An Extractive Spectrophotometric Method of Determination of Molybdenum(VI) Using 3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one

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3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one (HL) behaved as a sensitive spectrophotometric reagent for molybdenum(VI). The metal ion formed a yellow complex with the reagent in acetic acid medium. The complex was extractable into 1,2-dichloroethane and the absorbance values remained unchanged for more than one week. Spectral data showed the formation of $1:2$ species with λ_{max} value at 411 nm. Beer's law was obeyed over the concentration range of 0—2.3 ppm. The molar absorptivity and Sandell's sensitivity were calculated to be 5.61×10^4 $dm^3 mol^{-1} cm^{-1}$ and 0.0017 $\mu g\,Mo\,cm^{-2}$ respectively, at 411 nm. The effect of as many as 41 cations and 28 anions and complexing agents was studied. Out of these only Sn(II), Ce(IV), citrate, oxalate, disodium dihydrogen ethylenediaminetetraacetate, and hydrogen peroxide interfered seriously. For ten replicate determinations of 1 $\mu g\,Mo\,cm^{-3}$ the standard deviation was 0.008 with a relative mean error of $\pm0.09\%$. The method is simple, selective, precise and rapid. It has been applied satisfactorily to the determination of molybdenum in steels, waters and flue dust samples.

The classical methods for spectrophotometric determination of molybdenum, based on its reaction with thiocyanate in the presence of a reducing agent[1a] and with 3,4-toluenedithiol[1b] are not too selective as they are subject to interference from many other elements and need masking in many cases. Methods using chromenone derivatives[2—6] reported in literature are also not suitable for routine analysis of the metal as these are prone to many interferences[4—6] and suffer from low sensitivity.[2—6] We have observed that 3-hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one (HL) compared with above mentioned chromenones gives the most sensitive and selective reaction with molybdenum(VI) when the colored species is extracted into 1,2-dichloroethane from weakly acetic acid medium. The proposed method is rapid and can be utilized in the analysis of a wide variety of commercial samples with a better accuracy.

Experimental

Apparatus, Reagents and Solutions: U-2000 (Hitachi) Spectrophotometer with 10 mm matched cells was used for the absorbance measurements. Solutions of molybdenum and other ions were prepared as reported earlier.[7] 3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one (HL) was prepared by the reported method[8] and dissolved in ethanol to give 0.002 $mol\,dm^{-3}$ solution. 1,2-Dichloroethane (Qualigens SQ) was distilled and the fraction distilling at 82.5—83 °C was used for extraction.

Steels: Steel sample (0.1 g) was dissolved in 3 cm^3 concentrated HCl and 1 cm^3 concentrated HNO$_3$ by heating slowly on a sand bath and the solution was evaporated to dryness. The cold residue was treated with 10 cm^3 0.5 $mol\,dm^{-3}$ HCl, transferred into a 100 cm^3 volumetric flask and volume made up to the mark; 1 cm^3 (BCS 406/1), 2 cm^3 (BCS 219/4) and 5 cm^3 (BCS 261/1) aliquots were neutralized with aqueous ammonia, acidity was adjusted to 0.6 $mol\,dm^{-3}$ with acetic acid (pH 2.8), 40 mg ascorbic acid (in each case) and 4 mg NaF (for BCS 219/4) were added

and analyzed for Mo by the proposed procedure.

Flue Dust Sample: Reverberatory flue dust (0.1 g) from copper manufacture, containing no molybdenum, was mixed with a solution of known Mo content and dried in an oven. After fusion of the dried dust sample with sodium peroxide (0.8 g), the leach was neutralized with concentrated H$_2$SO$_4$, made slightly alkaline with aqueous ammonia, boiled and the hydroxide precipitate was filtered and washed well with deionized water. The filtrate was adjusted to 0.6 $mol\,dm^{-3}$ CH$_3$COOH and Mo determined by the proposed method.

