THE ESTIMATION OF COBALT

by

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ABSTRACT.

A critical survey of the methods and primary standards used in the estimation of macro quantities of cobalt has been made. This indicates that even the most recommended methods contain unsatisfactory features. Further, it shows that not only have a wide variety of cobalt compounds been used as primary standards, but many stock solutions prepared for use in investigating some methods, have been standardised using other methods, very often of doubtful accuracy.

A number of cobalt primary standards have been compared by analysis under strictly controlled conditions. The results indicate that many standards, including Co(II) sulphate and electrolytic cobalt should be rejected. $\left[Co(NH_3)_5Cl\right]Cl_2$ is recommended as a good standard.

A number of cobalt analytical methods have been examined experimentally. The electrolytic and sulphate methods have been rejected for the accurate estimation of cobalt. In the former a contaminated deposit was obtained under all conditions used. The α nitroso β naphthol, ferricyanide, cyanide, E.D.T.A., and perborate methods have likewise been rejected for accurate work. The anthranilate method has been found to give slightly high results, probably due to contamination by the reagent. Its use is not recommended.

The methods chosen for the most detailed examination were the phosphate, electroytic, anthranilate and carbonato-complex methods. It has been hoped that a comparison might be made of the accuracy and precision of these methods. Where a potentially good method has not been acceptable previously because of some defect, an attempt has been made to remedy this, and where methods have been thought capable of further development, this has been attempted. The phosphate method is an example of the former; a drawback in this method, the solubility of cobalt ammonium phosphate, has been overcome by incorporating a rapid spectrophotometric method of estimating the filtrate cobalt with Nitroso-R-salt. As an example of the latter, the now standard ferrous iron-dichromate titration has been used in a volumetric method based on initial oxidation of cobalt by hydrogen peroxide in the presence of potassium bicarbonate. Both these methods, in the forms developed, have been found to give high accuracy. Where this is desired, their use is recommended in place of other methods shown to be unsatisfactory in the present work.

CONTENTS

A. INTRODUCTION AND APPROACH TO PROBLEM.

1. Introduction.

Although cobalt compounds were used in very early times for colouring glass, it was not until 1742 that Brandt isolated the metal. The name cobalt is derived from the German 'kobald' (gnome, goblin) applied by miners in former times to certain ores found in the Hartz mountains, on account of difficulty in smelting and the bad effects on their health.

Cobalt when polished is silver white with a faint bluish tinge. Its main physical properties together with those of iron and nickel for comparison, are shown in Table I.

Table I

	Fe.	Co.	Ni.
Density	7.85	8.80	8.80
Atomic volume	7.11	6.70	6.67
M. pt.	1535°	1490°	1452°
B. pt.	2735°	3100°	2840°
Atomic weight	55.85	58.94	58.69
Atomic radius	1.27	1.25	1.24
Outer electronic configuration	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$

The oxidation states of iron, cobalt and nickel are shown in Table II.

Table II

	Fe.	Co.	Ni.
Ionic	$\underline{\underline{2}}$ $\underline{3}$	$\underline{\underline{2}}$ 3 (4)	0 1 $\underline{\underline{2}}$ (3)
Covalent	$\underline{2}$ $\underline{\underline{3}}$ 6	$\underline{2}$ $\underline{\underline{3}}$	

$\underline{\underline{N}}$ commonest

$\underline{N}$ next most stable

N definite but few

(N) doubtful

The +2 oxidation state is the most stable for simple ionic cobalt compounds, and in this state cobalt resembles Fe(II) and Ni(II). The cobaltous ion is not easily oxidised to the simple cobaltic ion owing to the instability of the latter in acid solution. This becomes evident from the oxidation potential of the system

$$Co^{++} \rightleftharpoons Co^{+++} + e^- \qquad E^0 = -1.80 \text{ volts}^*$$

which indicates that Co^{+++} is a very powerful oxidising agent. Such is its instability under normal conditions that it attacks water (provided its concentration is sufficiently high) with the liberation of oxygen. The overall reaction can be

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* All potentials are expressed using the convention used in "The oxidation states of the elements and their potentials in aqueous solutions." by W. M. Latimer.

represented thus:-

$$4Co^{+++} + 2H_2O = 4Co^{++} + 4H^+ + O_2$$

Recently Bricker and Loeffler$^{(1)}$ have attempted to utilize the fact that a cobaltic sulphate solution in 10 N sulphuric acid can be kept stable for long periods at -7°C as a means of estimating Cr(III), Mn(II) and Ce(III) for which high potentials are required.

Few cobalt complexes exist in the +2 state, and they are unstable. In contrast, the +3 state is perfectly stable for co-ordination compounds, and complexes in this oxidation state are very numerous, the co-ordination number always being six. The extent to which the +3 oxidation state can be stabilized due to formation of complexes or sparingly soluble compounds may be measured in terms of the magnitudes of the appropriate oxidation potentials. Some of these are shown in Table III.

Table III

System	E^o
$Co(OH)_2 + OH \rightleftharpoons Co(OH)_3 + e^-$	-0.17
$Co(NH_3)_6^{++} \rightleftharpoons Co(NH_3)_6^{+++} + e^-$	-0.10
$Co(CN)_6^{----} \rightleftharpoons Co(CN)_6^{---} + e^-$	-0.81
* $CoY^{--} \rightleftharpoons CoY^- + e^-$	-0.60

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* denotes complex with Ethylenediaminetetra-acetic acid (E.D.T.A.)

The values of E^o show that oxidation to the +3 state is much easier in the presence of precipitating or complexing agents. Cobaltic hydroxide is easily obtained by air or peroxide oxidation of the cobaltous compound. CN^- stabilizes the +3 state to such an extent that the Co(II) compound is oxidised by water and has no stable existence. It is also oxidised by air.

In the Co(IV) oxidation state, CoO_2 appears to be produced by powerful oxidising agents in alkaline solution (analagous to NiO_2 and MnO_2). Like NiO_2 it attacks water rapidly.

From what has already been said it will be realized that there can be no counterpart in cobalt analysis to the simple permanganate or dichromate oxidations used in the estimation of iron.

Most of the volumetric methods can be classified into one of the three following groups:-

(i) $\text{Co(II)} \xrightarrow[\text{presence of ZnO, HgO etc.}]{\text{oxidised by KMnO}_4\text{ in}} \text{Co(OH)}_3$

$KMnO_4$ may be added in excess and back titrated with a suitable reductant. This group of methods is now obsolete.

(ii) $$\mathrm{Co(II)} \xrightarrow[\text{hydrogen peroxide, sodium perborate or sodium hypochlorite}]{\text{oxidised by iodine, bromine,}} \mathrm{Co(III)} \left[\begin{array}{c} \mathrm{Co(OH)_3} \\ \text{ammine} \\ \text{or} \\ \text{carbonate} \\ \text{complex} \end{array}\right]$$

The excess of oxidant is removed, and the Co(III) compound reduced with standard reductant in acid solution.

(iii) depending on initial precipitation of the cobalt by an organic precipitant.

e.g. Cobalt may be precipitated as cobalt anthranilate, which on treatment with HCl yields anthranilic acid. This is estimated volumetrically by a bromination method.

Many other volumetric methods, for example the alkalimetric titration of cobalt ammonium phosphate with HCl, cannot be conveniently grouped.

In the field of gravimetric analysis, about thirty different methods have been proposed. A critical survey of existing methods will be made in Part 2.

2. The Estimation of Cobalt - Critical Survey.

(a) Methods

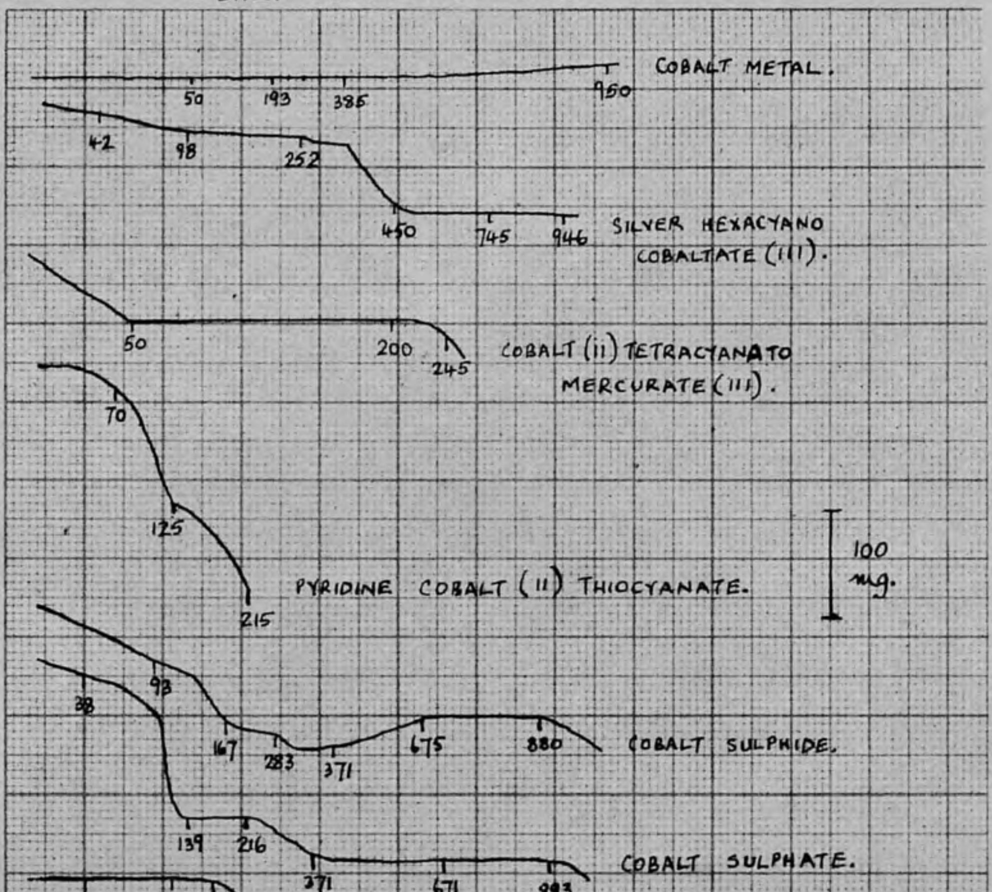
Before surveying existing methods for estimating cobalt it is necessary to mention a technique which has played a great part in assessing the merits of analytical methods, viz. Thermogravimetric Analysis. The method, which has been largely developed by Duval in France, consists of measuring weight changes during the heating of a solid. A curve showing weight change against temperature is obtained. For a possible weighing form, the thermogravimetric or pyrolysis curve indicates whether there is continuous change in weight over a certain range of temperature. In this case erratic results would be obtained if ignition were carried out under these conditions. If there is practically no change in weight over the range, a very good gravimetric method might be possible. In the latter case it would also be important to verify that the horizontal portion of the curve represented one particular compound rather than a mixture due to co-precipitation.

In his comprehensive study of inorganic thermogravimetric behaviour, Duval has included an investigation of cobalt precipitates used in analysis(2). The resulting pyrolysis curves will be referred to when the particular methods are dealt with. (FIGS 1 AND 2)

THE α NITROSO β NAPHTHOL METHOD.

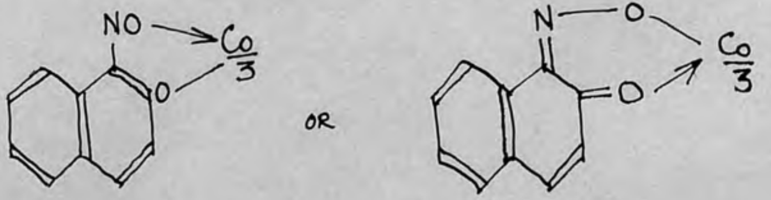
The precipitation of cobalt by α nitroso β naphthol introduced by Ilinski and Knorre(3) in 1885 was one of the first methods used for estimating a metal with the aid of a selective organic reagent. In spite of its many defects, and

FIG. 1. THERMOGRAVIMETRIC BEHAVIOUR OF SOME COBALT COMPOUNDS USED IN ANALYSIS.



the very large number of other methods proposed for estimating cobalt since then, it remains, in modified form one of the most used methods in cobalt analysis. For example in the 1956 edition of A.S.T.M.[*] Methods for Chemical Analysis of Metals, it alone is recommended as the method for macro estimation of cobalt in various materials; ~~and~~ it is given, very often uncritically, in most textbooks of inorganic analysis.

