vanadium, tungsten, palladium and chromium. The use of the 8-quinolinol method is restricted by the non selectivity nature of 8-quinolinol, and suffers serious interferences due to tungsten, vanadium, titanium and uranium. According to Majumdar the BPHA method[5] calls for a digestion of 1 h and is neither sensitive nor selective. Niobium, tantalum, tin, zirconium and other ions interfere in this method. The use of *N*-salicylhydroxamic acid[6] and analogues of BPHA, has also been recommended, but without any notable improvement. However, *N*-(o-toluoyl)-*N*-(o-tolyl)-hydroxylamine[7] has been reported to be quite selective in acidic medium.

In the present paper *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-(2-methyl-4-chlorophenyl)benzamidine hydrochloride, I, a member of the recently investigated chelating agents known as hydroxyamidines[8], has been used as a highly selective reagent for the gravimetric determination of molybdenum(VI). Though this reagent does not afford a directly weighable precipitate, yet, it can advantageously be applied to selectively estimate molybdenum in the pH range 2.8—6.6 in the presence of a large number of various ions such as



I

vanadium, titanium, chromium, iron, copper, uranium, niobium, tantalum, etc. which is an advantage over other existing methods. The present method can be successfully applied for the determination of molybdenum in ores and alloys.

EXPERIMENTAL

Apparatus

A Systronic pH meter type-322 was used for all pH measurements. A single pan semimicro balance VEB. Analytik type SAHM-6B was employed for weighing.

Standard Molybdenum(VI) Solution

A standard solution of molybdenum(VI) was prepared by dissolving BDH AnalaR quality ammonium molybdate in glass distilled water. The metal content of the solution was determined using 8-quinolinol[3].

Preparation of the Chelating Agent (HCPMCPBH)

N-hydroxy-*N*-*p*-chlorophenyl-*N*'-(2-methyl-4-chlorophenyl)benzamidine hydrochloride was prepared by the condensation of equimolar ratios of *N*-(2-methyl-4-chlorophenyl)benzimidoyl chloride and *N*-*p*-chlorophenyl hydroxylamine in ether at 0—5 °C[9]. The resulting hydrochloride was filtered and crystallized from absolute ethanol containing few drops of A. R. hydrochloric acid. Elemental analysis suggested satisfactory C, H and N values. A 3% (w/v) solution of HCPMCPBH in 90% ethanol was used throughout the experiments.

All the chemicals and reagents used were of A. R. grade.

Procedure

Dilute a suitable aliquot of molybdenum solution containing 4—40 mg of the metal to 150 ml and adjust the pH between 2.8—6.6 with acetic acid and ammonium acetate. Warm the solution to 60—70 °C and add the requisite volume of the 3% reagent solution (15 ml/25 mg of molybdenum) slowly with constant stirring till complete precipitation. Digest the orange-yellow complex for about 15—20 min over a boiling water bath and filter through a Whatman filter paper (No. 42, 11 — cm). Wash the complex with hot water and dry at 105 °C for 10—20 min. Transfer the

TABLE I

Determination of Molybdenum at pH 4.5 ± 0.1

Molybdenum taken/mg	Molybdenum found/mg	Number of experiment	Standard deviation	
			mg	%
3.98	3.96	5	±0.0158	±0.39
7.96	7.97	5	±0.0165	±0.20
11.94	11.96	5	±0.0158	±0.13
23.88	23.85	5	±0.0199	±0.08
31.84	31.87	5	±0.0234	±0.07
39.80	39.76	5	±0.0186	±0.04

complex along with the filter paper to a silica crucible and carefully ignite at 500—550 °C and weight as MoO_3. The weight of molybdenum trioxide multiplied by the conversion factor 0.66654 gives the amount of molybdenum. Table I shows that 4—40 mg of molybdenum can be determined satisfactorily.

DISCUSSION

Effect of pH

The formation of the molybdenum complex starts at pH as lows as 1.0, but it is not quantitative upto pH = 2.7. However, in the pH range 2.8—4.0, the complex separate in a fine form and requires very long digestion periods. Therefore the most suitable pH ranges for the determination of molybdenum by the present method is 4.1—6.6 in which a granular, easily digestable and filtrable precipitate is obtained. At and above pH 7.0 the complex has a sticky nature and hence is not suitable for gravimetric determination.