Well Water: To a 10 cm^3 aliquot of well water added a known amount of molybdenum (10μg), 20 volume hydrogen peroxide (1 cm^3) and aqueous ammonia (2 cm^3). The solution was boiled and evaporated to dryness. The residue was dissolved in 2 $mol\,dm^{-3}$ acetic acid (3 cm^3) and subjected to analysis for Mo by the proposed method.

Procedure: To an aliquot of the solution containing $\le23\mu g$ Mo(VI) in a 100 cm^3 separatory funnel added 3.0 cm^3 of 2 $mol\,dm^{-3}$ CH$_3$COOH and 1.0 cm^3 of 0.002 $mol\,dm^{-3}$ HL reagent. The final volume of aqueous phase was adjusted to 10 cm^3 with deionized water. The content was well mixed and then equilibrated with 10 cm^3 1,2-dichloroethane for 30 s. The two phases were allowed to separate and the organic phase was collected into a 10 cm^3 measuring flask after passing through Whatman No. 41 (9 cm size) filter paper to remove water droplets. The absorbance of the extract was measured at 411 nm against a similarly treated reagent blank. Molybdenum content in the samples was computed from a calibration curve prepared as per the proposed method.

Modifications for V, Fe, Ti, Zr, and W: For each mg of V(V) and Fe(III), 14 mg and 5 mg ascorbic acid respectively, can be added as a masking agent. Thus up to 15 mg each of V(V) and Fe(III) ions can be tolerated in the presence of proportionate amounts of ascorbic acid. Up to 0.5 mg Ti(IV), 1 mg Zr(IV) and 10 μg W(VI) can be suppressed by adding 4 mg sodium fluoride in each case.

Results and Discussion

In alkaline medium the reagent itself imparts a dark

yellow color which is not extracted into organic solvents. In neutral medium Mo(VI) does not give any colored reaction with the reagent but in acidic media an intense yellow complex is formed which is highly extractable into organic solvents.

Spectral Characteristics, Beer's Law and Sensitivity: Under the optimum conditions of the proposed method the absorption spectrum of yellow Mo-(VI)–HL complex against reagent blank shows two absorption maxima at 352 and 411 nm. The spectrum of the reagent blank against pure solvent shows that the reagent absorbs strongly up to 400 nm and thereafter the absorbance decreased to a negligible value. Measurements at 352 nm show a regular increase in the absorbance of the complex with time along with an increased interference due to a large number of cations which otherwise do not interfere at 411 nm. Therefore, for high stability of the complex and minimum interference of foreign ions, all the measurements are carried out at 411 nm. Coleman's test[9] indicates the formation of single species over the entire range of wavelength from 380 to 440 nm. Beer's law is obeyed over the concentration range 0—2.3 ppm, however, the practical range of determination of molybdenum obtained from Ringbom's curve is 0.17—1.82 ppm at 411 nm. The method has a molar absorptivity of 5.61×10^4 $dm^3 mol^{-1} cm^{-1}$ and Sandell's sensitivity equal to 0.0017 $\mu g Mo cm^{-2}$ at 411 nm. For ten replicate determinations of 1 $\mu g Mo cm^{-3}$ the standard deviation is 0.008 absorbance units with a relative mean error of $\pm 0.09\%$.

Choice of the Solvent: Maximum and equal value of absorbance of the complex is observed in both dichloromethane and 1,2-dichloroethane solvents but the latter shows higher stability (more than one week) than the former (less than 10 min). In case of other solvents the absorbance decreases in the order: benzene > chloroform > carbon tetrachloride > toluene > isopentyl acetate > butyl acetate > ethyl acetate > isobutyl methyl ketone > diethyl ether > isopentyl alcohol > 1 − butanol > cyclohexane. The complex is transferred quantitatively (100%) into 1,2-dichloroethane, dichloromethane, benzene, and chloroform through a single extraction with an equal volume (10 cm^3) of each solvent. In each case, the aqueous phase after single extraction is found void of molybdenum as confirmed by the more sensitive thiocyanate–pyrogallol method.[10] Other solvents extract the complex partially.

