

Spectrophotometric Determination of Cobalt, Nickel Palladium, Copper, Ruthenium and Molybdenum Using Sodium Isoamylxanthate in Presence of Surfactants

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Received 14.04.2000

A direct method has been developed for the spectrophotometric determination of microamounts of Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI) using sodium isoamylxanthate as a reagent in the presence of surfactant as solubilising agent. The method has been applied to the determination of these metal ions in various alloys and in environmental samples (fly ash).

Key Words: Sodium isoamylxanthate, surfactants, metal ions, environmental samples.

Introduction

Thio compounds play a vital role in analytical chemistry due to highly sensitive colour reaction, stability and selectivity towards various metal ions¹⁻¹². Xanthates have -CS₂ group which makes them more reactive towards various metals. These compounds form water-insoluble complexes with most of the metal ions; therefore, their complexes are either dissolved in water or extracted in a suitable organic solvent for their spectrophotometric determination, which is quite tedious and time consuming, and so there is a need for simpler and more rapid methods. In this method sodium isoamylxanthate has been used as a reagent for the spectrophotometric determination of Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI), which form water insoluble complexes and can be solubilised in micellar media. The present method has been found to be simple, rapid and sensitive for the determination of these metal ions.

Experimental

Equipment: A digital pH meter and an SP-20 Spectronic spectrophotometer were used.

Reagents: All the chemicals used were of analytical reagent (AR) grade. Doubly distilled water was used throughout the present study.

*Preparation of sodium isoamylxanthate*¹³: Stoichiometric quantities of isoamyl alcohol, sodium hydroxide and carbon disulphide (1:1:1) were used. Isoamyl alcohol was taken in a beaker and kept in an ice-salt mixture. Saturated solution of sodium hydroxide in water was added while stirring and carbon disulphide was added gradually with vigorous shaking for about 40 minutes and the xanthate formed was filtered by suction through a sintered funnel. Sodium isoamyl xanthate was dissolved in acetone, and filtered. Benzene was added to the filtrate slowly, while stirring. The precipitate formed was filtered by suction. The product was recrystallised by dissolving again in acetone and petroleum ether (b.p. 40-60°) was added to obtain precipitates, which were filtered and transferred to a vacuum dessicator and dried for 24 hours. A 0.5% solution of sodium isoamylxanthate was prepared in distilled water and standardised titrimetrically¹⁴ using mercuric acetate as a titrant and diphenylcarbazone as an internal indicator.

Metal ion solutions: Stock solutions of Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI) from their salts were prepared separately in distilled water and standardised¹⁵.

Effect of pH: Dilute solutions (0.1M) of NaOH, perchloric acid and ammonia were used for the study of pH effect on absorbance. Sodium acetate - acetic acid buffer (0.2 M, pH 5.0-5.8) was used for keeping the pH constant. *Solutions of interfering ions:* A 10% (w/v) solution of alkali metal salts and 0.2% (w/v) solution of different metal salts were used to study the interference of diverse ions.

Surfactant solutions: Sodium lauryl sulphate (SLS, 1%, w/v), Triton X-100 (TX-100, 5%, w/v) and cetyltrimethyl ammonium bromide (CTAB, 1%, w/v) were prepared in distilled water.

General procedure: To an aliquot of Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI) taken separately in the Beer's law range given in Table 1 was added sodium isoamylxanthate reagent solution (Table 1) and the pH was adjusted in the range given in Table 1 using 2.0 ml of acetate buffer, or adding 2 ml of 5M hydrochloric acid solution in the case of molybdenum. The complexes formed were solubilised in water by adding 1.0 ml of surfactant (Table 1) and diluted up to 10 ml in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar conditions.

Results and discussion

Absorption spectra: The absorption spectra of Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI) isoamyl xanthate complexes were recorded in the presence of surfactants against a reagent blank prepared under the similar conditions. The complexes absorb strongly at their respective absorption maxima (Table 1). The absorption spectra of metal complexes in acetone-water (1:1) in the absence of surfactant give less enhanced absorbance. Thus, adding the surfactant was preferred. The characteristic absorption spectra are shown in Figure 1.

