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Extraction and Trace Determination of Molybdenum(V) Using 6-Chloro-3-hydroxy-2-(5-methyl-2-furyl)-4*H*-chromen-4-one as an Analytical Reagent

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Molybdenum(V), obtained from Mo(VI) by reduction in presence of ascorbic acid in sulfuric acid medium, has been determined spectrophotometrically. Mo(V) formed an intense yellow 1:2 complex with 6-chloro-3-hydroxy-2-(5-methyl-2-furyl)-4*H*-chromen-4-one (CHMFC); the complex is extractable into 1,2-dichloroethane having $\lambda_{\max}$ at 437 nm. The proposed method is free from interference of many analytically important elements, with a molar absorptivity and Sandell's sensitivity of 5.32×10^4 dm^3 mol^{-1} cm^{-1} and 0.0018 μg Mo cm^{-2}, respectively.

Molybdenum(VI) can be determined spectrophotometrically by using various chromone derivatives[1–7] in different acid media. In most of these cases the sensitivity, selectivity, and Beer's law range were low. We have observed that Mo(V) obtained by reducing Mo(VI) with ascorbic acid gives an intense yellow color with 6-chloro-3-hydroxy-2-(5-methyl-2-furyl)-4*H*-chromen-4-one (CHMFC) in sulfuric acid medium after extracting the Mo(V)–CHMFC complex into 1,2-dichloroethane. The proposed method is highly simple and more sensitive and selective than most of the methods reported earlier[1–7] and can be successfully applied for the determination of various analytically important metal ions in various synthetic mixtures and standard samples.

Experimental

Apparatus and Reagents. An Elico SL164 double beam UV–vis spectrophotometer with 10 mm matched cells was used for absorbance measurements.

A stock solution of molybdenum(VI) (1 mg cm^{-3}) was prepared by dissolving sodium molybdate dihydrate (Thomas Baker, A. R.) in deionized water. The lower concentrations at μg Mo cm^{-3} level were obtained by suitable dilutions of the stock solution.

Solutions of other diverse metal ions were prepared by dissolving their salts (A. R.) in deionized water or dilute acids. Ascorbic acid (Thomas Baker, A. R.) was dissolved in deionized water to give 5% (w/v) solution.

6-Chloro-3-hydroxy-2-(5-methyl-2-furyl)-4*H*-chromen-4-one (CHMFC) was synthesized by a literature method[9,10] and was dissolved in ethanol to give 0.1% (w/v) solution.

Sulfuric acid 5 mol dm^{-3} was prepared by suitable dilutions of concentrated sulfuric acid 17.8 mol dm^{-3} (Qualigens, SQ).

1,2-Dichloroethane (Qualigens, SQ) was distilled and the fraction distilling at 82.5–83 °C was used for extraction.

Samples. Synthetic samples were prepared by mixing sodium molybdate dihydrate and other metal ion solutions to get the desired composition. Well water, varieties of steel (BCS 406/1, BCS 261/1, and BCS 219/4) and reverberatory flue dust samples were prepared as reported earlier.[8]

Procedure. An aliquot (1 cm^3) of the sample solution containing $\leq$26.2 μg Mo and other ions was taken in a 100 cm^3 separatory funnel. To this were added 2 cm^3 of 5 mol dm^{-3} H_2SO_4, 2 cm^3 of 5% ascorbic acid, 1 cm^3 of 0.1% (w/v) ethanolic solution of CHMFC, and 4 cm^3 of deionized water to raise the total aqueous volume to 10 cm^3 and the solution was mixed gently. The contents were then equilibrated with an equal volume 10 cm^3 of 1,2-dichloroethane for 30 s. After separation, the organic solvent phase was passed through a piece of Whatman filter paper No. 41 (9 cm size, pretreated with organic solvent) to remove water droplets. The absorbance of the extracted complex was measured at 437 nm against a similarly treated reagent blank. The molybdenum content was computed from the standard curve drawn under identical conditions of the method.

Modification for Masking Nb, Ta, and W. When $\leq$0.5 mg each of Nb(V) and Ta(V) or $\leq$0.02 mg of W(VI) were present, 7 mg of sodium fluoride or 10 mg of sodium citrate were added, respectively, to the aqueous phase well before the addition of CHMFC. In the case of 1 mg cm^{-3} each of Fe(III) and Cr(VI), 3 cm^3 ascorbic acid solution was required. Otherwise, the *procedure* remains the same.

