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2-(2-Furyl)-3-hydroxy-4*H*-chromen-4-one as an Analytical Reagent for Molybdenum(VI)

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2-(2-Furyl)-3-hydroxy-4*H*-chromen-4-one (FHC) has been used as an analytical reagent for the spectrophotometric determination of molybdenum. Molybdenum(VI) in the presence of several cations except Sb(V), Bi(III), and Ce(IV), anions and complexing agents except oxalate forms a yellow 1 : 2 complex with FHC. The complex was extractable into chloroform from 0.01—0.25 mol dm^{-3} acetic acid (pH 4.2—2.9) and was stable for 2 h. The complex showed an absorption maximum at 414 nm with a molar absorptivity of 4.99×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity equal to 0.0019 μg Mo cm^{-2}. Beer's law was obeyed over the concentration range of 0—2.9 ppm. The equilibrium constant was found to be 6.70×10^{-12}. For 1 μg Mo cm^{-3} the standard deviation was 0.004 with a relative mean error of ±0.7%. The method is simple, selective, precise and rapid and has been applied to the determination of molybdenum in synthetic and standard samples.

Various chromenones[1—5] have been applied to the spectrophotometric determination of molybdenum. In course of investigations it has been observed that another similar reagent 2-(2-furyl)-3-hydroxy-4*H*-chromen-4-one (FHC), which possesses similar chelating ability but differing in sensitivity and selectivity with the above reagents, forms a colored complex with molybdenum(VI) in acetic acid medium extractable into chloroform. This forms the basis of the present method which can be successfully applied for the determination of the metal ion in various synthetic mixtures and standard samples.

Experimental

Apparatus and Reagents: UV-visible (Shimadzu-140-02) and UV-2000 (Hitachi) spectrophotometers with 10 mm matched cells were used for absorbance measurements and spectral studies, respectively.

A stock solution of molybdenum was prepared by dissolving sodium molybdate dihydrate (E. Merck) in deionized water to give 10 mg Mo cm^{-3} and standardized by oxine method. Aliquots were suitably diluted to give solutions at μg Mo cm^{-3} level.

The solutions of other ions were prepared by dissolving their commonly available chemically pure salts in water and dilute hydrochloric or sulfuric acid to give $\leq$10 mg cm^{-3} concentration of the ions.

2-(2-Furyl)-3-hydroxy-4*H*-chromen-4-one (FHC) was prepared by the reported method[6] and dissolved in ethanol to give 0.1% (w/v) solution.

Chloroform (Qualigens SQ) was distilled and the fraction distilling between 60—61 °C was collected for use.

Samples: Synthetic samples were prepared by mixing sodium molybdate and other metal ion solutions to get the desired composition.

Reverberatory flue dust sample (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_2SO_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 0.2 mol dm^{-3} CH_3COOH and Mo determined by the proposed method.

Steel sample (0.1 g) was dissolved in 3 cm^3 concentrated HCl and 1 cm^3 concentrated HNO_3 by gentle warming on a sand bath. The solution was evaporated to a thick mass and treated with water (10 cm^3) and diluted HCl (1.5 cm^3). It was then transferred into a 100 cm^3 volumetric flask and volume made up to the mark. To an aliquot (1.0 cm^3) were added ascorbic acid (30 mg) and aqueous ammonia, pH was adjusted between 2.9 to 3.0 and Mo was determined by the proposed method as described below.

Procedure: To an aliquot containing up to 20 μg Mo(VI) were added 1 mol dm^{-3} CH_3COOH (2.0 cm^3), 0.1% ethanolic solution (1.0 cm^3) of FHC, followed by adding deionized water to make the volume of aqueous phase 10 cm^3. This was then equilibrated with chloroform (10 cm^3) for 30 s. After phase separation, the organic extract was passed through Whatman No. 41 (9 cm size) filter paper to remove water droplets. Finally the absorbance of the yellow extract was measured at 414 nm against a similarly prepared reagent blank using 10 mm cells. Amount of molybdenum in the samples was computed from a calibration curve prepared previously under identical conditions of the procedure.

