Spectrophotometric Determination of Cobalt (II)

MAZHER I. KHAN AND S. ARIF KAZMI

Department of Chemistry, University of Karachi, Karachi-32, Pakistan.

(Received 21st November 1978)

Summary: A new colorimetric estimation of cobalt is described. The procedure involves converting the cobalt containing sample into $CoCl_2$ and dissolving it in acetone and measuring the absorbance at 680 nm. Common cations which otherwise give blue-green solutions do not interfere. The recovery in all cases is better than 98% and the extinction co-efficient is large enough (560 M^{-1} cm^{-1}) to allow submillimolar concentrations in a one cm cell.

Introduction

While there are several reported methods of gravimetric and volumetric analysis of Co(II) in the literature[1,2], they are generally tedious, time consuming and unsuitable for submillimolar quantities. The only reported method for spectrophotometric determination of Co (II) which does not employ any special type of reagent is with conc. HCl as $CoCl_4^{2-}$ (λ = 692 nm)[3]. While this peak is intense, its sharpness makes it unsuitable as an analytical procedure when the equipment available is a colorimeter rather than a spectrophotometer. This difficulty is particularly magnified when Ni^{2+}, Fe^{2+} or Cr^{3+} are also present since their chlorides also have a significant absorbance in this region. Furthermore, the concentration of HCl also significantly effects the results in this procedure due to the equilibria between $CoCl_4^{2-}$, $CoCl_3H_2O^-$, $CoCl_2\ (H_2O)_2$ etc.[4,5]. On the other hand spectrophotometric methods for Co (II) determination using special reagents, while more sensitive, are applicable only under specific set of circumstances. For example in the method utilizing l-Phenyl-4-phenylamino-1,2,4-triazolium chloride[6], there is interference by Cu(II), Fe(III) as well as nitrate.

Halides of Co(II),CoX_2 (where X is Cl or Br) give an intense blue color in non-aqueous solvents, possibly forming CoX_4^{2-}. Utilizing this property, we have devoleped a procedure for colorimetric estimation of Co(II) in acetone in which most commonly encountered ions donot interfere.

Experimental

In this study cobaltous chloride hexahydrate, cobaltous carbonate, cobaltous nitrate hexahydrate, sodium cobaltinitrite, nickel chloride hexahydrate, nickel sulphate hexahydrate, nickel acetate, copper sulphate pentahydrate, copper chloride hexahydrate, ferric chloride, hydrochloric acid and acetone used were obtained from E. Merck. All chemicals including acetone were used without further purification.

Solutions were made by weighing the requisite quantities of compounds to yield the indicated concentrations in 25 ml. Volumetric flasks. One ml of conc. HCl was added first and then acetone was used to make up the remainder of the volume. Optical densities were recorded on Pye-Unicam SP 500 spectrophotometer and Bosch and Lomb Spectronic 20.

In the recovery experiments the compounds were first digested with conc. HCl in a long necked round bottom flask. The flask was then heated to near dryness This semi-dried mass was then extracted with acetone.

Possible interference was investigated by dissolving the substance, if soluble, and then recording the optical densities at 670 and 680 nm.

Results and Discussion

A plot of optical density vs. the concentration of $CoCl_2.6H_2O$ in acetone shows that in the region of our study (2.0×10^{-4} to 1.2×10^{-3} M), Beer's law is obeyed (ϵ =560 M^{-1} cm^{-1}). Where one ml. of concentrated HCl is not added the extinction co-efficient is considerably lower. This is probably because the species fromed is $Co[CoCl_4]$ and not all Co(II) is in identical environment.

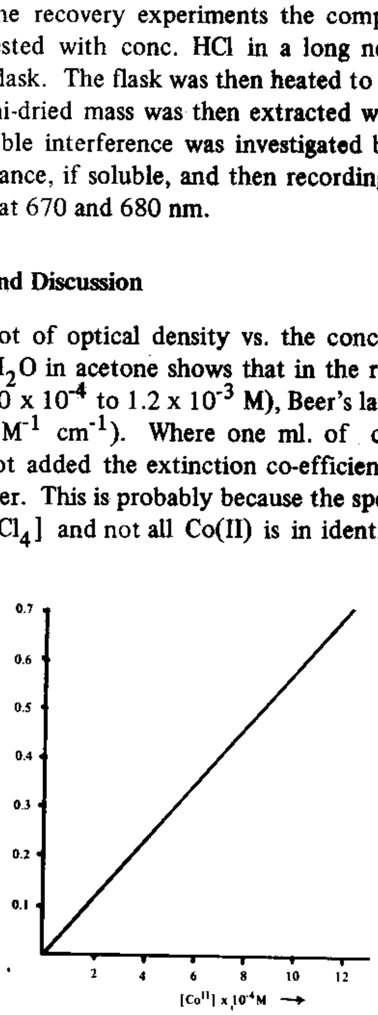

Figure 1. Beer's law plot for Co (II) in acetone in presence of excess chloride

Table I shows optical densities of different compounds at 680nm when dissolved in acetone. It is evident that none of these compounds can interfere in this estimation.

Table I. Absorbance of Potentially Interfering Ions.

Compound	Concentration	Optical Density
$CuSO_4.5H_2O$	Insoluble	–
$CuCl_2.6H_2O$	$2.4 \times 10^{-3}M$	0.04
$NiSO_4.6H_2O$	Insoluble	–
$Ni(CH_3COO)_2$	Sparingly soluble	Zero
$NiCl_2.6H_2O$	Sparingly soluble	Zero
$FeCl_3$	$3.0 \times 10^{-3}M$	0.03

Table II. Percent Recovery of Cobalt compounds

Compound	Moles of Co present	Moles of Co practically obtained	Percent Recovery
$CoCO_3$	2.173×10^{-4}	2.145×10^{-4}	98.8
$Co(NO_3)_2$	1.84×10^{-4}	1.83×10^{-4}	99.3
$CoCl_2$	1.98×10^{-4}	1.975×10^{-4}	99.9
$Na_3Co(NO_2)_6$	2.00×10^{-4}	1.96×10^{-4}	98.0
Percent recovery*			

---

*All cobalt compounds were converted into $CoCl_2$ with HCl.

Table II shows percent recovery of different Co(II) compounds by this procedure. In one case, $Na_3Co(NO_2)_6$, Co(III) was converted to Co(II). In all cases the recovery experiments are extremely encouraging.

In conclusion, we may cite three distinct advantages in favour of this procedure. Firstly, handling of acetone is much safer and easier. Secondly, since the absorption maximum used in the present study is a broad one (670 nm to 690 nm) use of colorimeters not equipped with monochromators is possible. Thirdly, the most distinct advantage of this rapid and very simple determination is that it can be carried out in presence of Cu^{2+}, Ni^{2+} and Fe^{3+} ions which posed a problem of interference in all previous spectrophotometric methods.

References

1. R.S. Young, *"The Analytical Chemistry of Cobalt"*, Pergamon Press, (1966).
2. A.I. Vogel, *"Quantitative Inorganic Analysis "*, Longmans, (1961).
3. E.S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 420, (1964).
4. F.A. Cotton, D.M. L. Goodgame and M. Goodgame, *J.Am. Chem.Soc.* **83**, 4690, (1961).
5. A.H. Zeltman, N.A. Matwiyoff and L.O. Morgan, *J. Phys. Chem.* **72**, 121, (1968).
6. C. Calzolari and L. Favretto, *Analyst,* **93**, 494, (1968).