α nitroso β naphthol exists in two isomeric forms which react with cobalt salts to form inner complex compounds of composition



Complexes in which cobalt is divalent and trivalent are possible. Much controversy has existed on the exact nature of the precipitate with cobalt, and the method has undergone a great deal of modification since its introduction. In its present form the compound is essentially a means of separation, the cobalt being finally weighed in another form.

Ilinski and Knorre found that on adding the potassium salt of α nitroso β naphthol to a neutral cobalt solution, a

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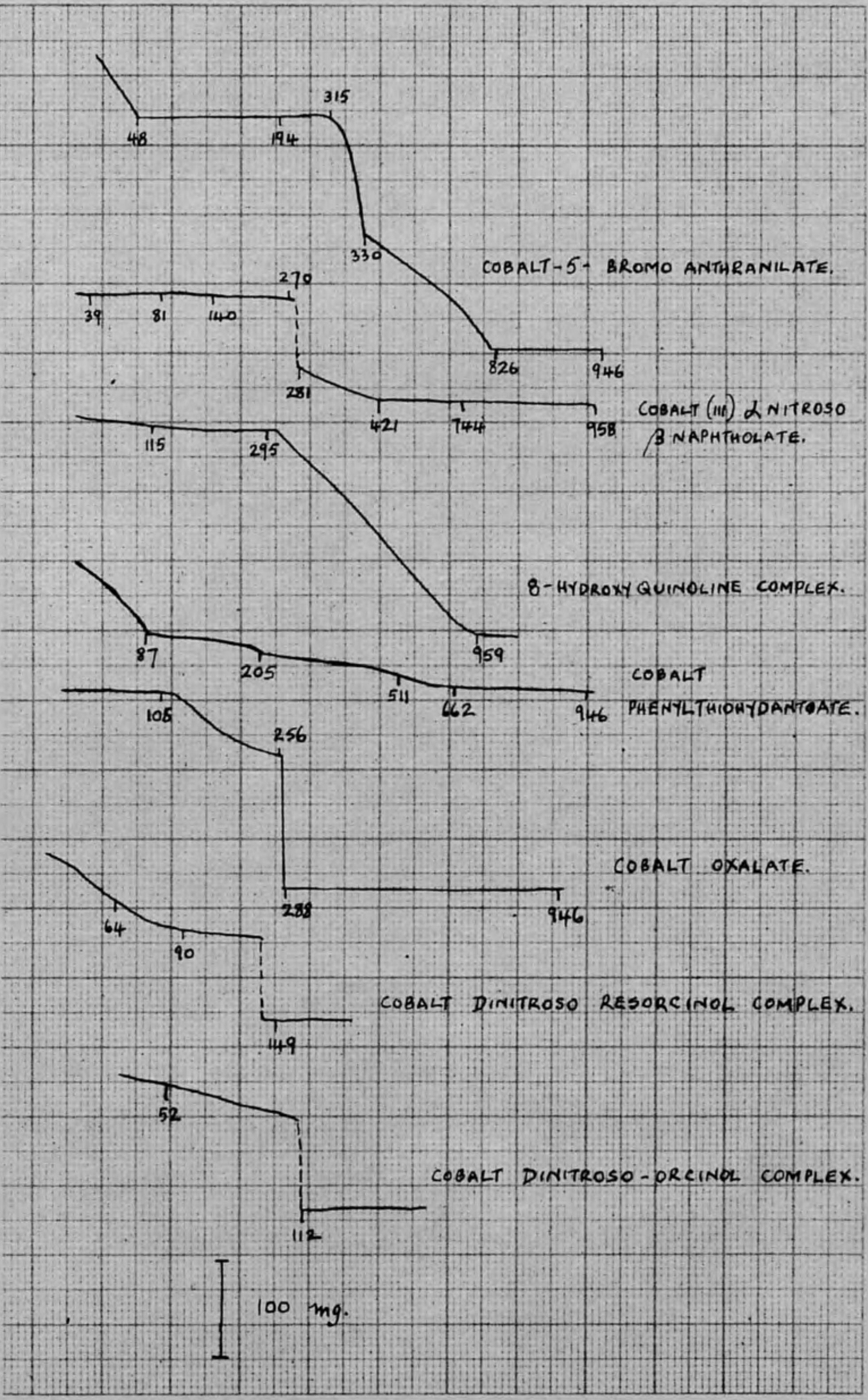
[*] American Society for Testing Materials.

FIG. 2. THERMOGRAVIMETRIC BEHAVIOUR OF SOME COBALT COMPOUNDS USED IN ANALYSIS.



reddish brown precipitate was formed. Upon heating with dilute acids it became purple, and they assumed that in it the cobalt was trivalent. The same precipitate was obtained upon adding a solution of the reagent in acetic acid or alcohol to a weakly acid cobalt solution. According to Atack(4), if a solution of the reagent in 50% acetic acid was used, the cobalt was gradually but never completely precipitated owing to its solubility in acetic acid.

Mayr and Feigl(5) believed the cobalt in the precipitate to be partly divalent and partly trivalent. In order to obtain it entirely in the trivalent state they first precipitated cobaltic hydroxide using sodium hydroxide and hydrogen peroxide, dissolved this in a large excess of hot acetic acid, and then treated it with α nitroso β naphthol. The complex was dried at 130° and weighed as $CoR_3.2H_2O$. The accuracy of the method was given as within 2%.

In an amperometric study of the reaction between cobalt and α nitroso β naphthol, Kolthoff and Langer(6) expressed doubt at Mayr and Feigl's formula, and indicated that on dissolving the $Co(OH)_3$ in hot acetic acid the greater part of the cobalt was reduced to the divalent state. A number of gravimetric determinations in which the cobalt was precipitated under various conditions, dried at 135° and weighed, generally confirmed this. No indication was found that the precipitate obtained in acid medium contained trivalent cobalt.

The reaction has been investigated very recently by Bobtelsky and Jungreis(7), but in view of the fact that modern forms of the method do not involve weighing the actual complex, it will not be discussed here.

Slawik(8) and Eder(9) ignited the complex and weighed the resulting oxide. A difficulty in this procedure was the explosive decomposition of the complex at 270°, a feature clearly indicated in Duval's pyrolysis curve for the material. Eder covered the precipitate with oxalic acid prior to ignition; this procedure is still in general practice.

Much doubt was thrown on the composition of the oxide resulting from ignition of the complex. It was assumed to have the composition Co_3O_4, and on this assumption Congdon and Chen(10), when assessing the method, obtained an accuracy of 1%.

A further modification was reduction of the oxide to metal for final weighing, and it is in this form that the method is claimed to be most accurate. By means of a Rose crucible, hydrogen is passed into the ignited oxide; and when reduction is thought to be complete, the finely divided cobalt metal is allowed to cool with the stream of hydrogen still passing over (finely divided cobalt is pyrophoric). Conversion of the metal so obtained, to sulphate has also been recommended, this being ignited at red heat. A further extension still, that of electrolysing the sulphate for final weighing also appears in the literature. All these modifications can be looked upon as separate methods, the α nitroso β naphthol being used simply to separate the cobalt. Each will be discussed later. Harris and Sweet attempted to utilize the specificity of the reagent in separating cobalt by dissolving up the precipitate and finally estimating the cobalt using E.D.T.A. The cobalt α nitroso β naphtholate was found to be too resistant to acid for the procedure to be used.

No matter which modification of the method is used, the nitroso naphthol method is open to much criticism. The precipitate is impure, partly due to the two valency states of the cobalt in it, and partly due to the reagent acting as oxidant, itself being reduced to products which further contaminate the precipitate. The bulky nature of the precipitate and its tendency to stick to glassware makes filtration difficult. The maximum quantity of cobalt capable of being estimated owing to the bulkiness is given as low as 25 mg. and never higher than 100 mg. On heating, poisonous fumes are given off, and the solubility of the precipitate in acetic acid solutions remains doubtful. The results of earlier investigations make it clear that the dried complex is an unsuitable weighing form, and this to a lesser extent is also true of the "Co_3O_4" resulting from ignition of the complex.

THE α NITRO β NAPHTHOL METHOD.

Recent work by Blay and Warren(11) has confirmed the doubts expressed about this reagent. Pure α nitro β naphthol gives no precipitate with cobalt; the reagent used by earlier investigators probably contained α nitroso β naphthol as impurity.

THE ELECTROLYTIC METHOD.

The electrolytic method is probably the most important in cobalt analysis and is recommended by many sources as the best method where large amounts of cobalt are involved and high accuracy desired. It is often given as the means of estimating cobalt after preliminary separation of the metal by precipitation, e.g. as dipotassium sodium cobaltinitrite.

Electrolytic cobalt has been used as a primary standard and the method is often used to standardise stock solutions for use in assessing other cobalt methods. This particular aspect will be dealt with later.

The classical electrogravimetric method was developed independently by Luckow and Gibbs in about 1864. They and others established that neither nickel nor cobalt was deposited from acid solutions, but they were deposited from solutions of their cyanides in KCN, as well as from solutions of their neutral sulphates after addition of acetates, citrates or tartrates. Later, Fresenius and Bergmann deposited both metals from solutions containing ammonium sulphate and a large excess of free ammonia. In the case of cobalt, the ammonia helped to prevent the formation of Co_2O_3 on the anode. Improvements, such as the use of rotating electrodes, were employed by Exner(12) and Smith(13). Others including Benner and Ross(14) used gauze electrodes and stationary anodes as a rapid means of depositing the metals; the use of a higher current being made possible because of the free circulation of electrolyte caused by convection currents.

In order to prevent the slight anodic deposit of cobalt which sometimes occurred in ammonical solution, Wagenmann(15) added small quantities of hydrazine sulphate to the electrolyte. Later Lundell and Hoffmann(16) used sodium bisulphite for the same purpose. The addition of reducing agents also helped to prevent rough deposits, said to be due to oxidation of the cobaltous-ammine ion. Their method was as follows:- To the cobalt solution was added 10 mls. conc. H_2SO_4 followed by sufficient 0.880 ammonia to neutralize and 35 mls. excess. 2 gms. sodium bisulphite was added and the volume adjusted to about 150 mls. Electrolysis was carried out for 6 to 8 hours at 0.2 - 0.3 amp/dm^2. *

Willard and Hall(17) in assessing this method claimed excellent results. In 1931 Brophy(18) by using a high rate of stirring ($>$ 800 r.p.m.) and a higher current density (4 - 7 Amp/dm^2) claimed complete depostion in 30 mins. Again sodium bisulphite and hydrazine sulphate were employed.

By this time doubts were hald as to completeness of deposition, so that the version of Lundell and Hoffmann's method appearing in Hillebrand and Lundell's "Applied Inorganic Analysis" 1929 contains treatment of the spent electrolyte with H_2S and estimation of the residual cobalt by igniting the sulphide to Co_3O_4 (this does not necessarily represent the composition of the oxide). A similar procedure appears in the textbook by Treadwell and Hall(19).

Many variations of the electrolytic method are to be found in the literature. Scott and Furman(20) recommend a low current density over a period of 12 to 15 hours; Young

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* 0.2 - 0.3 amp/sq.dm. cathode surface area.

and Hall(21) carry out the deposition rapidly at 90°, testing for absence of cobalt with Nitroso-R-salt.[*] Kallman(22) using the method for final determination of cobalt following cobaltinitrite separation, used a low current density and 6 - 8 hours for deposition. Because sodium bisulphite was used, he found the cobalt deposit contaminated with sulphur; this he estimated gravimetrically as $BaSO_4$ and corrected the weight of deposit accordingly.

A new form of the electrolytic method was proposed by Torrance in 1939(23) based on earlier work by Coehn and Glaser(24) in 1903. The cobalt was deposited as Co_2O_3 on the anode at pH 5. The deposit was not adherent for quantities of Co greater than 40 mg.

Internal electrolysis i.e. with no external electrical supply was recommended by Schleicher(25) and more recently a rotating mercury electrode by Tutundžić and Stojković(26).

There are said to be many unsatisfactory features to the method, the main ones being:-

(i) incomplete deposition,

(ii) an occasional slight anode deposit in the absence of a reducing agent,

(iii) a contaminated deposit in the presence of reducing agents,

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[*] This is a standard colorimetric method for estimating cobalt. See 2.c.

(iv) a tendency for solution of the platinum anode during prolonged electrolysis. It is assumed that any platinum lost from the anode in this way is deposited on the cathode, but some may be lost in the form of 'mud'.(27)

Of these criticisms (i) and (iv) are the easiest to establish, and there can be little doubt that they occur. The contamination of the deposit, (iii) has been assumed indirectly from the high results obtained.