To the samples containing V, Zr, Ti, W, Cr, Fe, and Ru the optimum amounts of masking agents added before the addition of FHC were: 0.7 mg disodium dihydrogen ethylenediaminetetraacetate for V(V) up to 110 μg, 3.0 mg sodium fluoride for each of Zr(IV) and Ti(IV) up to 0.5 mg and 1.0 mg respectively, 0.3 mg sodium citrate for W(VI) up to 30 μg, 10 mg ascorbic acid for each of Cr(VI) and Fe(III) up to 16 mg and 0.25 mg, respectively. The system tolerated up to 8 mg Fe(III) in presence of proportionate amounts of ascorbic acid inspite of the fact that the latter was much larger than the optimum tolerance level for pure Mo(VI) solution. Ru(III) up to 20 μg did not interfere in presence of 50 mg thiourea. Sn(II) up to 0.3 mg did not interfere when 0.1 mg Pd(II) ions (0.166 mg $PdCl_2$) were added to the solution before extraction.

Results and Discussion

Molybdenum(VI) reacts with FHC giving a light yellow color in neutral medium which intensifies in acidic medium. The spectral characteristics, effect of variables and diverse ions on Mo(VI)–FHC absorbance and applications of the system are discussed below.

Spectral Characteristics, Beer's law and Sensitivity: The absorption spectrum of yellow Mo(VI)–FHC complex against reagent blank in chloroform at optimum conditions shows an absorption maximum at 414 nm (Fig. 1, Curve A). The spectrum of reagent blank against pure solvent (Fig. 1, Curve B) shows that the reagent practically does not absorb above 400 nm. Beer's law is obeyed over the concentration range 0—2.9 ppm. However, the optimum range of determination of molybdenum obtained from Ringbom's curve at 414 nm is 0.29—2.13 ppm. The equilibrium constant of the complex has been found[7] to be 6.70×10^{-12}. The molar absorptivity and Sandell's sensitivity are calculated to be 4.99×10^4 dm^3 mol^{-1} cm^{-1} and 0.0019 µg Mo cm^{-3} respectively at 414 nm. Ten replicate determinations containing 1 µg Mo cm^{-3} give mean absorbance of 0.517 with a standard deviation of 0.004 and a relative mean error of ±0.7%.

Choice of Extraction Solvent: The complex is quantitatively extracted in a single contact with equal volume (10 cm^3) each of chloroform, carbon disulfide, carbon tetrachloride, benzene, dichloromethane, and 1,2-dichloroethane. In each case, the aqueous phase after extraction is free from molybdenum as indicated by the more sensitive pyrogallol-thiocyanate method.[8] Maximum molar absorptivity is observed with chloroform and hence preferred in this system. The complex is extracted up to 50% into toluene, butyl acetate, isobutyl methyl ketone, ethyl acetate, isopentyl alcohol, diethyl ether, and cyclohexane and negligibly into isopentyl acetate and 1-butanol. The absorbance of the complex remains practically constant for 2 h in chloroform.

Effect of Acidity: The magnitude of Mo(VI)–FHC absorbance is independent of the nature of the acid. Same absorbance (0.520) is obtained from solutions of 0.1 mol dm^{-3} CH_3COOH and H_3PO_4 and also a buffer solution of pH 2.9. But the maximum stability (2 h) of the color is found in acetic acid medium. The color is less stable (30 min) when extracted from a buffer solution(glycine+HCl) of pH 2.9. Solutions of 0.1 mol dm^{-3} H_2SO_4 and HCl (pH$\leq$1) also give the same absorbance value but the color is least stable in these cases. Better stability (1 h) is obtained when pH is adjusted between 4.2—2.9 by adding ammonia to a solution containing mineral acids before the extraction. In acetic acid medium the absorbance is maximum and constant (0.520) in the range 0.01 to 0.25 mol dm^{-3} CH_3COOH (pH 4.2 to 2.9) beyond which a slight decrease in absorbance is observed (Table 1). Hence, the aqueous phase is adjusted to 0.2 mol dm^{-3} CH_3COOH for further studies.

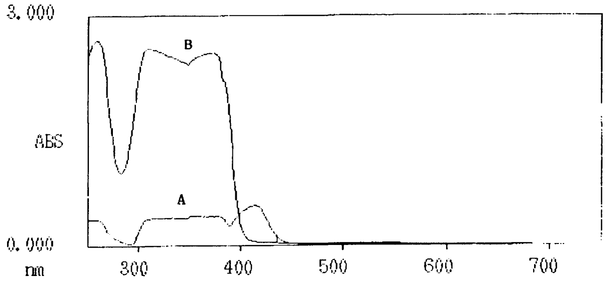

Fig. 1. Absorption spectra of Mo(VI)–FHC complex. (A) Complex against reagent blank, (B) Reagent blank against pure solvent. Conditions: Mo(VI) = 10 µg; FHC [0.1%(w/v)] = 1 cm^3; 1 mol dm^{-3} CH_3COOH = 2 cm^3; aqueous volume = solvent volume = 10 cm^3; solvent = chloroform; equilibration time = 30 s; number of extractions = 1.