Effect of Acidity: Effect of acidity on the system is examined in terms of absorbance of the complex in organic phase. The absorbance of the complex from solutions of the same acidity (0.5 equiv) adjusted with different acids decreases in the order: $CH_3COOH > H_2SO_4 \approx HClO_4 > HCl > H_3PO_4$. This decrease in strong acids may be due to the formation of oxonium salts of the reagent, whereas in H_3PO_4, it may be due to the masking effect of the excess phosphate ion concentra-

tion over the tolerance level. Maximum and constant absorbance is obtained in the acidity range 0.1—1.0 $mol dm^{-3}$ CH_3COOH (pH 3.43—2.75). Therefore, the aqueous phase is adjusted to 0.6 $mol dm^{-3}$ CH_3COOH (pH 2.8) for further investigations.

Effect of Reagent Concentration: During the variation of reagent concentration a maximum and constant absorbance is observed for 0.2—2.5 cm^3 of 0.002 $mol dm^{-3}$ HL. Organic phase of the reagent blank develops a slight turbidity at ≥ 3.0 cm^3 concentrations of the reagent. Consequently the absorbance of the complex decreases on increasing the reagent concentration beyond 3.0 cm^3. Hence, 1.0 cm^3 of 0.002 $mol dm^{-3}$ reagent is recommended for further studies.

Effect of Equilibrium Period: The Mo(VI)–HL complex formed under optimum conditions of the aqueous phase is transferred quickly into 1,2-dichloroethane giving a maximum and constant absorbance for the variation of shaking time from 10 to 300 s.

Composition of The Complex: Equimolar solutions of molybdenum and reagent HL (1.0×10^{-4} $mol dm^{-3}$) are utilized to find out metal to ligand ratio by Job's continuous variations method as modified by Vosburgh and Cooper. The absorbance values are measured at two different wavelengths namely 411 and 430 nm. The curves obtained are indicative of 1 : 2 stoichiometry in the extracted species. This is further confirmed by mole-ratio method[11] by taking two different concentrations (2.0×10^{-5} and 3.0×10^{-5} $mol dm^{-3}$) of molybdenum and measuring the absorbance in each case at two different wavelengths as mentioned above. The composition of the complex is verified by equilibrium shift method[12] at 3.0×10^{-5} $mol dm^{-3}$ molybdenum and 2.25×10^{-5}—1.2×10^{-4} $mol dm^{-3}$ reagent concentration which gives the slope of the plot to be 1.93 (Fig. 1).

Effect of Diverse Ions: Of the various anions and complexing agents, hydrogen peroxide, disodium dihydrogen ethylenediaminetetraacetate, citrate, and oxalate interfere seriously. A hundred mg each of sulfate, chloride, phosphate, nitrate, thiourea, iodide, and hydrogensulfate; 60 mg acetate; 50 mg each of peroxodisulfate, thiocyanate, and bromide; 40 mg ascorbic acid; 20 mg each of borate, carbonate hydrogencarbonate, and diorthophosphate; 10 mg each of sulfite, iodate, disulfite, and pyrosulfate; 4 mg fluoride and 0.5 mg each of tartrate and dithionite do not interfere. Glycerol can be tolerated up to 0.2 cm^3. All the anions are added before the addition of the reagent as sodium salts except iodide, hydrogensulfate, peroxodisulfate, thiocyanate, bromide, iodate, disulfite, and pyrosulfate which are added as potassium salts. The above determinations are carried out with 10 μg Mo(VI).