Table 1. Analytical characteristics of metal isoamylxanthate complexes in the presence of surfactants

Characteristic	Co(II),	Ni(II),	Cu(II),	Pd(II),	Ru(III)	Mo(VI)
Beer's law range ($\mu\text{g}/\text{ml}$)	3.0-35	2.0-37	2.2-30	3.0-38	3.5-77	3.5-80
Absorption maxima (λ max, nm)	400	360	410	360	350	470
Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	1.92×10^4	1.2×10^4	2.06×10^4	0.95×10^4	1.18×10^4	1.13×10^4
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.0031	0.0047	0.0052	0.0067	0.0085	0.0086
pH range	4.5-9.0	6.0-8.0	3.0-8.0	4.5-7.0	4.5-7.0	5M HCl (2 ml)
Surfactant used*	SLS	SLS	SLS	TX-100	SLS	TX-100
Amount of 0.5% reagent used (ml)	0.5	2.0	3.0	0.3	2.0	2.0
Relative standard deviation ($n = 10$)	0.72	0.65	0.81	0.71	0.92	0.83

*SLS, TX-100 and CTAB were used for the study; however, the best results were obtained with the given surfactant. The developed conditions are applied for the simultaneous determination of the metals as shown in Table 2.

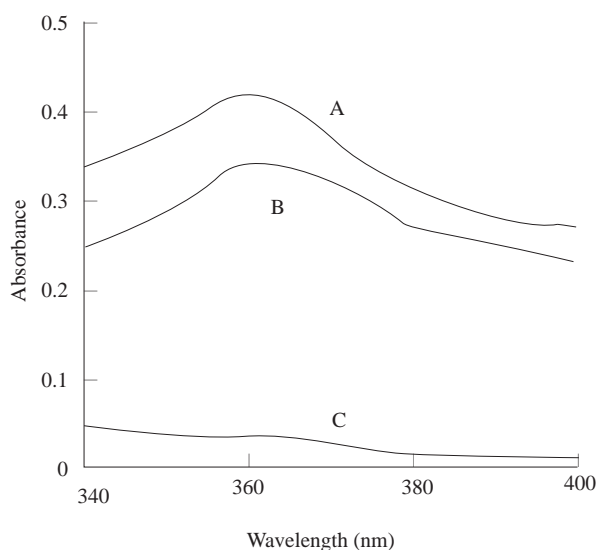


Figure 1. Absorption spectra of (A) palladium isoamylxanthate complex in the presence of surfactant Triton-X 100; (B) palladium isoamylxanthate complex in acetone -water mixture (1:1) and (C) reagent blank.

Effect of pH: The pH of metal complex solutions was adjusted using dilute solutions (0.1M) NaOH, perchloric acid and ammonia, and the effect on absorbance was studied. The absorbance of the complexes was maximum and constant in the pH range given in Table 1.

Calibration curves: The calibration curves were constructed at their respective absorption maxima and these were linear over a wide concentration range as given in Table 1 for each metal ion.

Effect of reagent concentration: Different amounts of 0.5% solution of reagent were added for each metal ion and it was observed that the absorbance was constant and maximum in the amounts given

in Table 1.

Effect of time: The absorbance was constant for more than 20 h in the case of Co(II), Ni(II), Cu(II), Pd(II) and Ru(III); however, the molybdenum complex was stable for only one hour in the presence of surfactants.

Effect of surfactants: The effect of various surfactants was studied on the absorbance of different metal complex solutions. The complexes were readily soluble in the presence of surfactants like SLS, TX-100, and CTAB, and an increase in absorbance was observed in all cases due to micellar action. Sodium lauryl sulphate (SLS) was preferred over other surfactants in cobalt, nickel and ruthenium; TX-100 in palladium; and SLS in copper and molybdenum, as it yields higher enhancement in absorbance than the to other surfactant.

Composition of the complexes: The composition of the complexes was studied in the excess of surfactant solutions by Job's method and the mole-ratio method. A break at a 1:2 (M:L) mole ratio suggested the formation of $M(C_6H_{11}OS_2)_2$ where $M = Co(II), Ni(II), Cu(II), Pd(II)$ and $Mo(VI)$ and in case of Ru(III) a break at 1:3 mole ratio suggested the formation $Ru(C_6H_{11}OS_2)_3$ under the given conditions.