In spite of the above, as mentioned earlier, many investigators and text books accept it as the best method for macro estimation of cobalt. This can be explained in many ways. For example, a combination of (i) with (iii) might give a seemingly good result. Loss of platinum to the solution combined with (iii) might also yield good results. The matter is further complicated by the following factor which is common to all cobalt methods. Some primary standards contain less than the theoretical amount of cobalt; others contain more. This source of error, in assessing the method, may combine with any of the above sources of error to give 'accurate' results. The field of primary standards will be discussed more fully in a later section.

The electrolytic method has been carried out with a much greater diversity of technique than any other method. Each of the following factors may be varied:-

(a) Chemical composition of solution being electrolysed,

(b) time,

(c) current density,

(d) temperature,

(e) type of electrode,

(f) rate of stirring,

(g) pH solution.

Recently, the electrochemical behaviour of the system Co - H_2O has been studied by establishing the diagram of electrode potential versus pH(28). The conditions necessary for producing electrolytic cobalt free from $Co(OH)_2$ are established. Similar information for the electrolysis of cobalt solutions containing ammonium sulphate and ammonia would involve a knowledge of the system Co - NH_3 - H_2O.

THE COBALTINITRITE METHOD.

Separation of cobalt as potassium cobaltinitrite was first recommended by Fischer(29) and introduced by Stromeyer.(30) Later, modifications were made by Brunck(31), Rose(32) and Gauhe(33).

In the Fischer-Brunck modification a 50% solution of potassium nitrite was added to either an acetic acid solution of cobalt, or a mixture of cobalt and nickel. The solution was stirred and left for 24 hours. After filtering and washing with 10% potassium acetate, the precipitate was dissolved in sulphuric acid, heated until fumes of SO_3 appeared, dissolved in water and finally the cobalt determined by another method. (Rose reduced with hydrogen and weighed the metallic cobalt). The reaction may be represented by:-

$$CoCl_2 + 7KNO_2 + 2CH_3COOH = K_3Co(NO_2)_6 + 2KCl + 2CH_3COOK + NO + H_2O.$$

Hillebrand and Lundell (34) and Scott and Furman (20) also give this method, recommending as final operations the sulphate or electrolytic methods.

The first gravimetric method using $K_3Co(NO_2)_6$ appears to be Brauner's in 1877 (35). An attempt was made by Cumbers and Coppock in 1937 (36) to use dipotassium sodium cobaltinitrite which was well known in potassium estimation, and on which much work had been done. It had been found previously that the composition of the precipitate varied with the composition of the reagent, the speed and mode of precipitation, and the presence of other ions. The ratio K : Na was not exactly 2 : 1; if the solution contained sodium salts the ratio became much smaller. Furthermore, any alkaline earth metals present replaced part of the sodium or potassium. By using, as reagent, a mixture of sodium nitrite and potassium chloride solutions for which Na : K was 15 : 1, and other controlled conditions, Cumbers and Coppock claimed that the precipitate consisted of $K_2Na(NO_2)_6.H_2O$. Thermogravimetric studies on both $2K_3(NO_2)_6\ 3H_2O$ and $(KNa)_3\left[Co(NO_2)_6\right] nH_2O$ were made by Duval(2). His results show the former to be a good weighing form and the latter a bad one, and he expresses the opinion that it should not be used in gravimetric analysis.

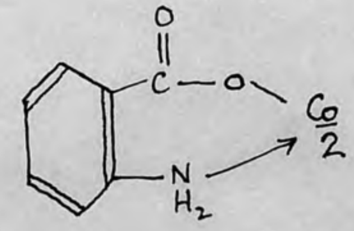
Volumetric procedures were introduced by Karlslake(37) and later by Barbieri(38), Vassiliev(39), Faleev(40) and Nikolow(41). They are very similar in principle. The cobaltinitrite precipitate is dissolved in excess standard $KMnO_4$ and sulphuric acid. Nitrous acid is formed, and the cobalt is reduced to the bivalent state owing to the instability of Co^{+++} in acid solution. Eleven equivalents of potassium permanganate are used for each mole of potassium cobaltinitrite. The excess of permanganate is determined in various ways. Karlslake and Faleev used oxalic acid, Barbieri used ferrous sulphate, and both Vassiliev and Nikolow used potassium iodide in acid solution, titrating the liberated iodine with thiosulphate. This variation now appears in Kolthoff and Sandell's textbook.(42)

The most recent work on the method was done by Kallman(22). He claims that the precipitation of cobalt in the presence of tartaric acid improves the scope of the method as a means of separating cobalt from other metals (including nickel). For the final determination of cobalt though, he recommends the electrolytic, ferricyanide, or αnitroso β naphthol methods.

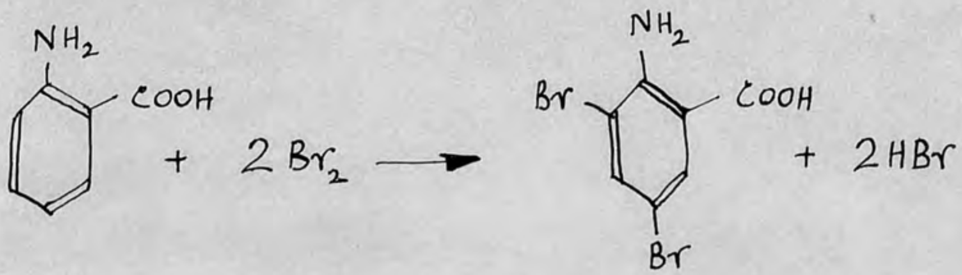
Many of the drawbacks in the cobaltinitrite method will be apparent from what has already been said. The long time required for complete precipitation (this is given as between six and twenty-four hours) is poor compensation for the separation of cobalt from iron and nickel. The exact solubility of the precipitate under analytical conditions has not been investigated; this is a factor that affects the volumetric as well as gravimetric procedures. There must be absence of sodium salts if a gravimetric procedure is used, or a precipitate of variable composition will result. Finally, in the volumetric procedures, on dissolving the precipitate in acid potassium permanganate, the absence of a strong reducing agent makes possible the loss of free oxygen by interaction of the Co^{+++} ion with water.

THE ANTHRANILIC ACID METHOD.

Anthranilic acid (o-amino benzoic acid) was introduced as a reagent in quantitative inorganic analysis by Funk and Ditt in 1933, and in the same year applied to the estimation of cobalt(43). It reacts with zinc, magnesium, lead, mercury, cobalt, nickel, cadmium and copper to form insoluble chelate compounds. The complex with cobalt can be represented thus:-



The method consists of adding an excess of 3% sodium anthranilate to a hot neutral or very slightly acid solution of cobalt. On boiling gently for five minutes, precipitation takes place. The solution is now allowed to stand for a short time, filtered, washed with cold 0.15% reagent followed by alcohol, dried at 105° - 110° and finally weighed as $Co(C_7H_6O_2N)_2$. Excellent results were claimed in unbuffered neutral solutions. A volumetric procedure was also proposed by Funk and Ditt (loc. cit.). It consisted of dissolving the anthranilate precipitate in 4N HCl and titrating with a potassium bromate-bromide solution using a misture of carmine and styphnic acid as indicator. The slight excess of bromine was determined by adding a few mls. of 0.2 N Kl and titrating the liberated iodine with thiosulphate.



Goto studied the effect of pH on the precipitation of cobalt with anthranilic acid(44). He found the minimum pH for complete precipitation, and the maximum pH at which no precipitation took place to be 4.41 and 3.36 respectively. These values have been criticised recently and re-determined.(45)

In the volumetric procedure, Shennan, Smith and Ward(46) found that if a large excess of bromate-bromide was used, or if the time taken was long, a tendency for some tribromination occurred, with high results. They therefore applied an indirect tribromination method which had been developed earlier for estimating anthranilic acid(47). Again a bromate-bromide mixture in HCl was used, the bromate being the carefully weighed constituent which determined the amount of bromine liberated. The excess was determined as in the other method, by titrating the iodine liberated from Kl. The sequence of reactions in the method can be shown thus:-

$$Co^{++} + 2C_6H_4(NH_2)\,COO\,Na \longrightarrow 2Na^{+} + \left[C_6H_4(NH_2)COO\right]_2 Co$$

$$\left[C_6H_4(NH_2)\,COO\right]_2 Co + 2HCl \longrightarrow CoCl_2 + 2C_6H_4(NH_2)COOH$$

$C_6H_4(NH_2)\ COOH + 3\ Br_2 \longrightarrow C_6H_2(NH_2)\ Br_3 + CO_2 + 3HBr.$

$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 3H_2O + 6KCl.$

$Br_2 + 2KI \longrightarrow 2KBr + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_2O_6$

The amount of cobalt present would be calculated according to the volume of standard bromate-bromide solution entering into the reaction.

Shennan _et_. _al_. (_loc. cit_.) also investigated the precipitation of cobalt anthranilate in solutions buffered with sodium acetate and sodium tartrate, presumably in the hope of separating cobalt quantitatively from other metals. Low results were obtained and it was assumed that the precipitate was appreciably soluble under these conditions. They finally concluded that although accurate results were possible in unbuffered solutions, the range of separations which could be effected was very limited and the method capable of little extension. The effect of pH on the precipitation of cobalt with anthranilic acid from acetate buffers has also been investigated recently by Harris(48) but details are not yet available.

An amperometric method for titrating up to 30 mg. cobalt with anthranilic acid has been described by Zhdanov _et_. _al_.(49).

The solubility of cobalt anthranilate in N acetic acid was determined by Treadwell and Ammann (50) who found it to be 0.00412 moles/litre.

There are many good features to the anthranilate method. The purity of the reagent can be checked, and the precipitate is easy to wash and filter. A strong point in its favour is the thermogravimetric curve of the precipitate (2) which indicates it to be a good weighing form. The fact that the precipitate is soluble in buffered solution, though a disadvantage for some purposes, does not affect the accurate estimation of cobalt when present on its own. A great disadvantage in the volumetric procedures is that precipitation followed by filtration and washing must be carried out as initial steps.

Shennan (51) used 5-bromo anthranilic acid for cobalt estimation. Again the precipitate was found to be soluble in the presence of acetates and tartrates, but use of a greater excess of reagent diminished this. As in the case of cobalt anthranilate itself, the 5-bromo anthranilate is stable over a large temperature range which makes it suitable for gravimetric analysis. Shennan's results were within 0.25% of the cobalt present.

THE FERRICYANIDE POTENTIOMETRIC METHOD

This method is based on the oxidation of cobalt in ammoniacal solution by potassium ferricyanide. It was introduced in 1935(52). The reaction may be represented thus:-

$$[Fe(CN)_6]^{---} + [Co(NH_3)]^{++} = [Fe(CN)_6]^{----} + [Co(NH_3)_6]^{+++}$$

The end-point is determined potentiometrically. It was found by the original workers that in the direct titration results were poor; the procedure then adopted was to add the cobalt solution to excess standard potassium ferricyanide containing ammonia and ammonium citrate, and back titrate the excess with a standard cobalt solution. The function of the citrate was to prevent the precipitation of the hydroxide.

The standard potentials of the individual couples are:- $[Fe(CN)_6]^{----} = [Fe(CN)_6]^{---} + e^-$ $E^o = -0.36$ volts

$[Co(NH_3)_6]^{++} = [Co(NH_3)_6]^{+++} + e^-$ $E^o = -0.10$ volts

Bagshaw and Hobson(53) raised doubts as to whether all the cobalt was oxidised at the point of inflection owing to the closeness of the two potentials. In order to determine them under experimental conditions, they prepared mixtures of oxidised and unoxidised cobalt nitrate in ammonia. The potentials were then determined in an ammonium citrate solution using platinum and normal calomel electrodes. The same procedure was used for the potassium ferrocyanide-ferricyanide system from the results:-

Couple:- cobaltous-cobaltic Potential -0.05 volt
" ferricyanide-ferrocyanide " -0.259 volt

and using the relationship:-

$$\log_{10} K = \frac{n}{0.591} (E_1 - E_2)$$

where K = Equilibrium constant,

E_1 and E_2 = potentials of the two couples,

n = no. of electrons involved in reaction,

it is found that $K = 4.21 \times 10^3$

This indicates that if 50 mls. of a cobaltous solution is titrated with 50 mls. of an exactly equivalent ferricyanide solution, at the point of inflection, 0.77 ml. of the cobaltous solution would remain unoxidised.

