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Extraction of Co(II) Spectrophotometrically by using Reagent 2-Acetyl Thiophene Thiocyanate

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2-Acetyl thiophene thiocyanate (ATT) was proposed as extractant for development of extractive spectrophotometric method for determination of Co(II). The reagent coordinates with Co(II) to produce yellow coloured complex which was then extracted into ethyl acetate at pH 10.8–11.2 having absorption maxima at 450 nm. The thermal study showed that the extraction reactions are exothermic in nature with the reagent, and the stoichiometric ratio of Co(II) to 2-acetyl thiophenethiocynate in organic phase was 1 : 2. The method permits separation and determination of cobalt from real and synthetic mixtures. The separation of Co(II) from bivalent metal ions has also been studied.

Key Words: Extraction, Cobalt(II), Spectrophotometrically, 2-Acetyl thiophene thiocyanate.

INTRODUCTION

The spectrophotometric determination of Co(II) with various reagents is known, but some of them show interference of foreign ions; in some the equilibriation time required is more, in some little amount of heating is required. Isonitrosopropiophenone[2], methylpyridylidene-*o*-aminobenzenethiol[3], isopropyltropolone[4], 1-nitroso-2-naphthol[5] and 2-nitroso-1-naphthol[6] used for spectrophotometric determination of cobalt are reported in literature. Extraction of cobalt by nitrosonaphtholate is slow and takes 30 min at room temperature for quantitative extraction of cobalt, which has serious interference of Fe(II), Sn(II), Pt(IV) and Pd(II) metals. Dithiazone[7] utilised for estimation of citrate buffer at pH - 8.0 suffers from coextraction of nickel. Thiocyanic acid[8] used for extraction suffer fram interference of copper(II) and iron(II). Tetraphenyl arsoniumthiocynate[9] used for determination of cobalt suffer froms Fe(III), Cu(II), Mo(II), Ni(II) and V(V). 1-(2-Pyridylazo)-2-naphthol[10] used for extraction of cobalt shows interference of Cu(II) and Ni(II). Promethazine hydrochloride[11] used for determination of cobalt in which many ions interfere. Munic acid[12] requires heating to 40–45°C whereas 4-(5-bromo-2-pyridylazo)-*m*-phenylenediamine and anthraquinone[13] require 10 min for full color development. 2,4-Dihydroxyacetophenone thiosemicarbazone[14] suffers from Fe(II), Cu(II), Mo(II), Pd(II) and Ni(II) interference in determining cobalt. Ethylthioxanthate[15] used for extraction of cobalt suffers from interference of Cu(II), Bi(II), Fe(II), EDTA and citrate. Cyclohexylthioglycolate[16] extracts cobalt from aqueous solution but shows serious interference of many metals. Extractive spectrophotometric determination of noble metals has been described earlier; however, the method adopted requires several extraction stages for quantitative recovery of metal ions, hence the present work is undertaken to develop a more effective method for extractive spectrophotometric determination of cobalt(II) using 2-acetyl thiophene thiocyanate[17] and its application in various commercial samples is carried out.

EXPERIMENTAL

Absorbance and pH measurements were carried out on a Shimadzu UV visible 2100 spectrophotometer with 1 cm quartz cells and a Control Dynamic digital pH-meter with combined glass electrode respectively.

The stock solution of cobalt(II) was prepared by dissolving 100 mg of equivalent cobalt(II) (1000 ppm) in 100 mL distilled water. The solution was standardized[18] and working solution of lower concentration was obtained by suitable dilution. 2-Acetyl thiophene thiocyanate (ATT) dissolved in methanol was used as extractant. A 0.1% solution of 2-acetyl thiophene thiocyanate was used for spectrophotometric determination of cobalt(II). All the other chemicals used were of analytical reagent grade.