Beer's law and sensitivity: Under the optimum conditions described above, calibration curves for different metal ions were constructed at their respective absorption maxima. Beer's law was obeyed over a wide concentration range of each metal ion (Table 1). The molar absorptivity and Sandell's sensitivity with RSD's are given in Table 1.

Interferences: The effects of diverse ions on the determination of these metal ions were studied in detail. To test the effect of diverse ions, Co(II) 20.98 μg , Ni(II) 37.0 μg , Cu(II) 12.7 μg , Pd(II) 15.0 μg , Ru(III) 38.66 μg and Mo(VI) 27.42 μg were determined by the general procedure, in the presence of their respective foreign ions. Each of these metal ions can be determined without any interference in the presence of a 50 fold excess of the following cations: Al(III), Bi(III), Ba(II), Cd(II), Cr(III), Mg(II), Mn(II), Pb(II), Sr(II), Rh(III), Zr(IV) and Zn(II). Amongst the anions examined (amount mg shown in parentheses), the following anions did not interfere: acetate(100), sulphate(70), thiosulphate(20), metabisulphite(30), citrate(90), bromide(70), thiocyanate(100), fluoride(95) and chloride(95). Iron(II and III) (50 fold in excess) in the determination of these metal ions was masked with 2.0 ml of 5% sodium fluoride solution. Pd(II) in the determination of these metal ions was separated by pre-extraction into chloroform at pH 2.5. EDTA interfered strongly in the determination of these metal ions due to its ability to form stronger complexes than isoamylxanthate.

Applications

Determination of metals in the presence of metal ions and alloys: A 0.1-0.5 g sample of the alloy was taken in a beaker and to this was added 10-15 ml of concentrated HCl and 5.0 ml of concentrated HNO_3 . It was heated on a hot plate until it dissolved and the final volume was reduced to about 5 ml. Then 10 ml of concentrated HCl was added and the solution was diluted with distilled water and filtered and final volume was increased to 25 ml in a standard flask. An aliquot of the resulting solution was determined by the general procedure. The results of the determinations are given in Table 2.

Table 2. Determination of metal ions in alloys/samples¹

Alloy/ Sample	Certified (%) composition	Amount of metal (μg) ^a		RSD(%)	
		taken	found		
Determination of cobalt					
JSS 607-6	Co:	4.72	14.01	14.02	1.98
	V:	0.82			
	W:	16.96			
High speed steel	Co:	9.25	20.51	20.51	1.96
	Mn:	0.40			
	Si:	0.005			
	S:	0.05			
	P:	0.05			
	Cr:	4.1-4.2			
	Mo:	5.5			
	W:	6.8-18.5			
Determination of nickel					
Stainless Steel no 306	Cr:	16.5	24.05	24.0	1.57
	Ni:	12.0			
	Mo:	2.0-3.0			
	^b Fe:	70-71			
Stainless Steel no. 304	Cr:	18.0	27.0	27.2	1.61
	Ni:	8-12			
	^b Fe:	70-71			
Monal alloy 400	Ni:	63	25.0	24.9	1.78
	C:	0.151			
	S:	0.00241			
	Mn:	0.071			
	Si:	0.51			
	^c Fe:	2.51			
	^b Cu:	31.01			
Edible oil	A		22.0	22.10	1.45
	B		30.0	30.20	1.66
Determination of copper					
Mallory	Cu:	99.2	25.0	25.10	1.47
	Cr:	0.81			
Steel	Cu:	0.54	32.0	32.15	1.85
	Ni:	0.441			
	^b Fe:	44.01			
Ca, Si, Mn and Cr:		55.021			
Determination of palladium					
Iridium alloy	Pd:	3.5	26.0	25.95	1.40
	Pt:	55.51			
	Rh:	7.01			
	^b Cu:	8.01			
	^c Fe:	3.51			
	Ir:	28.01			
Oakay alloy Pd:		20.5	22.10	1.63	
	Ni:	60.01			
	V:	19.51			
Determination of molybdenum					
Stainless Steel no 306	Cr:	16.5	40.0	41.15	1.63
	Ni:	12.01			
	Mo:	2-3.01			
	^c Fe:	70-711			
Eligiloy	Co:	40.0	70.0	69.85	1.73
	Ni:	15.01			
	Cr:	20.01			
	Mn:	2.01			
	Mo:	7.01			
	^c Fe:	15.01			
	Be:	0.051			
	C:	0.151			
Determination of ruthenium					
Synthetic Mixture	Ru(III) 10	60.0	60.13		1.47
	Ir(III) 151				
	Pd(II)	151			
	Os(VIII)	301			
	^c Fe(III)	30			