Later, Yardley(54), using changed conditions did not find this 'overlap' of the two systems, and obtained titration curves which could only be explained if the equilibrium constant was about 2×10^6. He claimed that extremely accurate results were possible.

Recently Cassy(55) found that in a citrate-sulphate solution the equilibrium constant was 9.8×10^4, indicating that 0.34% of the Co(II) remains unoxidised finally. Diehl and Butler(56) replaced the ammonia by ethylenediamine, the Co(II) ethylenediamine complex being a stronger reducing agent than the analagous Co(II) ammonia complex by some 0.5 volt. The potential break at the equivalent point is augmented by a similar amount, but it was found that dissolved oxygen became an interfering factor, and steps had to be taken to remove it.

Previous results and opinions are conflicting as to the use of the ferricyanide method for the accurate estimation of cobalt. Tomicek and Freiberger(57) claimed results within 0.09% of theoretical; Yardley claimed that all his results except one were with 0.06%. However, Hall and Young(58), and more recently Cassy (loc.cit.), the latter using improved conditions, state the method to be only 1% accurate. There is little doubt that the method is excellent for routine cobalt estimation in the presence of other metals (only Mn interferes) and where high accuracy is not required.

THE PHOSPHATE METHOD

The phosphate method is analagous to that for zinc and magnesium, but although much investigated, it has never received similar recognition. This is mainly due to the solubility of the precipitate. The overall reaction can be represented by the equation:-

$$CoCl_2 + 2(NH_4)_2HPO_4 + H_2O = CoNH_4PO_4.H_2O + NH_4H_2PO_4 + 2NH_4Cl.$$

On adding an ammonium phosphate solution to a heated cobaltous solution the initial precipitate is light blue and flocculent. Later, if further heated it passes through a deep royal blue stage, and finally into a purple form which is sometimes crystalline. Its composition now approximates to $CoNH_4PO_4 \cdot H_2O$. The chemical changes involved were studied by Bassett and Bedwell(59). Ignition of the ammonium phosphate yields cobalt pyrophosphate, an alternative weighing form.

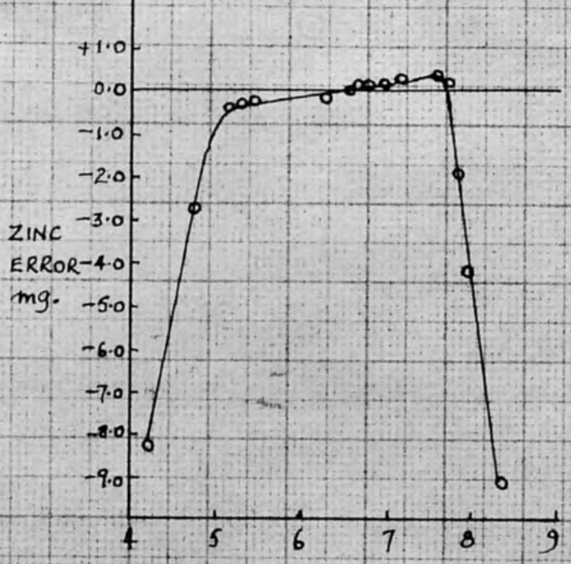
$$2\ CoNH_4PO_4 \cdot H_2O = Co_2P_2O_7 + 2\ NH_3 + 3\ H_2O.$$

The corresponding method for magnesium has been much studied. A good account of the difficulties and part of its extensive literature is found in Kolthoff and Sandell's textbook.(42) Magnesium ammonium phosphate is one of the most soluble precipitates used in quantitive analysis (13.6 mg./L in water at room temperature); it was found that co-precipitation of such substances as $Mg(H_2PO_4)_2$, $Mg_3(PO_4)_2$, and basic magnesium phosphates was possible, with resulting errors, both positive and negative, on ignition to the pyrophosphate.

In the case of zinc, it was found that the result on the basis of the pyrophosphate was a function of the pH during precipitation, the optimum value for the correct answer being 6.6 (60).

A method was devised using ammonium chloride and sodium acetate as buffer, to bring about this condition. The

FIG. 3.



EFFECT OF pH ON PRECIPITATION OF $ZnNH_4PO_4$ (BALL & AGRUSS).

results obtained are shown in Fig. 3. The negative error from solutions more acid than pH 6.6 can be explained by solubility loss. The positive error between pH 6.6 and 7.5 can only be explained in terms of composition variation in the precipitate, a factor not discussed by the authors.

Early work on the cobalt method was done by Debray(61), Chancell(62), Dirvell(63) and others. Clarke(64) used the following method:- To a mixture of cobalt and nickel in solution was added about five times the combined weight of ammonium phosphate and twenty-five times the weight of hydrochloric acid. The solution was boiled for a few minutes and then ammonia cautiously added until the precipitate first formed, dissolved. On vigorous stirring $CoNH_4PO_4.H_2O$ was precipitated; it was filtered, washed and ignited to the pyrophosphate. Although cobalt was detected in the filtrate, no correction was made for it.

Later Hope(65) used a somewhat similar method. Sulphuric acid was used instead of hydrochloric, and the amount of ammonia added was less. Schoeller and Powell (66) found that the precipitates produced by these methods had different properties. That produced by Clarke's method was granular, deep lilac, and not immediately soluble in dilute acid, whereas Hope's precipitate was silky, pale lilac and immediately soluble in the acid. In addition, the filtrate in Clarke's method contained a little cobalt, but in Hope's method it was almost cobalt free.

Dakin(67) in 1900 ignited the ammonium phosphate to the pyrophosphate, and later (68) developed a volumetric method based on dissolving the ammonium phosphate in excess standard sulphuric acid and back titrating with standard alkali. This was investigated by Schoeller and Powell (loc. cit) who found the methyl orange to be unsuccessful. They developed a method of direct titration in which the end point was indicated by the disappearance of the lilac colour given to the solution by the cobalt ammonium phosphate. This method has recently appeared in the new edition of Sutton's textbook on volumetric analysis.$^{(19)}$

An attempt to take into account filtrate cobalt was made by Dufty$^{(70)}$. The filtrate was saturated with H_2S, the resulting CoS filtered off and ignited to Co_3O_4, and the cobalt found in this way added to the major fraction as pyrophosphate. The same procedure was used by Schoeller and Powell (<u>loc. cit.</u>) who also used α nitroso β naphthol for determination of filtrate cobalt. Later Congdon and Chen$^{(10)}$ tried these variations and claimed accurate results. However, Willard and Hall$^{(17)}$ invariably obtained high results, probably owing to the method by which they precipitated the cobalt ammonium phosphate. Some later workers $^{(71)}$ $^{(72)}$ weighed the cobalt as the ammonium phosphate and ignored filtrate cobalt.

In a study of the method in 1951, Matsuo$^{(73)}$ investigated the effect of pH, and ammonium concentration on the precipitation of Cd, Ni and Co. The method for cobalt was as follows:- To the cobalt solution containing ammonium chloride, ten times the equivalent of ammonium phosphate was added. After heating on a water bath for a few minutes the pH was adjusted with normal NH_4OH and the precipitate left overnight. Duplicate analyses were made at each pH value, one being filtered and ignited at 500°, the other filtered, dried at 105° and the P_2O_5 contents determined using ammonium molybdate. The values of the latter were found to vary according to the pH of precipitation and the $Co^{++}:NH_4^+$ molar ratio. The results are shown in Fig. 4.

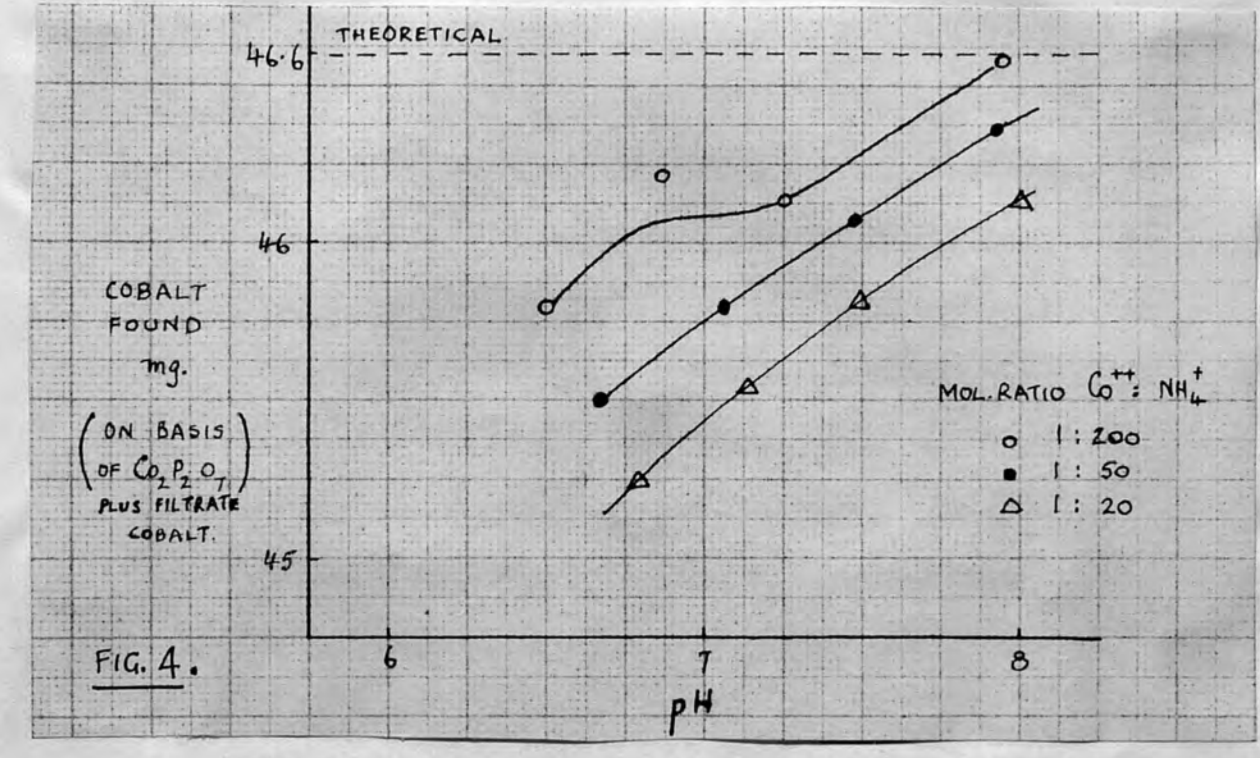


FIG. 4.

In each case the filtrate cobalt was determined spectrophotometrically using α nitroso β naphthol, the values obtained being added to the major fraction to give total cobalt. Matsuo's results were low, and he concluded that the method was incapable of producing a precipitate of satisfactory composition.

The pyrolysis curve for $CoNH_4PO_4.H_2O$ was investigated by Duval(2) and is shown in Fig. 1. He found a slow rise in weight up to 98° (a gain of 4 mg/139 mg) followed by a "sudden deep-seated decomposition." The pure pyrophosphate, he claimed, appeared at 580° and was a good weighing form.

The literature on the phosphate method is confusing and previous results difficult to assess. Most of the previous workers were concerned with separating nickel from cobalt as well as estimating the latter and little attention was paid to the best method of preparing a precipitate of good composition. The fact that Willard and Hall obtained high results and Matsuo low results suggests variation in the composition of their precipitates, although use of faulty primary standards may also account for the difference.

Again, the thermogravimetric behaviour of the precipitates supports the view that they vary in composition. In contrast to Duval's curve for cobalt ammonium phosphate, Kraus(72) dried his precipitate at 115°-120° and found no loss in weight even at 140°.

Some workers ignore the solubility of the precipitate. As in other methods, compensation of errors is possible e.g. if a primary standard which contains more than the theoretical amount of cobalt is used in a method which ignores filtrate cobalt, good results might be obtained. The volumetric procedures are all subject to errors due to the solubility of the precipitate. Again some methods involve ions which have been shown to affect the result. Congdon and Chen(10), for example, use cobalt nitrate as primary standard although Dufty (loc. cit.) showed that the presence of NO_3^- produced low results.

Matsuo's recent conclusion that the phosphate method gives low results under all conditions must be treated with doubt. He does not specify the standard used, and many features of his procedure are dubious, e.g. ignition of the cobalt ammonium phosphate at 500°. However, his results show the dependence of total cobalt on pH, which again indicates variation in composition of the precipitate.

Finally, in its present form, with the estimation of filtrate cobalt by sulphide precipitation followed by ignition to oxide, two gravimetric procedures are involved and this detracts from the value of the method.