Effect of Reagent Concentration: It is observed that 0.3—2.2 cm^3 of FHC (0.1% in ethanol) are sufficient to extract 10 µg of molybdenum in a single operation (Table 1). Higher amounts of the reagent give lower absorbance as the reagent blank becomes turbid with FHC concentration $\geq$2.5 cm^3. Therefore, 1.0 cm^3 of FHC solution is used for further investigations.

Effect of Equilibration Time: After complexation under optimum conditions, the extraction of Mo(VI)–FHC complex into chloroform is very fast and no change is observed in the absorbance when shaking time is varied from 10 to 300 (Table 1). The optimum equilibration time adopted is 30 s.

Stoichiometry of the Complex: Stoichiometry of the complex between Mo(VI) and FHC is established by Job's continuous variations method as modified by Vosburgh and Cooper. Taking equimolar solutions of molybdenum and FHC (1.04×10^{-4} mol dm^{-3}) and measuring the absorbance at two different wavelengths namely 414 and 430 nm, the curves indicate 1 : 2 stoichiometry in the extracted species. This is further confirmed by a clear break at 1 : 2 metal-ligand ratio in mole ratio method utilizing two different concentrations (2.08×10^{-5} mol dm^{-3} and 3.13×10^{-5} mol dm^{-3}) and measuring the absorbance in each case at two different wavelengths (414 and 430 nm). The ratio of slopes 2.26 and 2.04 obtained in slope ratio method at wavelengths 414 and 430 nm respectively, also shows the formation of 1 : 2 complex under these conditions.

Effect of Diverse Ions: The effect of diverse ions is studied by carrying out determination of 10 µg Mo(VI) in presence of each of these ions (mg amount in parentheses) added to the aqueous phase (10 cm^3) before the addition of FHC. The following ions do not interfere: nitrate (100), sulfate (100), thiourea (100), carbonate (70), bromide (60), peroxodisulfate (50), hydrogen carbonate (50), iodide (40), thiocyanate (40), disulfite (30), chloride (30), iodate (25), nitrite (20), borate (20), acetate (20), phosphate (15), ascorbic acid (10), sulfite (5), fluoride (3), disodium dihydrogen ethylenediaminetetraacetate (0.7), dithionite (0.5), tartrate (0.5), and citrate (0.3). All the anions are added as sodium salts except bromide, peroxodisulfate, iodide, thiocyanate, disulfite, and iodate which are added as

Table 1. Effect of Various Parameters on the Absorbance of Mo(VI)–FHC Complex

$CH_3COOH^{a)}$/mol dm^{-3}	0.00	0.01—0.25	0.3	0.4	0.5—0.7	0.8—0.9	
Absorbance	0.100	0.520	0.515	0.510	0.495	0.490	
FHC$^{d)}$(0.1% w/v)$^{b)}$/cm^3	0.1	0.2	0.3—2.2	2.5	2.7	3.0	4.0
Absorbance	0.400	0.485	0.520	0.510	0.510	0.495	0.415
Equilibration time$^{c)}$/s	1	2	3	5	10—300		
Absorbance	0.220	0.400	0.505	0.515	0.520		

a) Conditions: Mo(VI) = 10 µg; FHC [0.1% (w/v) in ethanol] = 1 cm^3; aqueous volume = solvent volume = 10^3; solvent = chloroform; equilibration time = 30 s; number of extractions = 1. b) Conditions: 1 mol dm^{-3} CH_3COOH = 2 cm^3; other conditions are the same as in (a) excepting variation in FHC content. c) Conditions: FHC [0.1% (w/v) in ethanol] = 1 cm^3; other conditions are the same as in (b) excepting variation in equilibration time. d) FHC = 2-(2-Furyl)-3-hydroxy-4*H*-chromen-4-one in ethanol.