¹First the amount of each metal taken was tested by standard methods. a: each result is average of five experiments; b: masked with 2.0 ml of 5% thiourea solution; c: masked with 2.0 ml of 5% sodium fluoride solution.

Determination of nickel in edible oils: A 4 - 20 g of the oil sample (vegetable oil) depending on the nickel content was taken in beaker and decomposed with concentrated HNO₃. The dried sample was heated in a muffle furnace at 600°C for 1 h and then allowed to cool. After the addition of a few drops of concentrated HNO₃ it was dried and again heated to 700°C for 1 h. The ash was dissolved in concentrated HCl and diluted with a small amount of distilled water and filtered, and the final volume was increased to 10 ml in a standard flask. An aliquot of this solution was taken for the estimation of nickel by the general procedure. The results of the determinations are given in Table 2.

Determination of copper in beers, wines and fly ash: A weighed amount of fly ash (10 g each) and 50 ml of beer or wine sample was transferred to a beaker and dissolved in concentrated HNO₃ and evaporated to dryness. The residue thus obtained was dissolved in distilled water and diluted up to 100 ml. All samples were standardised by the known method⁹, after which copper was determined by the general procedure. The results of the determinations are given in Table 3 which are comparable to those of the reported method⁹ in which copper was extracted as the potassium morpholine-4-carbodithioate complex into molten naphthalene and dissolved in CHCl₃ and absorbance was measured at 440 nm.

Table 3. Determination of copper in fly ash, beer and wine samples

Sample	Amount of copper taken [μg]	amount of copper found (μg) aRSD(%)	
		Present method	Naphthalene method
Fly ash	5.5	5.51 \pm 1.85	5.49 \pm 1.86
Beer (Bottle)	6.6	6.64 \pm 1.79	6.63 \pm 1.80
Wine (Bottle)	8.7	8.72 \pm 1.75	8.72 \pm 1.73

^a: Mean of five determinations.

Simultaneous determination of cobalt and nickel: An aliquot of solution containing nickel and cobalt was taken in a beaker to which the reagent, buffer and SLS solutions as required were added and the absorbance was measured at 350 nm. An another aliquot of the same solution was taken, 1:10 ammonia solution added and absorbance measured at 400 nm and 350 nm. The nickel complex was decomposed by ammonia to give nickel-ammine while the cobalt complex remained unaffected. The absorbance at 400 nm corresponds to the cobalt while the difference of absorbance obtained at 350 nm before the addition of ammonia and afterwards corresponds to nickel. Results of the determinations are given in Table 4.

Table 4. Simultaneous determination of cobalt and nickel

Amount taken (μg)	Amount found (μg) + RSD(%)	
	Cobalt	Nickel
10.0	9.5 \pm 2.25	14.7 \pm 1.98
12.0	12.3 \pm 1.96	20.1 \pm 1.87
15.0	15.31.42	24.7 \pm 1.67
20.0	19.9 \pm 1.41	30.3 \pm 1.55

Each result is average of five experiments.

Conclusions

Sodium isoamylxanthate reacts with Co(II), Ni(II), Cu(II), Pd(II), Ru(III) and Mo(VI), which form water insoluble complexes which can be easily dissolved in water in the presence of the surfactants. The surfactants

increase the sensitivity by their micellar action. The present method has been found to be simple, rapid and applicable for the determination of metals in the presence of each other, which makes it an alternative to the existing methods for the determination of these metals.

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