THE PYRIDINE-AMMONIUM THIOCYANATE METHOD

This method was introduced by Spacu and Dick(75) and consists of adding pyridine and ammonium thiocyanate to the cobaltous solution to produce the complex $Co(C_5H_5N)_4(CNS)_2$.

Later, almost simultaneously Spacu and Kuras(76) and Dobbins and Sanders(77) developed volumetric procedures based on precipitation with excess standard thiocyanate followed by back titration with standard silver nitrate.

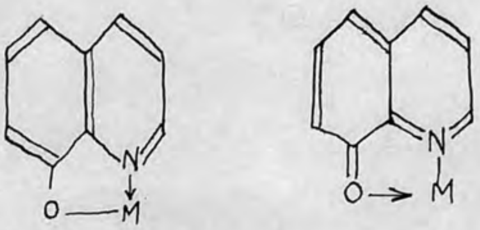
The thermogravimetric curve for the complex itself(2) indicates stability up to 60° followed by continuous loss of weight, so that if the gravimetric procedure is used, the precipitate has to be dried in a vacuum desiccator at room temperature.

As in other volumetric methods involving precipitation and filtration as an integral part of the determination, the solubility of the precipitate becomes a source of error. In testing Spacu's volumetric method Dobbins and Sanders found the complex to be partly soluble on washing. Ammonium salts were found to have a solvent action, and as the reagent contains NH_4^+ some solubility is inevitable.

The method cannot be seriously considered for the accurate estimation of cobalt.

THE OXINE METHOD.

This reagent was introduced independently by Berg and Hahn in 1926-7. It reacts with many metals under specified pH conditions, giving crystalline precipitates in which the metal atom may be co-ordinately bound either to the nitrogen atom or the oxygen atom of the carbonyl group, to form a stable five membered ring.



M = 1 EQUIVALENT METAL.

Berg(78) gave 4.2 to 11.6 as the pH for complete precipitation. He originally suggested 100° for drying the precipitate as $Co(C_9H_6ON)_2.2H_2O$ but later Fleck and Ward(79) and Cumbers and Coppock(36) found some uncertainty in the degree of hydration of the complex. Fleck and Ward found the gravimetric procedure unsuitable, the composition of the complex dried at 120° being approximately $Co(C_9H_6ON)_2.2H_2O$. They found, however, that the volumetric procedure, also suggested by Berg, gave excellent results. This consisted of liberating the oxine by adding dilute HCl to the washed precipitate, and then brominating to 5:7 dibromo-8-hydroxyquinoline with a standard potassium bromate-bromide solution. Either methyl red or indigo carmine could be used as indicator, the colour becoming yellow at the end point. Eight equivalents of bromine were required for each mole of the oxinate of a bivalent metal.

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr.$$

Owing to difficulty in detecting the end point, Fleck and

Ward added a small excess of the bromate and a little KI; the liberated iodine was titrated with thiosulphate. Cumbers and Coppock in assessing the gravimetric procedure found that between 90° and 95° the water of hydration was 1.75 H_2O, and became progressively less until there was none at about 120°. As a result they attempted to dry at room temperature, and found this effective, but a factor corresponding to 1.75 H_2O had to be used. Duval(2) however, found loss of both water and alcohol up to 115° followed by a period of almost constant weight up to 295°. Berg also recommended decomposing the complex by heating with oxalic acid and finally weighing the oxide. As in the anthranilate, cobaltinitrite, and pyridine ammonium thiocyanate volumetric methods, precipitation and filtration is an integral part of the oxine volumetric method, and this detracts from its value.

THE CYANIDE METHOD

McCulloch(80) attempted to estimate cobalt by oxidising a cobaltous solution in thepresence of potassium cyanide to potassium cobalticyanide using standard dichromate, and then adding an excess of standard ferrous ammonium sulphate, and back titrating with dichromate. Poor results were obtained. Later Rupp and Pfenning (81) added a cobalt solution to a standard potassium cyanide solution until a brown precipitate appeared indicating that the complex formation was complete. Results were worked out on the assumption that a 1:5 Co:CN ratio existed in the complex. This method now appears in Sutton's recent textbook(69). Glasstone and Speakman(82) confirmed the basis of the method by the electro~~nic~~metric titration of Co with KCN.

In 1937 Evans(83) developed what was claimed to be an accurate volumetric method by combining the above complex formation with Liebig's method for titrating cyanides with silver nitrate. This method consists of the following reactions:- When silver nitrate solution is added to a cyanide solution the white precipitate of AgCN dissolves on stirring to form a stable complex $K[Ag(CN)_2]$. Further addition of silver nitrate gives a precipitate of $Ag[Ag(CN)_2]$ As the turbidity due to this is hard to detect, ammonia is introduced to keep it in solution as a soluble complex. If KI is present, AgI will not be precipitated in the presence of CN^- ions, but as soon as the latter have been consumed AgI is precipitated, and this indicates the end-point.

Evans found many difficulties in developing his method. After running standard KCN into the cobalt solution containing ammonia and AgI until it turned clear, it was observed that cloudiness returned again. This, Evans attributed to formation of a lower cyanide which withdrew

CN^- ions from the soluble silver complex and caused AgI to be precipitated. The process of conversion was found to be slow, and became even slower as the cobalt remaining diminished. He then attempted to find the best conditions for-:

(i) conversion of the cobalt to the higher cyanide,

(ii) a stable end point,

(iii) no loss of cyanide.

Efforts to speed up the conversion by heat resulted in reaction between the cyanide and ammonia; of the alternatives to ammonia, sodium hydroxide was found unsuitable, but borax and sodium carbonate were found satisfactory. With mild oxidants less cyanide was used than corresponded to a 1:6 Co:CN ratio; it approximated to 1:5. Stronger oxidants produced a lower Co:CN ratio. The final procedure adopted by Evans is difficult to carry out in practice and contains many unsatisfactory features. Eight burette readings are required for each determination for example, and it is specified that the stream of air used for oxidation must be passed through the solution for six minutes. Low results are obtained for five minutes and high results for seven minutes.

Evans results are fair, but he does not specify the standard used. The method was examined by Hall and

Young$^{(58)}$ who found its accuracy to be only 1-3%.

VOLUMETRIC METHODS BASED ON Co(II) $\longrightarrow$ Co(III) ($Co(OH)_3$ AMMINE OR CARBONATO COMPLEX.)

Many of the older methods consisted of oxidising cobaltous solutions to $Co(OH)_3$ with $KMnO_4$ in the presence of such substances as HgO or ZnO, these serving only to mechanically to separate the hydroxide.

Winkler$^{(84)}$ added standard $KMnO_4$ to the cold cobaltous solution until a permanent pink colour appeared. The end-point, which was sluggish, was improved by Harris$^{(85)}$ who titrated the solution when hot. von Reis and Wiggert$^{(86)}$ treated the cobalt solution with a ZnO emulsion, brought it to the boil, added a known excess of standard $KMnO_4$ and back titrated with a standard ferrous solution.

Another larger group of methods consists of:-

$$\mathrm{Co(II)} \xrightarrow[\begin{array}{r l}&\text{sodium hypochlorite}\\&\text{iodine}\\&\text{bromine}\\&\text{sodium perborate}\\\text{or}&\text{hydrogen peroxide}\end{array}]{\text{oxidation by}} \mathrm{Co(III)} \qquad \left[\begin{array}{l}\mathrm{Co(OH)_3}\\ \text{ammine or}\\ \text{carbonato}\\ \text{complex}\end{array}\right]$$

The excess of oxidant is removed, and the Co(III) compound reduced with a standard reductant.

Fleischer$^{(87)}$ and later Bayley $^{(88)}$ used sodium hypochlorite in the presence of excess NaOH. The cobaltic hydroxide was dissolved in excess standard ferrous solution and back titrated with permanganate:

$$2\ Co(OH)_3 + 2\ FeSO_4 + 3\ H_2SO_4 = 2\ CoSO_4 + Fe_2(SO_4)_3 + 6\ H_2O$$

Donath(89) used iodine and NaOH. The precipitate was filtered off and distilled with HCl; the chlorine formed being passed into KI and the iodine liberated being titrated with thiosulphate.

Harris(85) after assessing the above methods concluded that they were highly empirical and none possessed a high degree of accuracy.

Many volumetric methods are based on the use of hydrogen peroxide. Of the early ones, that of Carnot(90) is interesting because it was the first to utilize a reaction involving a cobaltous solution, sodium or potassium bicarbonate and hydrogen peroxide. On mixing, a green soluble complex is formed in which the cobalt is trivalent. The excess peroxide is catalytically decomposed by the cobalt present. The complex itself is unstable except in a large excess of sodium or potassium bicarbonate. Its structure has been given as $Co\left[Co(CO_3)_3\right]$.(91)

One of the simplest analytical procedures was developed by Job(92). The cobalt was oxidised by peroxide in the presence of sodium bicarbonate and the carbonato complex reduced by ferrous pyrophosphate, the excess of which was determined with permanganate. His solution was large in volume (150 ml.) and therefore a large quantity (30 gm. excess) of sodium bicarbonate was used to stabilize it. As the final procedure involved reduction in an acid solution, this large excess had to be neutralized with care in order to avoid loss by effervescence. Also, the large volume made removal of excess peroxide difficult as the concentration of cobalt which catalysed the decomposition would be decreased. Further, the oxygen evolved during the decomposition would cause a greater error due to solubility if the volume were large, and this was so in Job's method. Willard and Hall(17) examined his method. They passed a current of CO_2 through the solution to remove oxygen, and gave attention to another feature of the method, the conditions necessary for the complete decomposition of excess H_2O_2 without decomposition of the complex itself. Heating the solution for five minutes at 63^o was claimed to bring this about. Subsequent operations were the same. The end-point was found to be permanent only in a CO_2 atmosphere, and their results were poor.

An iodometric procedure was used by Laitinen and Burdett(93) in 1951. They oxidised the cobalt to the green complex in the minimum volume, added KI, and made acid by carefully adding dilute sulphuric acid. The liberated iodine was titrated with standard thiosulphate. As an advantage of the method it was stated that only one stable standard solution was involved rather than two of less stability as in the previous methods. The iodine is liberated during the neutralisation of the bicarbonate with sulphuric acid, so that large quantities of CO_2 are generated at the same time.

Metzl(94) used hydrogen peroxide to produce $Co(OH)_3$ via the carbonato complex by decomposing the latter with excess sodium hydroxide. He also oxidised a cobaltous solution containing ammonium chloride to the cobaltammine and again produced $Co(OH)_3$ by decomposing it in the same way. In both cases excess hydrogen peroxide was removed by boiling, the trihydroxide dissolved in an acid KI solution, the liberated iodine being titrated with standard thiosulphate.

$$2\ Co(OH)_3 + 2\ KI + 3\ H_2SO_4 = 2\ CoSO_4 + I_2 + 6\ H_2O + K_2SO_4.$$

In a rather similar method Engle and Gustavson(95) used both hydrogen peroxide and sodium perborate as oxidants:

$$8\ CoSO_4 + 4\ NaBO_3 + 14\ NaOH + 5\ H_2O = 8\ Co(OH)_3 + Na_2B_4O_7 + 8\ Na_2SO_4.$$

Again the trihydroxide was estimated iodometrically. Others to use perborate were Willard and Hall(17) Sarver(96) and more recently Baker and McCutcheon(97). The excess perborate is easily removed by boiling for ten minutes. One difficulty mentioned by Willard and Hall, which is a disadvantage in all procedures which require dissolving $Co(OH)_3$ in reducing agents, is the long time required for complete solution. They found that between 0.5 and 2 hours was required to dissolve it in standard KI; in the case of ferrous sulphate, about half an hour was required, and even then the last traces were difficult to dissolve. Furthermore sources of error were found which depended on the procedure used. For example, when ferrous sulphate itself was added to the alkaline solution, air oxidation of the iron took place and results were high. On the other hand if acid ferrous sulphate was added, loss of free oxygen due to instability of the Co^{+++} ion in acid solution became a possible source of error. Willard and Hall did actually obtain consistently low results, and concluded that as a reducing agent ferrous sulphate was too weak.

