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Dithionite as a New Reductant in the Thiocyanate Method for the Spectrophotometric Determination of Molybdenum

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Sodium dithionite has been recommended as a new reductant in the thiocyanate method for the spectrophotometric determination of molybdenum. The study is based on prior extraction of molybdenum(VI)–thiocyanate species in ethyl acetate from 0.8 mol dm^{-3} HCl medium followed by reduction of the complex with dithionite in the organic extract. The orange yellow color so obtained is measured at $\lambda_{\max}$ 468 nm against a reagent blank. The 1:5 (Mo:SCN) complex is stable for 1 h in ethyl acetate and obeys Beer's law over the concentration range 0—2.6 ppm of molybdenum (optimum range for accurate determination is 0.7—2.5 ppm). The molar absorptivity and Sandell sensitivity of the complex are 1.79×10^4 dm^3 mol^{-1} cm^{-1} and 0.0053 μg Mo cm^{-2}, respectively. The relative standard deviation for nine replicate determinations of 2 μg Mo cm^{-3} is ±1.1%. Of the tested 40 cations and 24 anions including complexing agents only thiourea interferes in the procedure. The method is sensitive and highly selective. It is applicable to the determination of molybdenum in steels and flue dust samples with satisfactory results.

Thiocyanate[1—5] is extensively used for the colorimetric determination of molybdenum even though several other reagents may give better results. Tin(II) chloride[1,2] is often employed as a reductant to reduce molybdenum to pentavalence for the formation of molybdenum(V) thiocyanate complex but the reduction does not stop at molybdenum(V) only. This lowers the sensitivity and also produces uncertainties in the color system which adversely affect the accuracy and precision of the method. To overcome these difficulties, the presence of iron prior to reduction,[2] is reported to be necessary, but the role of iron is not well understood.[1] Various other elements, viz., vanadium, tungsten, uranium, chromium, rhenium are also reduced by tin(II) and form thiocyanate complexes in their lower oxidation states which interfere in the determination of molybdenum. Therefore, a milder reductant that would convert molybdenum only to molybdenum(V), is desirable and thus sodium dithionite has been recommended for this purpose in the present investigation. Accordingly, an effort has been made to develop highly selective, reproducible and sensitive method for the spectrophotometric determination of molybdenum at microgram levels in real samples. The method is based on prior extraction of molybdenum(VI) with thiocyanate in ethyl acetate from HCl solution. The organic extract is subsequently treated with solid sodium dithionite in order to reduce molybdenum(VI) to molybdenum(V) and to develop an intense orange yellow color.

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.[6] Potassium thiocyanate (s.d. Fine Chem. Extra pure) (9.7176 g) was dissolved in deionized water to give 100 cm^3, 1 mol dm^{-3} solution. Sodium dithionite (purified, LOBA Chemie, minimum assay 87%) was used as solid. The reagent was stored in a cool and dry place, tightly closed to prevent its exposure to air and moisture. Ethyl acetate (Qualigens 'SQ') was distilled and the fraction distilling at 76.5—77 °C was used for extraction.

Wash solution was prepared by mixing 1 cm^3 of 1 mol dm^{-3} KSCN and 1.6 cm^3 of 5 mol dm^{-3} HCl solutions and diluting to 10 cm^3 with deionized water.

Sample: Synthetic samples were prepared by mixing sodium molybdate and other metal ion solutions to get the desired composition. Steel (0.1 g) was dissolved as reported earlier[7] and the final solution was made to 100 cm^3 in 0.8 mol dm^{-3} HCl, 1 cm^3 (BCS 406/1), 5 cm^3 (BCS 261/1) or 3 cm^3 (BCS 219/4) aliquots were taken for determination of molybdenum. Reverberatory flue dust sample (0.1 g) from copper manufacture, containing no molybdenum, was mixed with solution of known molybdenum content and dried in an oven. After fusion of the dried dust sample with sodium peroxide (0.8 g), the mass was dissolved in water, neutralized with concentrated HCl and adjusted to 0.8 mol dm^{-3} HCl in 100 or 50 cm^3 volume. 1 or 5 cm^3 aliquots were used for molybdenum determination.