Results and Discussion

CHMFC reacts with Mo(VI) to give a light yellow color in neutral medium and an intense yellow color in acidic media. The reagent also combines with Mo(V) obtained by ascorbic acid reduction[11] in 1 mol dm^{-3} H_2SO_4, forming a more intensely colored complex having an absorption maximum at 437 nm. Reduction by hydrazine sulfate has given low absorbances in both HCl and H_2SO_4 media of 1 mol dm^{-3} acidity and hence is not advantageous. Reduction of Mo(VI) to Mo(V) is not quantitative using Sn(II)–HCl. Sn(II) also forms an highly extractable (more than 90%) greenish yellow complex with CHMFC and hence interferes seriously in the determination of molybdenum.

Beer's law is obeyed over the concentration range of 0–2.60 μg Mo cm^{-3} of organic solvent phase; however, the optimum concentration range for accurate determination, as evaluated from Ringbom plot[12] is 0.20–1.99 μg Mo cm^{-3} of organic solvent phase at 437 nm. The molar absorptivity and Sandell's sensitivity of the proposed method are calculated to be 5.32×10^4 dm^3 mol^{-1} cm^{-1} and 0.0018 μg Mo cm^{-2}, respectively. The relative standard deviation of the method is 0.2% for ten replicate analyses of 1 μg Mo cm^{-3}.

Stoichiometry of the complex between Mo(V)–CHMFC is established by Job's method[13] of continuous variations, as modified by Vosburgh and Cooper.[14] The curves obtained by

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Table 1. Effect of Various Parameters* on the Absorbance of Mo(V)–CHMFC Complex

H_2SO_4[a)]/mol dm^{-3}	0	0.05	0.1	0.25	0.5–2.0	2.5
Absorbance	0.482	0.511	0.520	0.540	0.555	0.545
H_2SO_4[b)]/mol dm^{-3}	0.05	0.1–1.5	1.75	2.0	2.5	3.0
Absorbance	0.515	0.555	0.542	0.535	0.520	0.495
5% Ascorbic acid[c)]/cm^3	0	0.1	0.2–3.0	4.0	5.0	6.0
Absorbance	0.518	0.535	0.555	0.540	0.516	0.510
CHMFC[d)] (0.1% w/v)/cm^3	0.1	0.3	0.5	0.7–2.2	3.0	4.0
Absorbance	0.089	0.240	0.395	0.555	0.520	0.480
Equilibration time[e)]/s	2	5	10–200	240	300	350
Absorbance	0.290	0.420	0.555	0.510	0.446	0.426

a) Conditions: Mo = 1 mL of 1.04×10^{-4} M solution; 5% ascorbic acid = 2 cm^3; CHMFC [0.1% (w/v) in ethanol] = 1 cm^3; aqueous volume = organic solvent volume = 10 cm^3; organic solvent = 1,2-dichloroethane; equilibration time = 30 s; number of extractions = 1. b) Conditions: 5 mol dm^{-3} H_2SO_4 = 2 cm^3; other conditions are the same as in (a) excepting variation in H_2SO_4 content before extraction. c) Conditions: other conditions are same as in (a) excepting variation in ascorbic acid content. d) Conditions: 5% ascorbic acid = 1 cm^3; other conditions are same as in (a) excepting variation in CHMFC content. e) Conditions: CHMFC [0.1% (w/v) in ethanol] = 1 cm^3; other conditions are same as in (d) excepting variation in equilibration time.

Table 2. Analysis of Samples by the Proposed Method

Sample		Mo added	Mo found[b)]
No.	Matrix[a)]	μg	μg
1.	[Fe(1.777), Ni(0.22), Cr(0.311), Mn(0.022)][c)]	10	10.00
2.	[Fe(0.0044), Ni(0.277), Cr(0.088), Cu(0.028), W(0.0088), Al(0.0044), Mn(0.0044)][c)]	22	21.80
3.	[Fe(0.145), Ni(0.0375), Cr(0.05), Cu(0.0025), Mn(0.005), Co(0.00025)][c)]	9.50	9.55
4.	[Fe(1.05), Ni(0.1368), Cr(0.285), Cu(0.015)][c)]	15.0	14.86
5.	Ce(1), Zr(1), Sr(2), Cd(3)	20	19.72
6.	Bi(2), Th(0.66), Os(0.066)	8	7.97
7.	Pt(0.2), Mg(2), Au(0.4)	20	19.90
8.	Ca(1), V(4), Rh(0.04)	5	5.04
9.	Al(1), As(2.5), Fe(2)	7.5	7.52
10.	Pd(0.05), Ti(0.2), Ag(0.2)	5	4.96
11.	Well Water	10	10.00 ± 0.09[d)]
12.	Flue Dust	20	19.62 ± 0.01[d)]
13.	BCS(406/1)	1%[e)]	0.977 ± 0.021%[d)]
14.	BCS(261/1)	0.11%[e)]	0.105 ± 0.002%[d)]
15.	BCS(219/4)	0.58%[e)]	0.579 ± 0.003%[d)]

a) Figure in brackets shows the amount of the metal ion added in mg/10 cm^3 aqueous phase. b) Average of the triplicate analyses. c) Sample numbers 1–4 are analogous to cast steel, cristite, stainless steel, and stainless U, respectively. d) Mean ± relative standard deviation ($n = 7$). e) Reported value.