Sarver (loc.cit.) attempted, by careful manipulation of taps, to suck into the alkaline $Co(OH)_3$, ferrous sulphate solution without air. Then, sulphuric acid was introduced in a similar manner and finally the excess of standard $FeSO_4$ was back titrated with $K_2Cr_2O_7$ using barium diphenylamine sulphonate. Recently Baker and McCutcheon (loc.cit.) in a modified form of Sarver's method, transfer the solution containing $Co(OH)_3$ in excess standard ferrous ammonium sulphate, into an excess of $K_2Cr_2O_7$. A back titration was then made potentiometrically, using the ferrous solution. The results they publish vary by up to 1%. Sarver's method was also examined by Evans(83) who found it to be not very reproducible.

The possibility of using reducing agents other than KI and $FeSO_4$ to reduce the $Co(OH)_3$ was investigated by Willard and Hall. Stannous chloride was found to be very good in that the trihydroxide dissolved easily, but a carbon dioxide atmosphere was necessary.

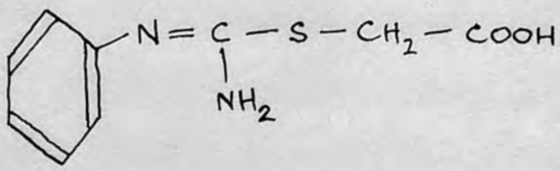
$$2\ Co(OH)_3 + SnCl_2 + 6\ HCl = 2\ CoCl_2 + SnCl_4 + 6\ H_2O.$$

The method used was to add an excess of standard $SnCl_2$ and determine the excess by back titration with iodine or potassium dichromate. Using the latter and potassium ferricyanide as external indicator good results were claimed. (This was before the introduction of diphenylamine indicators). They suggested that if the titration could be carried out electrometrically it would be the best volumetric method for cobalt estimation. A version of the method using diphenylamine as indicator has appeared recently in Sutton's textbook.

Reduction by titanous sulphate, sodium arsenite, antimony trichloride, potassium thiocyanate and hydrazine salts were tried by the above workers with unsuccessful results.

Methods involving oxidation to $Co(OH)_3$ as a first step were examined by Evans (loc.cit.) who concluded that they were incapable of giving consistent and accurate results.

THE PHENYLTHIOHYDANTOIC ACID METHOD



This reagent was introduced by Willard and Hall(17) in 1922, and precipitates cobalt in ammoniacal solution as a red-brown bulky complex of indefinite composition. Many metals from Group II are also precipitated; under controlled conditions cobalt may be separated from As, Al, Cr, Mn, Zn, Ti, etc... Both nickel and iron are partially precipitated, the extent being diminished by the presence of citric acid.

Owing to the indefinite nature of the precipitate, ignition to the oxide "Co_3O_4" was attempted; this invariably gave high results. When ignited with a Meker burner, more accurate results were obtained by assuming the oxide to be Co_2O_3, this being attributed to the more reducing atmosphere. In order to find the nature of the impurities causing high results with "Co_3O_4" Willard and Hall(17) analysed the oxide. It gave a distinct test for sulphate, showing that during ignition some of the sulphur in the precipitate was being converted into sulphate.

A further development of the method was the conversion of the oxide into sulphate for final weighing. This again led to high results after precipitation with phenylthiohydantoic acid, although conversion of pure cobalt to sulphate was claimed to give good results. The method was further investigated in 1929 by Cuvelier(98) who found errors to be as low as 0.1 - 0.2% on quantities of cobalt up to 200 mg. It is very doubtful whether the method is capable of this degree of accuracy. He used electrolytic cobalt, the purity of which is always open to doubt, as primary standard. The sulphate ignition at 600° involves possible loss of SO_3, and some of the sulphate itself was almost certain to have been the result of decomposition of the original precipitate. Again the apparently good results are probably due to cancellation of errors.

In 1947 Garrido(99) recommended diphenylthiohydantoin as a gravimetric reagent, but the thermogravimetric behaviour of the precipitate(2) indicates that the method is incapable of high precision. It appears to have no special advantages over other methods.

THE SULPHATE METHOD

Ignition to, and final weighing as cobalt (II) sulphate is the final procedure in many methods. This will now be discussed in more detail. It consists of adding a little nitric acid to the oxide to convert to nitrate, followed by sulphuric acid to convert to the anhydrous sulphate on ignition. After cooling a few drops of water are usually added and the sulphate is again heated to expel free sulphuric acid. The temperatures recommended vary between 400° and 600°. The important question is whether this can be carried out without thermal decomposition of the anhydrous sulphate itself.

$$CoSO_4 \longrightarrow CoO + SO_3$$

The extensive literature on this method, much of which is reported in Mellor(100), is very conflicting as to the temperature at which decomposition starts. It ranges from 440° to about 900°. Willard and Hall(17) found 550° as the upper limit for igniting the sulphate without decomposition, although in later work, Willard and Fowler(101) prepare anhydrous cobalt sulphate by heating to constant weight at 500°-650°.

Fairchild(102) recommended the following method for cobalt analysis. The cobalt is precipitated as CoS and then treated with HCl, HNO_3 and finally H_2SO_4 to convert into $CoSO_4$ which is ignited at 600°. Unfortunately his stock solution of cobalt nitrate was standardised by evaporating down an aliquot portion, treating with H_2SO_4 and igniting under the same conditions.

More recently Baker and McCutcheon(103) claim that $CoSO_4$ ignited at not higher than 550° gives accurate results. Yardley(54) in assessing the value of $CoSO_4$ as a primary standard found that ignition at 400°-550° always produces a product either containing a trace of water or deficient in SO_3.

Duval's thermogravimetric study of cobalt sulphate indicated the original substance to be $CoSO_4 + 8.5\ H_2O$. He concluded that dissociation took place over the whole range between 350° and 820°, and that results better than 1% accurate could not be obtained using the sulphate method.

The above work is concerned only with the ignition of cobalt sulphate; errors in operations carried out before the ignition would be in addition to the above.

REDUCTION TO METALLIC COBALT

Reduction by hydrogen to the metal has been recommended as the final procedure in many methods.

$Co^{++} \rightarrow Co(III)$ α nitroso β naphtholate $\rightarrow$ oxide $\xrightarrow{red'n}$ metallic Co.

$Co^{++} \rightarrow Co(OH)_3 \longrightarrow$ oxide $\longrightarrow$ metallic Co.

$Co^{++} \rightarrow$ Co phenylthiohydantoate $\longrightarrow$ oxide $\longrightarrow$ metallic Co.

$Co^{++} \rightarrow Co(II)$ sulphide $\longrightarrow$ oxide $\longrightarrow$ metallic Co.

The procedure itself is old, and was used as early as 1864 by Winkler(84). It needs great care, the stream of hydrogen having to be passed over the finely divided metal until this has cooled to room temperature. Yardley (loc.cit.) found the reduced metal very pyrophoric; this appears to depend on the temperature at which reduction is carried out.

The question of whether the oxide is completely reduced is important. Commercial cobalt "sponge" of 99.99% purity invariably contains some unreduced oxide. This will be dealt with more fully later.

Another drawback to the method is that in weighing the metal itself, weighing errors have the maximum effect, and this, no doubt, is the reason why conversion to the sulphate has also been recommended for final weighing.

E.D.T.A. METHODS

Ethylenedeiaminetetra-acetic acid was introduced in 1946 by Schwazenbach and has formed the basis of a number of methods for estimating cobalt.

Complexone III [*] forms both a divalent and trivalent complex with cobalt, the latter being more stable than the former.

$$Co^{++} + H_2Y^{--} \longrightarrow CoY^{--} + 2H^{+}$$

$$Co^{+++} + H_2Y^{-} \longrightarrow CoY^{-} + 2H^{+}$$

The redox potential for the system Co^{+++}/Co^{++} with E.D.T.A. was found by Pribil$^{(104)}$ to be -0.6 volt, which meant that oxidation to the trivalent state was possible using ceric sulphate. A method based on this was subsequently developed by Pribil and Malicky$^{(105)}$, the end-point being determined potentiometrically. Oxidation was found to be very slow, a considerable time lag occurring between addition of the reagent and potentiometric readings.

The most direct titration between cobalt and E.D.T.A. was proposed by Flascka in 1952$^{(106)}$. Murexide [**] was used as indicator; the maximum cobalt which could be determined in this way was only 0.38 mg.

In 1954 Harris and Sweet$^{(107)}$ attempted to utilize the standard zinc-E.D.T.A. method for estimating cobalt. Excess standard E.D.T.A. was added to an acid solution of cobalt, the excess being determined by a back titration with a standard zinc solution using Eriochrome Black T [***] as

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[*] Sodium salt of sequestric acid or Trilon "B".

[**] Ammonium salt of purpuric acid.

[***] Sod-1(1-hydroxy-2 naphthylazo)5-nitro-2-naphthol-4-sulphonic acid.

indicator at pH 10. For quantities of cobalt above 50 mg. the end-point was difficult to detect. More recently other indicators such as pyrogallol red and catechol violet have been proposed for titration of cobalt with E.D.T.A.

ALKALIMETRIC METHOD

Coetzee(108) has developed a method for titration of cobalt with 0.1 alkali using thymolphthalein as indicator. In order to observe the colour change more clearly, the blue hydroxide containing almost all the alkali required was boiled until the rose-coloured form was obtained. The solution was cooled and the last stages of the titration carried out at room temperature. Accurate results were claimed, but the method required previous separation of the cobalt.

THE SULPHIDE METHOD

Precipitation of cobalt as sulphide followed by conversion to oxide and then reduction to metal for final weighing is an old method(109). In 1930 Haring and Leatherman(110) studied precipitation of cobalt sulphide from buffered solution at various pH values. The precipitate was then treated as above. Accurate results were claimed.

The method has been criticised on the grounds that although precipitation appears to be complete, washing the sulphide introduces difficulties. Water carries it through the filter and ammonium salts dissolve it.

The final procedure of reduction to metallic cobalt has already been discussed. Thermogravimetric study of CoS(2) indicates that it is quite unsuitable as a weighing form.

Other methods, some of which have been proposed recently are the iodopentammine(111), mercury thiocyanate (112-116), silver hexacyano(117), dinitroresorcinol(118-119), hexamino tri-iodo mercurate(120), ferrocyanide (121-122), oxalate(123-124), and benzoquinaldinic acid(125) methods.

(b) Primary Standards

A survey of cobalt analytical literature reveals that a very wide selection of cobalt compounds has been used for preparing standards. Further, many investigators have standardised cobalt stock solutions of arbitrary strength for assessing a particular method, by using a range of existing methods of analysis, so that their final results only relate to these methods.

A large number of methods, some of which are very important, contain no reference at all to the standard used.

They merely state "...gms. of cobalt was taken." Table III shows the wide range of standards used. Table IV shows the methods which have been used to standardise stock solutions of cobalt for analysis.

Table III

Primary standard	Reference
$CoSO_4$	(125)(126)
$CoSO_4.7H_2O$	(77)(23)(71)(6)
$CoCl_2$	(72)
$K_3Co(CN)_6$	(54)
$[Co(NH_3)_4CO_3]NO_3$	(93)
J.M. Cobalt "sponge" 99.99% pure	(107)(56)(127)
J.M. Cobalt sheet, 99.8% pure	(55)
$[Co(NH_3)_5\ Cl]Cl_2$	(103)(97)
$Co(NO_3)_2.6H_2O$	(113)(10)
Metallic cobalt, (hydrogen-reduced)	(70)(84)(110)
Electrolytic cobalt	(17)(112)(98)

Table IV

Substance used to prepare solution	Method used to standardise solution	Reference
$Co(NO_3)_2$	Electrolytic	(125)(53)(108)
$CoSO_4$	Electrolytic	(126)(128)(96)(118)
Unknown	Electrolytic	(129)
$CoCl_2.6H_2O$	α nitroso β naphthol	(118)
$Co(NO_3)_2.6H_2O$	α nitroso β naphthol (reduced to metal finally)	(130)
$CoSO_4$	Anthranilate	(36)
$Co(NO_3)_2.6H_2O$	phosphate method (ignition to pyrophosphate)	(131)
$CoSO_4$	E.D.T.A.	(126)
$CoSO_4.7H_2O$	Ferricyanide (potentiometric)	(128)(132)
$CoCl_2.6H_2O$	Oxidation by H_2O_2 and iodometric procedure	(133)
$CoSO_4.7H_2O$	Sulphate	(128)(57)(118)(126)
$CoSO_4.7H_2O$	α nitroso β naphthol	(118)

$CoSO_4$ This has been discussed in connection with the analytical method based on it. It appears to be capable of giving high or low results.

$CoSO_4.7H_2O$ For accurate work it is questionable whether this substance can be dried without partial decomposition taking place, a difficulty often met in hydrated substances. Duval(2) states that the original substance contains 8.5 molecules of water of crystallisation.