Procedure for Extraction and Determination: To a sample solution containing ⩽26 μg molybdenum(VI) in a 100 cm^3 separatory funnel were added 1.6 cm^3 of 5 mol dm^{-3} HCl and 2.0 cm^3 of 1 mol dm^{-3} thiocyanate solution. The aqueous volume was adjusted to 10 cm^3 with deionized water. After mixing, the content was equilibrated with 10 cm^3 ethyl acetate for 3 min. The two phases were allowed to separate and the aqueous phase was discarded. To the organic phase, 10 cm^3 wash solution followed by 100 mg solid sodium dithionite were added and equilibrated immediately for 1 min again. The organic phase was poured over sodium sulfate anhydrate to remove water droplets and the absorbance of the orange yellow extract was measured at $\lambda_{\max}$ 468 nm against a similarly prepared reagent blank. Molybdenum content was obtained from a standard curve drawn under identical conditions of the proposed method.

Modifications for Cr(III,VI), Ti(IV), W(VI), Nb(V), and Fe(II,III): In 10 cm^3 aqueous phase, 100 mg ascorbic acid was added to mask ⩽10 mg Cr(III,VI) when present, whereas $\leqslant$ each of 5 mg Ti(IV), 3 mg W(VI) and 0.5 mg Nb(V) were masked with 100 mg sodium fluoride. For 20 µg molybdenum, the tolerance level for ascorbic acid (giving $<1\%$ error) is only 50 mg. The excess 50 mg amount added in case of Cr(III, VI) may be consumed in reduction/masking of the ions and is without any adverse effect. When 12 mg of Fe(II,III) were present, the organic extract was shaken with another 10 cm^3 portion of wash solution for 1 min, after adding another 100 mg portion of solid dithionite.

Results and Discussion

Dithionite is known for its rapid and powerful reducing action in alkaline medium.[8)] Keeping this fact in view, we studied different possibilities to reduce molybdenum(VI) to molybdenum(V) so as to achieve maximum color intensity of the thiocyanate complex by changing the order of addition of reagents and other solution conditions. When dithionite is added to molybdenum(VI) solution containing thiocyanate, as solid and adjusted to 0.1 mol dm^{-3} NaOH, no color is observed at room temperature or on heating the contents to boiling. However, when the solution is acidified, an intense orange yellow color is obtained which is extracted into organic solvents. On the other hand, if dithionite is added directly to acidic aqueous solution containing molybdenum(VI) and thiocyanate, only a white turbidity is observed. As the aqueous solution of dithionite disproportionates rapidly into thiosulfate ion and finally to elemental sulfur in presence of acids, it is considered appropriate to minimize the contact of dithionite with acidic aqueous solution as far as possible. This is done by first extracting molybdenum(VI)–thiocyanate complex into the organic phase at optimum conditions and then reacting molybdenum(VI)–thiocyanate species in the organic extract with solid dithionite as given in the procedure. The maximum absorbance value obtained in this case is the same as that obtained by first reducing molybdenum complex in alkaline medium and then extracting it from acidic solution. This study shows that the reduction of molybdenum(VI)–thiocyanate complex with dithionite can be accomplished in acidic medium as well. It is also found that dithionite added directly to the organic extract, as solid and shaking the content for 5 min (without any aqueous phase), gives only 95% of color intensity. The effect of various parameters on molybdenum(VI)–thiocyanate extraction into organic solvents is discussed below:

Optimum Conditions for Extraction of Molybdenum(VI)–Thiocyanate Complex: Molybdenum(VI)–thiocyanate species is extracted into various oxygenated solvents and high molecular weight amines but quantitative (100%) recovery is obtained in ethyl and isopentyl acetates with single extraction, using equal volumes of solvents, after equilibrating for 3 and 5 min, respectively, when molybdenum content is kept within Beer's law range. On reacting the extracted species with dithionite, the maximum and constant absorbance is shown only in ethyl acetate extract. Thus ethyl acetate is chosen for the purpose. Of the various acids studied, HCl in 0.6—1.5 mol dm^{-3} range gives maximum (100%) extraction which decreases in the order: $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HClO}_4 > \text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{CH}_3\text{COOH}$. Potassium thiocyanate, 1.8—3.0 cm^3 of 1 mol dm^{-3} concentration, added per 10 cm^3 of aqueous solution, is found sufficient to give quantitative extraction of the complex when aqueous phase is equilibrated with equal volume (10 cm^3) of ethyl acetate, for 3—10 min. Hence, 0.8 mol dm^{-3} HCl acidity, 2.0 cm^3 of 1 mol dm^{-3} KSCN and 3 min equilibration time, are chosen for further studies in this system.

After the extraction of molybdenum(VI)–thiocyanate complex into ethyl acetate, a large number of elements such as Sr(II), V(IV,V), Ce(IV), Cd(II), Ba(II), Ca(II), Mg(II), Mn(II), Be(II), Ni(II) (1 each); U(VI) (0.5); Pb(II) (0.2); Re(VII) (0.1); Au(III), Pt(IV), Ir(III) (0.01 each), and Ta(V) (0.05) are left unextracted completely alongwith Cu(II), Bi(III), Sb(III) (1 each); Se(IV) (0.2); Ag(I) (0.1) 50—90%; Hg(II) (1) and Pd(II) (0.01) 20—30% (figure in parentheses shows the mg amounts added cm^{-3} aqueous phase). If dithionite is added to the raffinate at this stage as solid and content is shaken immediately for 1 min with the same organic extract, an orange yellow color of molybdenum(V)–thiocyanate species is obtained in the solvent but V(V) and Re(VII) are also reduced to their lowervalent states and form colored thiocyanate complexes in solution which are coextracted 80 and 60%, respectively, causing a positive error. On the other hand, Se(IV), Cu(II), Pd(II), Hg(II), Bi(III), Sb(III), and Ag(I) present in both aqueous and solvent phases form colored precipitate which settle at the interface and affect the absorbance value considerably. To overcome these difficulties, the raffinate after extraction is rejected and the organic extract is shaken again with 10 cm^3 of the wash solution after adding solid dithionite to the contents of the separatory funnel. The effect of various variables (taken in the wash solution) on the development of molybdenum(V)–thiocyanate color in ethyl acetate extract, is discussed below:

Optimum Concentration of Variables in the Wash Solution and Order of Addition of Dithionite for Maximum Color Development in Ethyl Acetate Extract: Effect of Acidity: The ethyl acetate extract containing molybdenum(VI)–thiocyanate complex, gives a very little absorbance when shaken with neutral or alkaline wash solution having desired concentration of thiocyanate and adding solid dithionite before shaking. However, a constant and maximal absorbance is obtained when the wash solution is adjusted to 0.2—1.2 mol dm^{-3} HCl before shaking (Table 1). Thus, 0.8 mol dm^{-3} HCl concentration is found convenient for maximum color develop-

Table 1. Effect of Various Variables in the Wash Solution on the Absorbance of Mo(V)-SCN$^-$ Species

HCl[a)]/mol dm^{-3}	0.00	0.05	0.1	0.2—1.2	1.4	1.5	2.0
Absorbance	0.058	0.320	0.370	0.410	0.390	0.370	0.300
1 mol dm^{-3} KSCN[b)]/cm^3	0.0	0.2	0.4	0.5—2.5	3.0	3.5	4.0
Absorbance	0.021	0.360	0.395	0.410	0.390	0.380	0.375
Sodium dithionite[c)]/mg	0.0	10	20	40	50—150	200	500
Absorbance	0.031	0.175	0.250	0.395	0.410	0.400	0.320
Equilibration time[d)]/s	5	10	15	20	30—300		
Absorbance	0.270	0.380	0.395	0.405	0.410		