taking equimolar solutions of Mo and CHMFC indicated 1:2 = metal:ligand ratio in the extracted species. This is further confirmed by the mole-ratio method[15] results.

The complex is quantitatively (100%) extractable into 1,2-dichloroethane, dichloromethane, chloroform, carbon disulfide, and carbon tetrachloride, but maximum and constant absorbance is obtained in 1,2-dichloroethane. The complex is stable for more than one day in the extract. Therefore, it is chosen for further studies. The complex is partially extracted in other organic solvents. The aqueous phase after single extraction contains no molybdenum detectable by the more sensitive pyrogallol–thiocyanate method.[16] The complex shows maximum absorption at 437 nm and the reagent blank absorbs negligibly in this region. Therefore, absorbance measurements are carried out at 437 nm against the pure organic solvent.

The effect of variables on the absorbance of the Mo(V)–CHMFC complex was studied, keeping the concentration of molybdenum at 1.04×10^{-5} mol dm^{-3}. Conditions were the same as in the *procedure*, except where the relevant parameter is being varied, as shown in Table 1. It is concluded that the optimum conditions for transferring the complex quantitatively into an organic layer in a single extraction using an equal volume (10 cm^3) of 1,2-dichloroethane are 1 mol dm^{-3} H_2SO_4 for both the reduction and extraction steps, 1 cm^3 of 5% ascorbic acid, 1 cm^3 of 0.1% (w/v) ethanolic solution of CHMFC and 30 s equilibration time. These conditions giving maximum and constant absorbance are incorporated into the given *procedure*.

By taking 1 μg Mo cm^{-3} under optimum conditions of the procedure, one can study the effects of various anions, cations, and complexing agents on the absorbance of the Mo(V)–CHMFC complex. Nitrate (50), sulfate (45), chloride (40), thiourea (35), acetate (30), carbonate, iodate, iodide, peroxomonosulfate, and borate (7 each); phosphate (3.5), tartrate, and citrate (1 each); EDTA (0.8), fluoride (0.7), and oxalate (0.5) caused $<1\%$ error. All the anions and the complexing agents are added in the mg cm^{-3} amounts given in parentheses as their solid sodium salts except iodide, iodate, peroxomonosulfate, and bromide, which are added as potassium salts. These are added well before the addition of CHMFC. Thiocyanate and hydrogen peroxide caused $>12\%$ error even when present in traces.

Under the optimum conditions, Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Zn(II), Cd(II), Co(II), Cu(II), Hg(II), Fe(II), Cr(III), As(V), Al(III), Bi(III), and V(IV,V) (1 mg cm^{-3} each); Ag(I) (0.8 mg cm^{-3}), Pb(II), U(VI), and Th(IV) (0.5 mg cm^{-3} each); Zr(IV), Ni(II), Se(IV), and Ce(IV) (0.2 mg cm^{-3} each); Ti(IV) (0.06 mg cm^{-3}), Nb(V) and Ta(V) (0.05 mg cm^{-3} each); Rh(III), Os(VIII), Pd(II), Re(VII), Pt(IV), Ru(III), Ir(III), and Au(III) (0.02 mg cm^{-3} each, higher amounts were not tested); and W(VI) (0.002 mg cm^{-3}) cause $<1\%$ error in the absorbance of the Mo(V)–CHMFC complex. Sb(V) and Sn(II) even in traces give $>1\%$ error. Fe(III) and Cr(VI) (1 mg cm^{-3} each) cause $<1\%$ error in presence of 0.3 cm^3 of 5% ascorbic acid solution added per cm^3 of aqueous phase.

The proposed procedure is more simple, sensitive and selective than most of the existing methods[1–7,17–20] and has better precision and accuracy with a wider Beer's law range. The synthetic samples prepared by mixing several analytically important and frequently interfering elements were analyzed satisfactorily having an error of $<1\%$. The usefulness and applicability of the method to a wide variety of synthetic and technical samples, especially varieties of steel and flue dust, are shown (Table 2) by the satisfactory accuracy and precision.

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