$CoCl_2$ and $CoCl_2.6H_2O$ The hexahydrate is sufficiently efflorescent to make its use inadvisable. The anhydrous form is easily made but cannot be weighed with certainty without the most extreme precautions.(134)

$[Co(NH_3)_4CO_3]NO_3$
$K_3Co(CN)_6$
$[Co(NH_3)_5Cl]Cl_2$

These complexes have many favourable features as primary standards. They may be re-crystallised and dried without difficulty, and their high molecular weights reduce weighing errors to the minimum. The pyrosulphate fusion required before preparing the solution presents no difficulty. Yardley(54), one of the very few investigators to discuss and examine primary standards, finally chose $K_3Co(CN)_6$.

J.M. 99.99% cobalt "sponge" * This product is described as 99.99% pure, excluding gas content, and this has encouraged some recent workers to use it as a primary standard. It is

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* Purchased from Johnson Matthey and Co. Ltd., Hatton Garden, London, E.C.1.

stated by the manufacturers that the "sponge" contains a little unreduced oxide. The purity figure is obtained by subtracting from 100 the sum of the metallic impurities determined spectrographically. Clearly its value as a primary standard will depend on how much unreduced oxide is present initially, and the extent to which oxidation takes place on storing the material. Further, in using cobalt "sponge" as primary standard, weighing errors have the maximum effect.

$\underline{Co(NO_3)_2.6H_2O}$ This is subject to the same difficulty as the hydrated sulphate, namely that of drying.

Metallic cobalt This will be considered as finely divided hydrogen-reduced metal similar to the "sponge". Yardley(54) found it extremely pyrophoric but his procedure for preparation was not given. The temperature used in reduction is important. At 250° the product is a pyrophoric black powder; at 700° it is not.(135) Metallic cobalt has the defects of cobalt "sponge".

Electrolytic cobalt Willard and Hall(17) electrolysed a solution of $[Co(NH_3)_5Cl]Cl_2$ using a platinum foil cathode covered with a thin film of vaseline. The cobalt deposit was peeled off as a sheet and ignited in hydrogen at bright red heat. After cooling, the product was used as a standard. Many investigators state "electrolytic cobalt was used as standard", without giving details.

It will be shown later that electrolytic cobalt is invariably impure, the degree of impurity depending on the procedure used in its preparation.

As for the use of existing cobalt methods for standardising stock solutions, it has already been shown that many are open to serious criticism. Furthermore, where a particular method has been used to standardise a stock solution, knowledge of the exact procedure would be required to assess its value. In many methods a different result would be obtained if the conditions were varied. This occurs strikingly in the phosphate method. Kolthoff and Waters(131) standardised a cobalt nitrate solution using the phosphate method although Dufty(70) established that the presence of nitrate ion interferes with this method, giving low results.

Another example has already been mentioned. Fairchild(102) standardised a stock solution using the same procedure that he proposed to assess, using it, ignition to $CoSO_4$ at 600°. Even if the $CoSO_4$ treated in this way was deficient in SO_3 his results might not indicate this.

To summarise, many methods have been used to prepare standard cobalt solutions for assessing methods of analysis. Some involve substances and procedures that are invalidated by previous work. Others involve assumptions which are dubious and require further investigation.

This, coupled with the fact that primary standards have been ignored by many workers, means that apart from relatively few cases where care has been taken, it is very doubtful whether great importance can be attached to the degree of accuracy claimed in the published results on cobalt analytical methods.

(c) the Nitroso-R-salt method.

As use will be made of the Nitroso-R-salt * method for estimating small amounts of cobalt a brief reference will be made to it here. It is one of a very large number of methods available for the spectrophotometric estimation of cobalt. The complex with cobalt is orange-red, the development of colour taking place in the presence of sodium acetate. Three molecules of Nitroso-R-salt react with each cobalt atom. Such variables as pH, time of boiling, etc. have an influence on the colour development.

A great advantage of the method is that although Nitroso-R-salt forms coloured complexes with most of the common metals, all except the cobalt complex are destroyed by nitric acid. An account of earlier work on the method

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* sod-1-nitroso-2-hydroxy-naphthalene 3:6 disulphonate.

and a discussion of the best methods for its use is given in Sandell's textbook.(136)

3. Aim and Scope of Present Work.

The present work originated some years before the war, when Dr A. G. Foster was investigating the possibility of developing an accurate volumetric method based on the green carbonato complex produced by oxidising a cobaltous solution with hydrogen peroxide in the presence of sodium bicarbonate. In order to standardise a cobalt stock solution for this purpose a survey was made of existing cobalt analytical methods, in order to find one capable of accurate, reproducible results.

No such method was found, many weaknesses in recommended methods became apparent, and it was concluded that a full investigation of the whole field was needed. Initial work, including a study of the catalytic decomposition of hydrogen peroxide in connection with the above method was carried out, but progress was delayed by the war. The present investigations began in 1953.

The aim and scope of the present work will be apparent from what has already been said and from the critical survey of methods. They indicate that even the most recommended methods i.e. electrolytic, αnitroso βnaphthol, and sulphate contain unsatisfactory features.

The first aim therefore has been to examine critically the literature on the estimation of macro quantities of cobalt. In order to limit the scope somewhat, the effects of interference by metals other than cobalt have not been considered when assessing the merits of individual methods, although in some cases it is difficult to ignore this aspect.

A study of the methods reveals that, not only have a wide variety of cobalt compounds been used as primary standards, but in addition, many of the stock solutions prepared for use in investigating some methods have been standardised using other methods, very often of doubtful accuracy.

The second aim therefore, has been to compare, using a reproducible method under strictly controlled conditions, a number of cobalt primary standards, some of which have not been used hitherto for this purpose. It should be pointed out that the method of analysis chosen for this need not be accurate in an absolute sense, but only reproducible, as its function is simply to indicate how the available amount of cobalt stands in relation to the theoretical amount implied by the formula.

The third aim has been to examine experimentally a number of cobalt methods using a reliable primary standard. The methods chosen for the most detailed examination were the phosphate, electrolytic, anthranilate, and carbonato (peroxide-bicarbonate method). Others examined were the α nitroso β naphthol, ferricyanide, cyanide, E.D.T.A. and perborate.

It has been hoped that a comparison might be made of the accuracy and reproducibility of these methods. Where a potentially good method had not been acceptable previously because of some defect, an attempt has been made to remedy this, and where methods have been thought capable of further development, this has been attempted. The phosphate method is an example of the former; initial work was done during and immediately after the war. A drawback in this method, the solubility of cobalt ammonium phosphate, has been overcome by incorporating a rapid spectrophotometric method of estimating the filtrate cobalt with Nitroso-R-salt. As an example of the latter, the now standard ferrous iron-dichromate titration has been used in a volumetric method based on initial oxidation of cobalt by hydrogen peroxide in the presence of potassium bicarbonate.

B. EXPERIMENTAL

4. General Technique and Calibration of Apparatus

Weighing This was carried out using an Oertling 62 FM balance with multiweight carrier for weights less than one gram.

Weights. A set of Baird and Tatlock Series 1 nickel-chrome alloy weights was calibrated and kept for the purpose of calibrating all other weights used. The latter operation was carried out using a semi-micro balance; by reading to half a division on the illuminated scale, corrections of ± 0.01 mg. were applied.

The ring weights 0.01 - 0.5 gm. incorporated in the Oertling 62 FM balance were removed and calibrated in the same way.

Volumetric Apparatus

(a) **Standard flasks.** All those used were Grade A; they were calibrated by weighing with distilled water in the usual way.

(b) **Burettes.** All those used were Grade A; they were calibrated in intervals of 10 ml.

In addition, burettes were modified according to a recommendation by Bishop(137), in order to improve further their accuracy. The tips were ground as shown in Fig. 5 and the lower surface smeared with a thin layer of wax, to

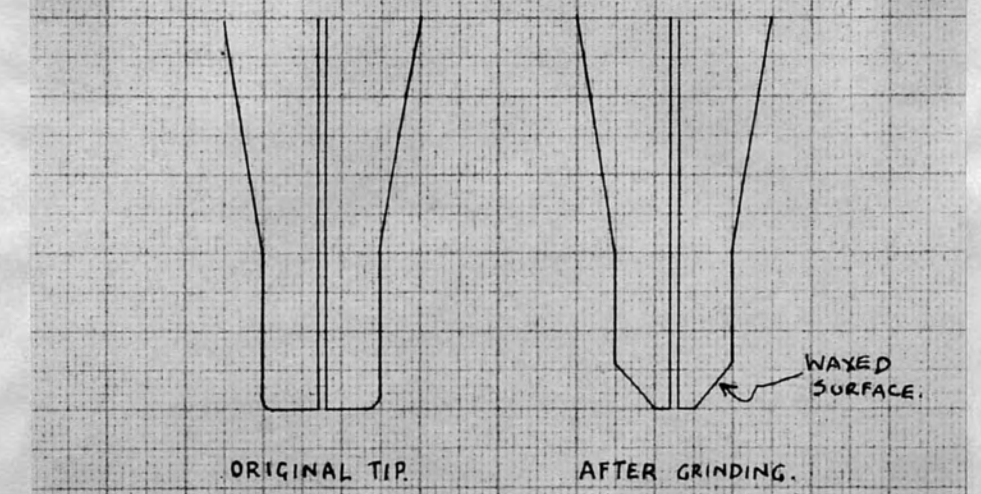

FIG. 5. MODIFICATION OF BURETTE TIPS.

enable smaller drops to fall completely away.

(c) Pipettes. Generally Grade A pipettes were used. They were calibrated in the usual way.

In weighing previously heated crucibles, it was found that a longer time was required for cooling to constant weight than the literature generally recommended. Whenever possible, heated crucibles etc. were left in the balance room overnight before weighing; they were never weighed in less than two hours after ignition at high temperatures.

Recent research by Agterdenbos(138) has confirmed that cooling for 45 mins. can lead to a final temperature difference of 10^o between the crucible and the balance, and as eadh degree may cause a difference in weight of 0.16 mg., large errors are possible unless longer periods of cooling are employed.

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pH measurements A Cambridge pH meter was used with glass and saturated calomel electrodes. The instrument was standardised using $\frac{M}{20}$ potassium hydrogen phthalate (pH 4.00) and a sodium phosphate-potassium phosphate buffer solution (pH 6.81 at 18^o).

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5. Primary Standards

Standards examined:

(a) $CoSO_4$ (b) $K_3Co(CN)_6$
(c) $CoSO_4.K_2SO_4.6H_2O$ (d) $[Co(NH_3)_6]Cl_3$
(e) $[Co(NH_3)_5Cl]Cl_2$ (f) J.M. 99.99% cobalt sponge.
(g) J.M. cobalt wire

Notes: (i) Electrolytic cobalt as a potential primary standard will be dealt with in Chapter 7.

(ii) Some substances such as $Co(NO_3)_2.6H_2O$ were rejected as possible standards for reasons given earlier.

Preparation of Standards.

All materials used for the preparation of standards were B.D.H. 'Analar' grade unless otherwise stated.

(a) Cobalt (II) sulphate. Cobalt (II) sulphate was re-crystallised three times from almost boiling water. The crystals were dried in air, ground up, and then ignited in an electric furnace at various temperatures between 500° and 550°. The anhydrous sulphate was stored in a vacuum desiccator.

(b) Potassium cobalticyanide. This method was used by Yardley(54). A solution of 48 gm. of $CoCl_2.6H_2O$ in 100 ml. of hot water was slowly added to a nearly boiling solution of 80 gm. of KCN in 100 ml. of hot water. When effervescence had ceased, 5N HCl was added until the mixture was acid to litmus, and the whole was boiled for a few minutes. Further small amounts of solid KCN were added until the precipitate slightly re-dissolved. The solution was again made acid. The alternate addition of KCN and acid was continued until the faintly acid solution was almost clear and yellow-green in colour. A further 5 ml. of 5N HCl was added, and the solution boiled until solid commenced to separate. The crude product was filtered, washed with alcohol, and after air-drying, re-crystallised from the minimum amount of hot water. The re-crystallisation was repeated three times, the hot solution being filtered through asbestos. The purified material was washed with alcohol and ether, dried in vacuo, ground up, and stored in a vacuum desiccator before use.

(c) Potassium cobaltous disulphate. Equimolecular amounts of cobalt sulphate and potassium sulphate were mixed and the disulphate re-crystallised three times from hot water. The crystals were washed with a little water and acetone, ground up and dried in a vacuum desiccator.