Conditions: a) Extraction of 20 μg Mo(VI) as thiocyanate complex at optimum conditions; 1 mol dm^{-3} KSCN=1 cm^3, total volume of wash solution=10 cm^3, sodium dithionite=100 mg, equilibration time=1 min, wavelength for absorbance measurement=468 nm. b) 5 mol dm^{-3} HCl=1.6 cm^3; other conditions are same as in (a) excepting variation in KSCN concentration. c) 1 mol dm^{-3} KSCN=1 cm^3; other conditions are same as in (b) excepting variation in sodium dithionite content. d) Sodium Dithionite=100 mg; other conditions are same as in (c) excepting variation in equilibration time.

ment. This shows that both extraction and reduction of molybdenum(VI)–thiocyanate take place in acidic conditions and occur at the same optimum acidity (0.8 mol dm^{-3} HCl).

Effect of KSCN Concentration: Wash solution containing HCl and dithionite but no thiocyanate, does not provide any color to the extract. It has been found that 0.5—2.5 cm^3 of 1 mol dm^{-3} KSCN added to 10 cm^3 wash solution, are sufficient to give maximum absorbance (Table 1).

Effect of Equilibration Time: Ethyl acetate extract on equilibration with wash solution containing HCl, KSCN, and dithionite in the optimum range, attains a full color intensity within 30—300 s (Table 1). Therefore, 1 min shaking time is preferred for further studies.

Effect of Nature of Reductants: After adding 10 cm^3 of wash solution to ethyl acetate extract and various reductants as solids or solutions, the content is shaken for 1 min at room temperature. The absorbance of the complex is found to increase in the order: ascorbic acid < hydroxyl ammonium chloride ≈ hydrazinium sulfate < thiourea < mercury < tin(II) chloride < zinc amalgam < sodium dithionite. It is noted that 50—150 mg sodium dithionite added as solid, last in the order and equilibrating the two phases immediately, gives a maximal and constant color of the complex. Hence, 100 mg amount of sodium dithionite is used for further studies. If shaking of the phases is done after 10 and 30 min, the absorbance value decreases to 40 and 10%, respectively. The colored complex formed under optimal conditions is found to be stable for 1 h in ethyl acetate extract at room temperature. Thereafter, the absorbance value increases gradually with time showing 2.5 to 6% increase after 2 and 5 h, respectively.

Spectral Characteristics, Beer's Law, Sensitivity and Composition: Under the optimum conditions of the method, molybdenum(V)—thiocyanate complex shows maximum absorbance at 468 nm. The reagent blank does not absorb in this region. Beer's law holds good over the concentration range 0—2.6 ppm of Mo with molar absorptivity and Sandell sensitivity of 1.79×10^4 dm^3 mol^{-1} cm^{-1} and 0.0053 μg Mo cm^{-2}, respectively. The optimum concentration range of molybdenum that can be measured accurately, as evaluated from Ringbom plot, is 0.7—2.5 ppm. The relative standard deviation for nine replicate determinations of 2 μg Mo cm^{-3} is ±1.1%. Job's method of continuous variations as modified by Vosburgh and Cooper, gives metal to ligand ratio as 1 : 5 in the extracted species. This composition is further confirmed by equilibrium shift method[9)] which gives the slope of the plot to be 5. Thus the complex may be formulated as $[\mathrm{MoO(SCN)_5}]^{2-}$. Presence of Mo–O bond is confirmed by IR spectra.

Effect of Diverse Ions: The ions (added in mg amounts are shown in parentheses per 10 cm^3 of aqueous phase) such as sulfate, acetate, citrate, oxalate, phosphate, tartrate, fluoride, carbonate, hydrogencarbonate, sulfite, borate, peroxodisulfate, bromide, disulfate, diphosphate, hydrogensulfate, iodide, disodium dihydrogen ethylenediaminetetraacetate, disulfite (100 each); nitrate, ascorbic acid (50 each); chloride (10); 20 volume hydrogen peroxide (1 cm^3), and glycerol (0.2 cm^3) cause < 1% error in the determination of 2 μg molybdenum cm^{-3}. All the anions are added as sodium salts except bromide, peroxodisulphate, iodide and disulfite which are used as potassium salts. Thiourea (20) lowers the absorbance to 15%.