Amount of Reagent

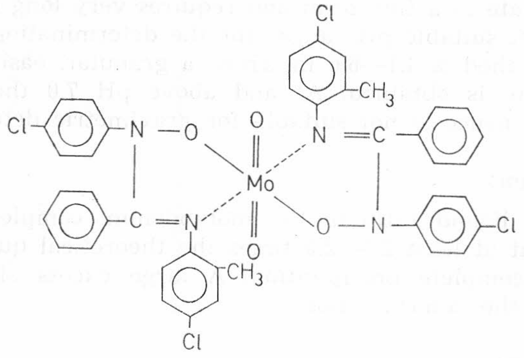
The metal to ligand ratio in the molybdenum complex is 1 : 2. It has been observed that at least 2.0—2.5 times the theoretical quantity of reagent is necessary for complete precipitation. A large excess of reagent has no adverse effect on the determination.

Nature of Complex

The dried dioxomolybdenum complex was analysed for molybdenum by ignition of a weighed portion to molybdenum trioxide and also by digesting with a mixture of concentrated nitric acid, sulphuric acid and perchloric acid, and subsequent gravimetric determination employing 8-quinolinol. The carbon, hydrogen and nitrogen were estimated by usual combustion methods. Found: Mo 11.03; C 55.12; H 3.28; N 6.32%; Calc. for $MoO_2(C_{20}H_{15}N_2OCl_2)_2$ requires Mo 11.06; C 55.29; H 3.45; N 6.45%.

The complex is diamagnetic and behaves as a nonelectrolyte in methanol. The electronic spectra of the chelate in ethanol shows an intence absorption maximum at 328 nm (recorded on Specord Carl-Ziess) which is probably the charge transfer band of the ligand. The complex is transparent in the visible region. All these are characteristics expected for a $4d^0$ system and agree well with the observation made in other dioxomolybdenum complexes[10,11]. Moreover, the IR spectral band at 930 cm^{-1} assignable as N—O stretching band[12,13] in the reagent is displaced to 960 cm^{-1} with an increase in intensity on complexation. These facts indicate the deprotonation of the hydroxyl hydrogen and the formation of a M—O bond. The C=N stretching band[14,15] in the reagent assigned at 1610 cm^{-1} is shifted to the lower frequency side (1575 cm^{-1}) in the complex. Thus it is very likely that the deprotonation of the $C{=}\overset{+}{N}{-}H$ hydrogen of the hydroxylamine hydrochloride takes place during complex formation. This is also supported by the fact that the broad band of the reagent at 2550 cm^{-1} assignable to $=\overset{+}{N}{-}H$ stretching is absent in the complex. All these facts suggest the deprotonation of the azometine nitrogen $=\overset{+}{N}{-}H$

and formation of a N—O—H bond, and the metal coordination through azomethine nitrogen atom by forming a C=N . . . M type of the bond. The existance of a cis-dioxomolybdenum group, O=M=O in the chelate is indicated by two very strong IR reobserved bands, one at 875 and the other at 914 cm^{-1}. The lower value of the symmetric stretching frequency (914 cm^{-1}) is truly indicative of the MoO$_2$ group, as an oxometal cation involving a single oxygen--metal multiple covalent bond absorbs at a considerably higher region around 970—980^{-1}[16,17]. Based on these studies, the following structure has been suggested for the molybdenum complex.



Effect of Diverse Ions

The influence of foreign ions on the gravimetric determination of molybdenum has been investigated. The procedure for the determination is the same with the only difference that the adjustment of pH as well as the precipitation of the complex were done after the addition of a definite amount of a foreign ion to the molybdenum solution. Under the conditions employed Cu(II), Fe(III), Ni(II), and VO$_3^+$ formed water insoluble complexes with the reagent and interfered seriously. However, EDTA masked these reactions and removed their interferences without causing any harm to the precipitation of the molybdenum complex. The presence of Li(I), Na(I), K(I), Ba(II), Sr(II), Ca(II), Mg(II), Be(II) (15 fold amount) and reasonable amount of Cl$^-$, Br$^-$, F$^-$, I$^-$, SO$_4^-$, NO$_3^-$, oxalate, tartrate, citrate and arsenate (40 folds) have no interfering effect on the determination of molybdenum. Rare earths do not interfere with the determination. Al(III), Zr(IV), Th(IV), and Se(IV) do not interfere with the method. In the presence of Nb(V) and Ta(V) tartaric acid (1 g) and NH$_4$HF$_2$ (500 mg) should be added. EDTA (1 g) should be present while precipitating molybdenum in the presence of Hg(II), Cd(II), Bi(III), Cr(III) and Pd(II). Ti (IV) was effectively masked with 5 ml of H$_2$O$_2$ (20%) and 20 ml of EDTA (10% w/v). For the separation of molybdenum from uranium the determination should be carried out at pH 3.0. Cr(VI) oxidises the reagent giving a reddish tinge to the precipitated complex. However, there is no change in the final weight of the ignited complex. Tungsten seriously interferes in the determination of molybdenum. The results are listed in Table II.