Among the cations, the following have no effect on the determination of 10 μg Mo(VI) under optimum conditions even when present up to 10 mg each of Mg(II), Ca(II), Ba(II), Sr(II), Mn(II), Co(II), Cu(II), Zn(II),
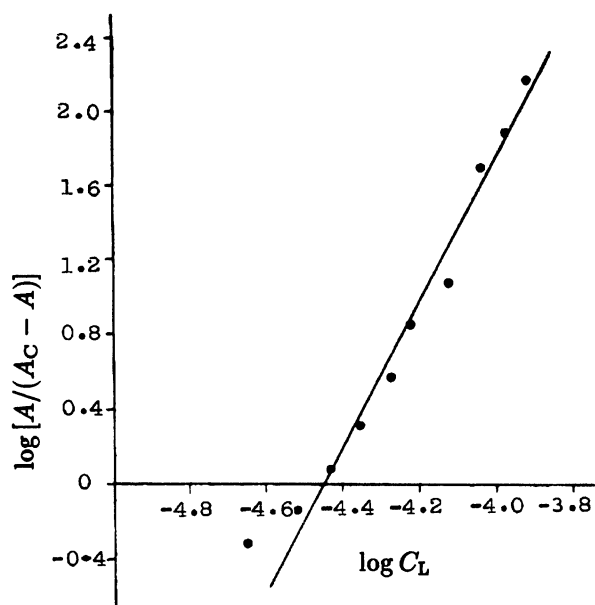
Fig. 1. Equilibrium shift method showing plot of $\log[A/(A_c - A)]$ vs. $\log C_L$ A = absorbance at a reagent concentration C_L, A_c = absorbance at complete formation of the complex, and C_L = total concentration of the reagent added. Conditions: Concn of $Mo(VI) = 3.0 \times 10^{-5}$ $mol\,dm^{-3}$; concn of $HL = 2.25 \times 10^{-5}$—1.2×10^{-4} $mol\,dm^{-3}$; 2 $mol\,dm^{-3}$ $CH_3COOH = 3$ cm^3; aqueous volume = solvent volume = 10 cm^3; solvent = 1,2-dichloroethane; equilibration time = 30 s; wavelength for absorbance measurement = 411 nm; number of extraction = 1. HL = 3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one.

Cd(II), Ag(I), Hg(II), U(VI), Pb(II), Cr(III), Fe(II), and V(IV); 4 mg Cr(VI); 3 mg each of Th(IV) and As(V); 2 mg Ni(II); 1 mg each of La(III), Al(III), Bi-(III), Nb(V), and Ta(V); 0.4 mg Sb(III); 0.2 mg each of Au(III), Pt(IV), Pd(II), Rh(III), Os(VIII), and Re-(VII); 0.1 mg Ir(III); 0.04 mg Ru(III) (higher amounts of platinum metals and Re are not tested except Ir and Ru). Interference due to 1 mg Zr(IV), 0.5 mg Ti(IV) and 0.01 mg W(VI) can be prevented by the addition of 4 mg sodium fluoride as masking agent. Up to 15 mg each of V(V) and Fe(III) can be tolerated in presence of 200 mg and 75 mg of ascorbic acid, respectively. The higher amounts of ascorbic acid than the permissible limit (40 mg) do not affect Mo(VI)–HL absorbance in the presence of these metal ions. Sn(II) enhances the absorbance while Ce(IV) decreases it significantly and thus are interfering.

Applications: The applicability of the method straightway to a wide variety of technical samples especially steels, flue dust and waters is shown (Table 1) by the satisfactory analyses. The proposed method has a better sensitivity[2—7,13,14] with a good precision and accuracy and tolerance of several important elements such

Table 1. Analysis of Samples by the Proposed Method

Sr. No.	Name of sample	Mo(VI) added μg	Mo(VI) found[a] μg
1.	Flue dust	20	19.1
2.	Well water	10	10.0
3.	BCS No. 406/1	1%[b]	0.969%
4.	BCS No. 219/4	0.58%[b]	0.585%
5.	BCS No. 261/1	0.11%[b]	0.103%

a) Average of duplicate analyses. b) Reported value.

as W, V, Cr, Mn, Fe, Co, U, Pt, Rh, Ru, Se, As, Ni, Cu, Th, Au, Re, Nb, Ta, Al, Zr, and Ti which interfere in most of the existing methods[1c,4—6)] of molybdenum determination. The method is simple and takes only 10 min in a single determination and much less for series operatinos.

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