In an aqueous phase (10 cm^3) containing 20 μg molybdenum and adjusted to optimum conditions for extraction, the cations (amounts in mg are shown in parentheses) extracted are Fe(III) (12), 90%; Pd(II) (0.1), Sn(II) (10), 80% each; Co(II), Hg(II) (10 each), 70% each; Os(VIII) (0.1), Fe(II) (12), 60% each; Se(IV) (2), Ti(IV) (5), Nb(V) (0.5), W(VI) (3), 50% each; Cu(II) (10), 40%; Sb(III) (10), 30%; Th(IV) (10), 20%; Bi(III) (10), 15%; Cr(III,VI), Zn(II) (10 each), Ag(I) (1), Ru(III) (0.01), 10% each; Zr(IV) (10), 8% and Al(III) (10), 5%. The amounts of Hg(II), Pd(II), Se(IV), Cu(II), Bi(III), Sb(III), and Ag(I) present in the extract are within permissible limits whose colored precipitate

Table 2. Analysis of Samples by the Proposed Method

Sample[a]	Mo added/µg	Mo found[b]/µg
Co(5), Bi(2), Re(1), Zn(5)	15.0	15.0±0.1 (RSD=0.85%)
V(5), W(0.5), U(2), Fe(6)	20.0	20.2±0.2 (RSD=0.93%)
Reverberatory flue dust (1 mg)	25.0	24.9±0.2 (RSD=0.74%)
	17.0	17.0±0.0 (RSD=0.02%)
Reverberatory flue dust (10 mg)	3.0	3.0±0.1 (RSD=2.75%)
BCS 261/1	0.11%[c]	0.11±0.00% (RSD=2.32%)
BCS 219/4	0.58%[c]	0.59±0.01% (RSD=1.39%)
BCS 406/1	1.0%[c]	1.00±0.02% (RSD=1.49%)

a) Figure in brackets indicates the amount of metal ion added in milligrams. b) Mean value±standard deviation (n=6). c) Certified value: RSD=Relative standard deviation.

formed on shaking with the wash solution after adding dithionite, do not affect the absorbance of molybdenum complex. Co(II) imparts green color to the extract which does not absorb at 468 nm. Ti(IV), W(VI), Nb(V), and Cr(III,VI) are not extracted in presence of respective masking agents as mentioned under modifications of the procedure. Iron(II,III) has a tendency to develop pink color in the organic extract due to the formation of iron(III)–thiocyanate complex. This can be easily avoided by back washing the organic phase with another 10 cm^3 portion of wash solution to which another 100 mg portion of dithionite is added before shaking. Cations such as Zn(II), Sn(II), Zr(IV), Th(IV), Os(VIII), Ru(III), and Al(III) present in the extract do not interfere. Thus none of the cations that are extracted in the solvent interfere with the color development i.e. reduction of molybdenum(VI)–thiocyanate with dithionite.

Applications: Table 2 shows a few synthetic and real samples (flue dust, steels) which can be analysed by the proposed method with satisfactory results. The method is of special value when the samples contain titanium, niobium, tantalum, tungsten, nickel, platinum metals, uranium, vanadium, chromium, and rhenium as they are not extracted at all under the conditions of the procedure. Dithionite has been used as a reductant for the first time in molybdenum(VI)–thiocyanate system. Its addition to the wash solution before shaking it with the ethyl acetate extract, makes the proposed method better than the most widely used tin(II) chloride–thiocyanate method[2)] and many others[1,3—5,10,11)] in respect of selectivity, precision and accuracy. The sensitivity is found comparable with some[2,10)] or better than most[1,3—6,10)] of the above mentioned methods. Also molybdenum(VI) is not reduced to lower than molybdenum(V) and it does not require the presence of iron for quantitative reduction. The proposed method is the most selective one amongst the existing molybdenum- thiocyanate systems.

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