General procedure

Extraction experiments were performed by shaking the appropriate organic and aqueous solution at an organic/aqueous phase ratio of 1 for 10 min. The distribution studies were carried out at 25°C, except the effect of temperature. The initial concentration of Co(II) was maintained 50 μg throughout the experiment. The ATT extractant forms a complex with cobalt(II), which was transferred in separating funnel and it was extracted in ethyl acetate (2 × 5 mL) and was transferred to a 10 mL volumetric flask with some amount of sodium sulfate in order to absorb trace amounts of water. The amount of cobalt metal present in the organic phase was determined quantitatively by spectrophotometric method The distribution coefficient, D was calculated as the ratio of Co(II) in the organic phase to that of the aqueous phase. Triplicate experiments and assays were routinely performed. In general, D had a standard deviation of ±5%. The uncertainty interval was higher for the very high ($D > 100$) or very low ($D < 0.01$) D values. Determination of cobalt(II) in the organic phase was calculated by taking absorbance at 450 nm spectrophotometrically and that in the aqueous phase was determined by known method.

RESULTS AND DISCUSSION

Effect of equilibrium time: The influence of shaking time for the extraction of Co(II) was studied for 30 s to 120 s. The quantitative extraction of Co(II) was achieved after 30 s with ATT. With further increase in shaking time, percentage extraction remained quantitative. The stability of the complex was studied as a function of time and it was found that the complex was stable for 48 h.

Influence of diluents: The suitability of the diluents was investigated using organic solvents such as ethyl acetate, chloroform, ethyl methyl ketone, methyl isobutyl ketone, *n*-butanol, carbon tetrachloride, toluene and hexane. The extraction of cobalt(II) was quantitative with ATT when both were dissolved in aqueous solution taking ethyl acetate. Ethyl acetate was used for further extraction studies as it gave better and quick phase separation.

Influence of temperature: The extraction study of Co(II) was performed at different temperatures from 303 to 343 K and it was found that the extraction of cobalt decreases as the temperature increases. The plot of log D against 1/T × 1000 (K) is shown in Fig. 1. The ΔH (change of enthalpy) is –18.54 kJ mol^{-1} for ATT respectively indicating exothermic reaction.

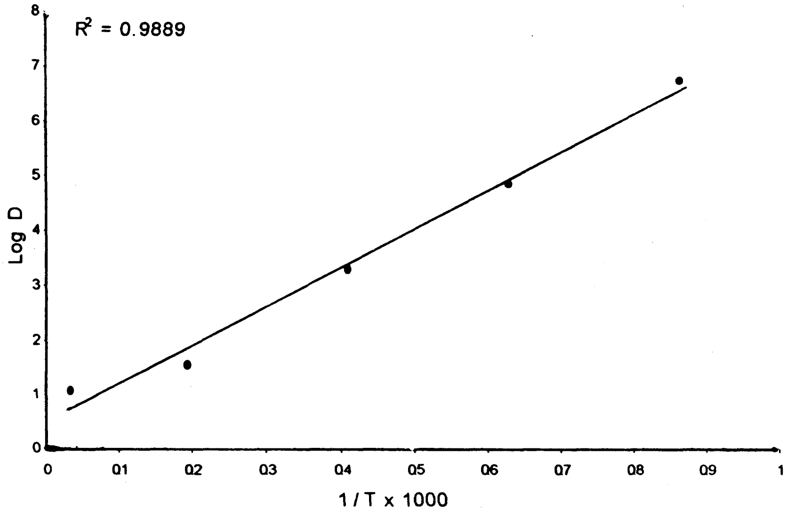

Fig. 1. Effect of temperature on extraction of Co(II) with ATT in ethyl acetate from aqueous media.

Effect of Reagent Concentration: Various volumes of 0.1% reagent solution were added to the sample solution containing 50 μg of cobalt at the respective pH values. The absorbances remained constant when the volume of the reagent solution used was more than 0.5 mL. Therefore 0.5 mL of 0.1% reagent was chosen for the quantitative determination of the metal.

Nature of Extracted Species: The nature of extracted species was ascertained from the plot of log D *vs.* log R from aqueous media (Fig. 2), where log D is the distribution coefficient of the complex and log R is the concentration of the reagent. The slope of the graph is 2.0366 for ATT. Thus stoichiometry ratio of metal to reagent was found to be 1 : 2 with the reagent.