TABLE II

Determination of Molybdenum in the Presence of Foreign Ions (Mo taken — 25.10 mg)

Ions	Amount added mg	Complexing agent	Mo Found mg	Error mg
Fe^{3+}	100	a	25.14	+0.04
Mn^{2+}	110	—	25.06	—0.04
Ni^{2+}	90	a	25.09	—0.01
Co^{2+}	100	—	25.10	—
Cu^{2+}	100	a	25.12	+0.02
V^{5+}	25	a	25.15	+0.05
Ti^{4+}	30	b	25.14	+0.04
Zr^{4+}	80	—	25.08	—0.02
Zn^{2+}	110	—	25.08	—0.02
Al^{3+}	85	—	25.13	+0.03
Bi^{3+}	100	—	25.07	—0.03
Hg^{2+}	70	a	25.11	+0.01
Pb^{2+}	65	a	25.13	+0.03
Cr^{3+}	120	a	25.12	+0.02
Th^{4+}	150	—	25.09	—0.01
Nb^{5+}	50	c	25.05	—0.05
Ta^{5+}	50	c	25.07	—0.03
Tl^{3+}	160	—	25.14	+0.04
La^{3+}	150	—	25.10	—
UO_2^{2+}	140	d	25.12	+0.02

a — disodium salt of EDTA;
b — 20% H_2O_2 (5 ml) + 10% EDTA (20 ml);
c — tartaric acid (1 g) + NH_4HF_2 (500 mg);
d — pH 3.0

TABLE III

Determination of Molybdenum in Ores and Alloys

Matrix	Certified value %	Molybdenum[a] found %	Standard Deviation
BCS 48bG	55.7	55.57	±0.0469
Ferrow molybdenum	58.9	58.84	±0.0349
Ore^{x}	2.9	2.85	±0.0374
Synthetic mixture V^{5+}(20), Cu^{2+}(50), Fe^{3+}(150), U^{6+}(20), Ni^{2+}(30), Co^{2+}(50), Mn^{2+}(40), Mo^{6+}(20.7)^{Y,Z}	20.7	20.67	±0.0629

BCS 48bG British Chemical Standard (Mo 55.7; Cu 0.56%).
Ferrow molybdenum (Mo 58.9; Cu 0.25%).
Ore^{x} Obtained from Indian Bureau of Mines, Nagpur.
a an average of six determinations.
Y numbers in bracket gives the amout in mg.
Z in presence of 2 g of EDTA.

Application to the Analysis of Ores and Alloys

A known amount of the sample was dissolved in aquaregia with addition of concentrated sulphuric acid, and heating was continued till dissolution was complete. The solution was evaporated to almost dryness 3—4 times and diluted with water. Undissolved silica and inorganic matter were filtered off and the solution was diluted to volume in a calibrated 250 ml volumetric flask. A suitable aliquot of the solution was diluted to 100 ml. To this 10 ml of 10% Na_2EDTA were added. pH was adjusted to around 4.5 with acetic acid and ammonium acetate and the amount of molybdenum in the sample was determined by the above procedure. The result is summarized in Table III.

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SAŽETAK

Gravimetrijsko određivanje molibdena(VI) upotrebom *N*-hidroksi-*N*-*p*-klorfenil--*N*'-(2-metil-4-klorfenil) benzamidin hidroklorida

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Ispitivana je mogućnost upotrebe *N*-hidroksi-*N*-*p*-klorfenil-*N*'-(2-metil-4-klorfenil)benzimidin hidroklorida (HCPMCPBH), kao strogo selektivnog kelirajućeg reagensa na molibden. Dioxomolibdenski kompleks $MoO_2(C_{20}H_{15}N_2OCl_2)_2$ se kvantitativno taloži u području pH = 2.8—6.6. Budući da se kompleks ne može isprati od suviška reagensa, za konačno određivanje osušeni talog je spaljen na 500—550 °C u MoO_3. Prisutnost većine uobičajenih iona (Mn^{2+}, Ni^{2+}, Cr^{3+}, V^{5+} itd.) ne smeta dok vanadij vrlo jako interferira pri određivanju molibdena.

Metoda je uspješno primjenjena pri određivanju molibdena u feromolibdenu i molibdenskim rudama.

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