Table 2. Analysis of Samples by Proposed Method

Sr. NO.	Composition of sample		Mo(VI)
	Matrix$^{a)}$	Mo(VI) added/µg	found$^{b)}$ µg
1.	Mn(2), Zn(1), Cu(1)	10	10.0
2.	Cu(2), Cr(0.5), Co(1)	10	10.1
3.	Sr(4), Cd(1), Al(0.2)	10	10.0
4.	Ni(1), Os(0.1), As(3)	10	10.0
5.	Pt(0.1), Au(0.1), Mg(2)	10	9.9
6.	Pd(0.1), Ti(0.5), Hg(1)	10	10.0
7.	Ca(2), Rh(0.01), Se(0.5)	15	15.1
8.	Ag(1), Ba(2), Re(0.1)	18	17.9
9.	Fe(2), Cr(1), Cu(1), Ti(0.1)	10	9.9
10.	U(0.5), W(0.03), Th(0.1)	8	7.9
11.	[Fe(0.29), Ni(0.075), Cr(0.1), Cu(0.005), Mn(0.01), Co(0.0005)]$^{c)}$	20	19.9
12.	[Fe(0.35), Cu(0.005), Ni(0.0456), Cr(0.095)]$^{c)}$	5	5.0
13.	[Fe(0.004), Ni(0.252), Cr(0.08), Cu(0.026), W(0.008), Al(0.004), Mn(0.004)]$^{c)}$	20	20.0
14.	[Fe(0.264), W(0.068), Cr(0.04)]$^{c)}$	10	10.1
15.	[Fe(2.665), Ni(0.033), Cr(0.466), Mn(0.033)]$^{c)}$	15	15.1
16.	V(0.1), U(0.5)	20	19.9
17.	Sn(0.05), Pd(0.1)	10	10.1
18.	BCS No. 406/1	1%$^{d)}$	0.96%
19.	Flue dust	15	14.98

a) Figure in bracket shows the amount of the metal ion added in mg/10 cm^3 aqueous phase. b) Average of the duplicate analyses. c) Sample numbers 11,12,13,14, and 15 are analogous to stainless steel, stainless U, cristite, steel CA-15 and cast steel, respectively. d) Reported value.

potassium salts. Glycerol does not interfere up to 0.5 cm^3. Oxalate and hydrogen peroxide interfere seriously.

Mn(II), Sr(II), Mg(II), Ca(II), Ba(II), Cu(II), Zn(II), Cd(II), V(IV), Hg(II), Co(II), Fe(II,III), Cr(III,VI) and As(V) (1 mg cm^{-3} each); Ag(I) (0.5 mg cm^{-3}); Ni(II) (0.2 mg cm^{-3}); Ti(IV), U(VI) and Se(IV) (0.1 mg cm^{-3} each); Al(III) and Zr(IV) (0.05 mg cm^{-3} each); Sn(II) (0.03 mg cm^{-3}); Th(IV) (0.02 mg cm^{-3}); V(V) (0.011 mg cm^{-3}); Pd(II), Pt(IV), Au(III), Os(VIII), and Re-(VII) (0.01 mg cm^{-3} each); Pb(II) (0.005 mg cm^{-3}); W-(VI) (0.003 mg cm^{-3}) and Ru(III), Ir(III) and Rh(III) (0.002 mg cm^{-3} each) do not interfere. V(V), Zr(IV), W(VI), Cr(VI), Fe(III), Ru(III), Sn(II), and Ti(IV) require masking agents/other metal ion as specified in the procedure. Sb(V) and Bi(III) get hydrolyzed under the conditions of the method. Ce(IV) intereferes seriously.

Applications: The wide applicability of the proposed method is tested by the satisfactory analysis of flue dust, steel and other synthetic samples containing molybdenum up to 20 µg in the aliquot (Table 2). This method is quite selective for the determination of molybdenum in the presence of large number of elements especially tungsten, tin, vanadium, chromium, manganese, iron, cobalt, uranium, platinum, rhodium, ruthenium, selenium, arsenic, nickel, copper, rhenium, thorium, gold, and aluminium which seriously interfere in most of the existing methods of molybdenum determination.[9] The total operation time in each run is less than 10 min. The method is found to be more sensitive ($\epsilon=4.99\times10^4$ dm^3 mol^{-1} cm^{-1}, sensitivity 0.0019 μg Mo cm^{-2}) than those reported earlier for molybdenum complex with chromenone derivatives such as 3-hydroxyflavone[1] ($\epsilon=3.7\times10^4$), 3-hydroxy-2-(2-sulfophenyl)-4*H*-chromen-4-one[2] ($\epsilon=1.4\times10^4$), morin[3] ($\epsilon=2.62\times10^3$) and other reagents[10—13] except pyrogallol-thiocyanate,[8] propylfluorone-antipyrine[10] and other fluorone derivatives, malachite green-thiocyanate[14] and quercetin-cetyltrimethylammonium bromide[15] which exhibit higher molar absorptivity. Thus the proposed method offers the advantages of better sensitivity, selectivity, wider Beer's law range, applicability to samples containing several interfering elements in concentrations higher than normally met with and is simple, rapid, precise, and accurate.

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