Beer's Law and Sensitivity: Calibration graphs for these metals were constructed under the optimum conditions. The graphs obey Beer's law in the range of 2–32 μg for cobalt. The molar absorptivity and Sandell sensitivity were calculated to be 0.12×10^4 L mol^{-1} cm^{-1} and 2.08×10^{-5} μg cm^{-2}.

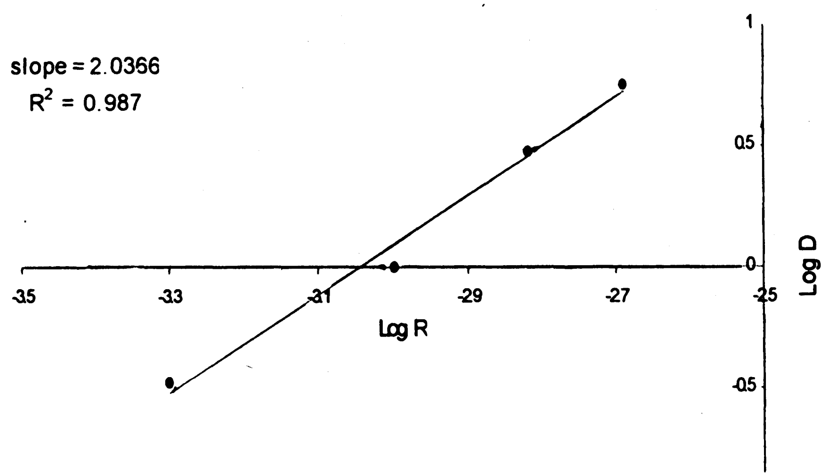

Fig. 2. Stoichiometric ratio of metal to reagent complex of Co(II) with ATT in ethyl acetate from aqueous media.

Influence of diverse ions on percentage extraction of Co(II): Varying amounts of foreign ions were added in the fixed amount (100 μg) of cobalt(II) to study the interference in the recommended extraction and the subsequent determination procedure. The tolerance limit was set at the amount of foreign ion required to cause ±2.0% error in the recommended procedure. The results are reported in Table-1.

TABLE-1
BINARY SEPARATION OF Co(II) WITH ATT IN ETHYL ACETATE FROM AQUEOUS MEDIA

Binary mixture metal taken (ppm)	Cobalt found (ppm)	
	Present method	Standard method
Co(5) + Mo(5)	4.98	5.01
Co(6) + Zr(4)	5.99	6.01
Co(5) + V(5)	5.02	5.01
Co(4) + Sn(6)	4.01	3.99
Co(5) + Cr(5)	5.01	4.99

*Each result is the average of three independent experiments.

Separation of Co(II) from other precious metal ions: The proposed method facilitates separation of cobalt (II) from its binary synthetic mixture with tin(II), molybdenum(VI), chromium(III), zirconium(IV) and vanadium(V). These metal ions do not extract and remain quantitatively in the aqueous phase under the optimum extraction conditions of cobalt(II) with ATT system facilitating separation of bivalent platinum quantitatively by the proposed method. The results are shown in Table-2. The proposed method also facilitates to determine cobalt(II) from various real samples.

TABLE-2
DETERMINATION OF Co(II) FROM REAL SAMPLES

Standard samples	Present (μg/mL)	Found (%)	Recovery (%)	R.S.D.*
Vitamin B_{12} injection	50	49.70	99.40	0.350
Macraberin Forte injection	36	35.96	99.88	1.010
$CoO\text{-}ZrO_7$ catalyst	157.13	157.12	99.99	0.045
$Co\text{-}Al\text{-}PO_4$ catalyst	202	201.60	99.80	0.076
Co-MgO catalyst	220	219.97	99.98	0.095

*Each result is the average of three independent experiments.

Conclusion

The results obtained show that newly synthesised ATT in ethyl acetate can be effectively used for quantitative extraction of Co(II) from aqueous media. The proposed method is quick and requires less amount of organic solvent. The equilibrium time required is very little, *i.e.*, only 30 s, and the complex is stable for 48 h. The results show good agreement with the standard method. The method is very precise. The ATT was first time used for extraction of Co(II) and successfully employed for separation of Co(II) from various binary mixtures

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