(d) Hexammine cobaltic chloride. Ordinary grade $[Co(NH_3)_6]Cl_3$ was re-crystallised three times from hot water, the crystals being filtered off after cooling the solution in a refrigerator. They were washed with 60% alcohol followed by 95% alcohol, and dried in a vacuum desiccator.

(e) Chloropentammine cobaltic chloride. This was prepared by the method of Willard and Hall(17)

To a cold solution of 50gm. cobalt chloride and 100 gm. ammonium chloride in 300 ml. 0.880 ammonia, 25 ml. 30% hydrogen peroxide solution was added at once, and then two or three mls. at a time until 50 ml. had been added in all. When the oxidation was complete, the solution was neutralised with conc. HCl, and 50 mls. excess added, after which the solution was heated to boiling and allowed to cool. The purple precipitate was filtered off, dissolved in 2% ammonia, filtered, acidified with hydrochloric acid and boiled. The pentammine was filtered off and re-precipitated three times in the above manner. It was then washed with water and finally with alcohol and a little ether. The product was dried in a vacuum desiccator.

(f) J.M. 99.99% cobalt sponge. This has been described previously. Two batches were purchased. They will be referred to as Sponge I and II.

(g) J.M. cobalt wire. This material is produced from spectrographically standardised cobalt sponge. The wire purchased was 0.5 mm diameter.

For both the sponge and the wire, an enclosed report gave an estimate of impurities based on spectrographic analysis.

Preparation of stock solutions.

The amounts of the various standards taken were such that their solutions contained approximately 100 mg.

cobalt in 50 ml.

In all cases except the mixed sulphate and three batches of the sponge, the final stock solutions contained cobalt (II) sulphate only.

Stock solutions from the anhydrous cobalt(II) sulphate and the mixed sulphate were made by simply weighing out accurately the appropriate amounts and making up the total volume to one litre.

For the complexes, pyrosulphate fusion was necessary to produce cobalt(II) sulphate. It was found convenient to carry this out in a rather long necked 500 ml. thick-walled pyrex bolt-head flask heated by means of a thermomantle. In this way possible loss of cobalt by splashing was minimised. After evaporation to dryness, twice using about 20 ml. of concentrated sulphuric acid for each 5 gm. of complex, the residue in each case was dissolved in water and made up to one litre.

Very much the same procedure was used for the cobalt sponge and wire. Each was first dissolved in nitric acid and evaporated to dryness twice with sulphuric acid. Three solutions of sponge were made by simply dissolving it in the minimum of nitric acid and making up to one litre as cobalt (II) nitrate. This is indicated in the results.

Stock solutions were kept in cupboards to avoid undue temperature fluctuations. Bottle stoppers were capped with small beakers.

Analysis of Standards.

In order to compare the actual cobalt content of each standard with the amount indicated by the stoichiometric formula it was necessary to employ a precise method of analysis. The method chosen was a development of the phosphate method, and in order to standardise conditions as much as possible, quantities of the standards containing about 100 mg. cobalt were taken for each analysis. The analyses themselves were carried out under strictly controlled conditions.

Method of Analysis.

To a neutral cobalt solution containing approximately 100 mg. cobalt, 5 gm. ammonium chloride and 10 ml. 2N sodium acetate were added. The total volume was adjusted to 120 mls. The solution was heated on a water bath; when hot, 12 ml. of 10% ammonium phosphate solution was slowly added, and the solution stirred occasionally until the precipitate turned violet. The beaker was now removed from the bath and left to stand for one hour.

The precipitate was filtered (X4 sintered crucible), washed with 1% ammonium phosphate solution which had been adjusted to pH 7.0, and finally with 5 ml. 50% alcohol.

After drying for about 15 minutes at 110°, it was ignited for one hour at 730°. Generally it was left in a desiccator overnight before weighing. The cobalt was calculated on the basis of $Co_2P_2O_7$.

The filtrate and washings were transferred to a 500 ml. volumetric flask and made up to the mark with distilled water. 25 ml. was withdrawn and analysed for cobalt spectrophotometrically using Nitroso-R-salt.[*]

This method is based partly on the analogous phosphate method for zinc(60) e.g. the use of ammonium chloride and sodium acetate as buffer.

The reproducibility of the method is illustrated by the following results obtained by analysing a cobalt sulphate solution containing approximately 100 mg. cobalt per 50 ml.

(i) 104.6 mg. cobalt
(ii) 104.7 mg. cobalt
(iii) 104.6 mg. cobalt
(iv) 104.6 mg. cobalt
(v) 104.6 mg. cobalt
(vi) 104.7 mg. cobalt

As it was not known at the time whether the result would depend on the final pH of the solution before filtering, these values were measured. Later it was found that under the conditions used in the analysis, there was no such dependence; they will not, therefore, be recorded.

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[*] This will be described at the end of the chapter.

Results.

Series I.

Standard	Cobalt taken mg.[*]	Total cobalt found mg.	% difference.
$CoSO_4.K_2SO_4.6H_2O$ A[**]	97.8	98.5	+0.7
" A	97.8	98.6	+0.8
" B	100.0	101.0	+1.0
" B	100.0	100.9	+0.9
" C	99.6	100.6	+1.0
" C	99.6	100.7	+1.1
$[Co(NH_3)_5Cl]Cl_2$ A	100.1	100.8	+0.7
" A	100.1	100.6	+0.6
" B	99.9	100.5	+0.6
" B	99.9	100.4	+0.5
" C	100.4	100.9	+0.5
" C	100.4	100.8	+0.4
" C	100.4	100.9	+0.5
J.M. Sponge (as nitrate) A	99.8	99.5	-0.3
" A	99.8	99.6	-0.2
" B	100.2	99.9	-0.3
" B	100.2	100.0	-0.2
" C	100.5	100.4	-0.1
" C	100.5	100.3	-0.2
" (as sulphate) D	101.0	101.2	+0.2
" D	101.0	101.2	+0.2

[*] Based on stoichiometric formula of standard.

[**] A,B, etc. refer to the different batches of the particular primary standard, except the sponge, where A,B,etc. refer to different stock solutions made from the same sample.

Series I (continued)

Standard		Cobalt taken mg.	Total cobalt found mg.	% difference.
$[Co(NH_3)_6]Cl_3$	A	100.1	100.5	+0.4
"	A	100.1	100.6	+0.5
$K_3Co(CN)_6$	A	100.2	100.9	+0.7
"	A	100.2	100.8	+0.6
"	B	100.2	100.7	+0.5
"	B	100.2	100.7	+0.5
$CoSO_4$	A*	100.1	100.4	+0.3
"	A	100.1	100.3	+0.2
"	B**	99.0	100.0	+1.0
"	B	99.0	100.0	+1.0
"	C***	100.2	100.3	+0.1
"	C	100.2	100.3	+0.1

* IGNITED AT 500° ** IGNITED AT 530° *** IGNITED AT 550°

Another variation of the phosphate method based on a procedure recommended by Schoeller(139) was also used to compare standards.

<u>Method</u>: To a neutral cobalt solution containing approximately 100 mg. cobalt was added 10 ml. conc. HCl and 10 ml. 10% ammonium phosphate solution. The total volume was adjusted to 150 ml. After heating on a water bath until hot, sufficient 1 : 1 ammonia was added to cause the precipitate formed to partly dissolve (25 ml. approximately). The

precipitate was left to stand for 1 - 2 hours, filtered through a X4 sintered crucible, washed with 1% ammonium phosphate solution followed by a little 50% alcohol and dried at 110°. It was then ignited for 1 hour at 730°. Subsequent operations including the filtrate cobalt estimation were as in the previous method.

Again the method itself was tested on an arbitrary cobalt solution, and found to give consistent results.

Results

Series II

Standard		Cobalt taken mg.	Total cobalt found mg.	% difference.
$[Co(NH_3)_5Cl]Cl_2$	A	100.2	100.4	+0.2
"	A	100.2	100.2	0
"	B	100.5	100.8	+0.3
"	B	100.5	100.6	+0.1
"	C	100.4	100.7	+0.3
"	C	100.4	100.7	+0.3
"	D	100.2	100.3	+0.1
"	D	100.2	100.4	+0.2
"	D	100.2	100.3	+0.1
"	D	100.2	100.3	+0.1
"	E	100.4	100.6	+0.2
"	E	100.4	100.5	+0.1

/continued over

Series II. (continued)

Standard		Cobalt taken mg.	Total cobalt found mg.	% difference
J. M. sponge II (as sulphate)	A	100.9	100.4	-0.5
"	A	100.9	100.5	-0.4
"	A	100.9	100.4	-0.5
"	A	100.9	100.4	-0.5
"	B	100.1	99.5	-0.6
"	B	100.1	99.6	-0.5
J. M. Co wire (as sulphate)	A	100.2	100.6	+0.4
"	A	100.2	100.6	+0.4
"	B	100.2	100.4	+0.2
"	B	100.2	100.4	+0.2
$K_3Co(CN)_6$	B	76.9	77.0	+0.1
"	B	76.9	77.0	+0.1
"	C	72.3	72.5	+0.2
"	C	72.3	72.4	+0.1
$CoSO_4$	D*	100.6	101.1	+0.5
"	D	100.6	101.2	+0.6

* Ignited at 530°

Summary.

Series I.

Standard.	Mean relative error for phosphate method used.
$[Co(NH_3)_5Cl]Cl_2$	0.54% high
$[Co(NH_3)_6]Cl_3$	0.45% "
$K_3Co(CN)_6$	0.57% "
Co sponge I (sulphate)	0.20% "
Co sponge I (nitrate)	0.22% low
$CoSO_4.K_2SO_4.6H_2O$	0.92% high
$CoSO_4$	0.45% " (but results erratic).

Series II.

Standard.	Mean relative error for phosphate method used.
$[Co(NH_3)_5Cl]Cl_2$	0.18% high
$K_3Co(CN)_6$	0.13% "
Co wire (sulphate)	0.30% "
Co sponge II (sulphate)	0.52% low
$CoSO_4$	0.55% high

In both series, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$ and $K_3Co(CN)_6$ give very similar results, the differences being of the same order as the experimental error for the method.

The cobalt wire gave slightly higher results.

The remaining standards gave different results to the three complexes; if it is assumed that the latter contain the theoretical amount of cobalt, then the sponge contains less, and the mixed sulphate more cobalt than the theoretical amount.

The fact that the group of complexes, and the cobalt wire gave similar results, led to the assumption that they contained the correct amount of cobalt. As the pentammine complex was the easiest to prepare, this was used as primary standard for all subsequent work. Stock solutions were made up and stored as described earlier.

The Nitroso-R-salt method.

This method has been investigated by many workers, and is now quite well established. It is exclusively recommended by the 1956 A.S.T.M. handbook for estimating small quantities of cobalt. Many variations of the method have been published, usually to overcome some specific interference, or to estimate cobalt in different concentration ranges.

At first, filtrates and washings from the phosphate method were evaporated down, and the reduced volume analysed for cobalt using Allport's method(140). Later, this cumbersome operation was rejected; instead, the filtrate and washings were made up to 500 ml. in a volumetric flask and 10 or 25 ml. analysed using a more sensitive form of the method.

Method: The filtrate and washings from the phosphate method were made up to 500 ml. To 25 ml. diluted to 40 ml., and containing one drop of phenolphthalein, 1 : 50 HCl was added until colourless and then a few ml. excess. The solution was boiled gently for a few minutes, 4 ml. 50% sodium acetate solution was added, and after further boiling, 4 ml. 0.2% Nitroso-R-salt solution was introduced. When the colour had developed fully (about 2 minutes' boiling), 2 ml. conc. nitric acid was added, the solution boiled for one more minute, and then cooled rapidly. It was made up to 100 ml. in a volumetric flask, and the optical density measured using a 4 cm. cell, No. 605 Ilford yellow-green filter (peak of transmission 545 mμ) and a blank treated similarly. A mercury vapour lamp was used as light source.

The calibration curve, for which $[Co(NH_3)_5Cl]Cl_2$ was used as standard, is shown in Fig. 6. The reported failure of Beer's Law at low cobalt concentrations(141) was not encountered, probably owing to the procedure used. The method is quite rapid; in practice it was found that four filtrates could be analysed within 30 minutes.

In order to ensure that no interference was caused by ammonium or phosphate ions under the analytical conditions, tests were carried out on dilute cobalt solutions of known strength and containing these ions. Neither was found to

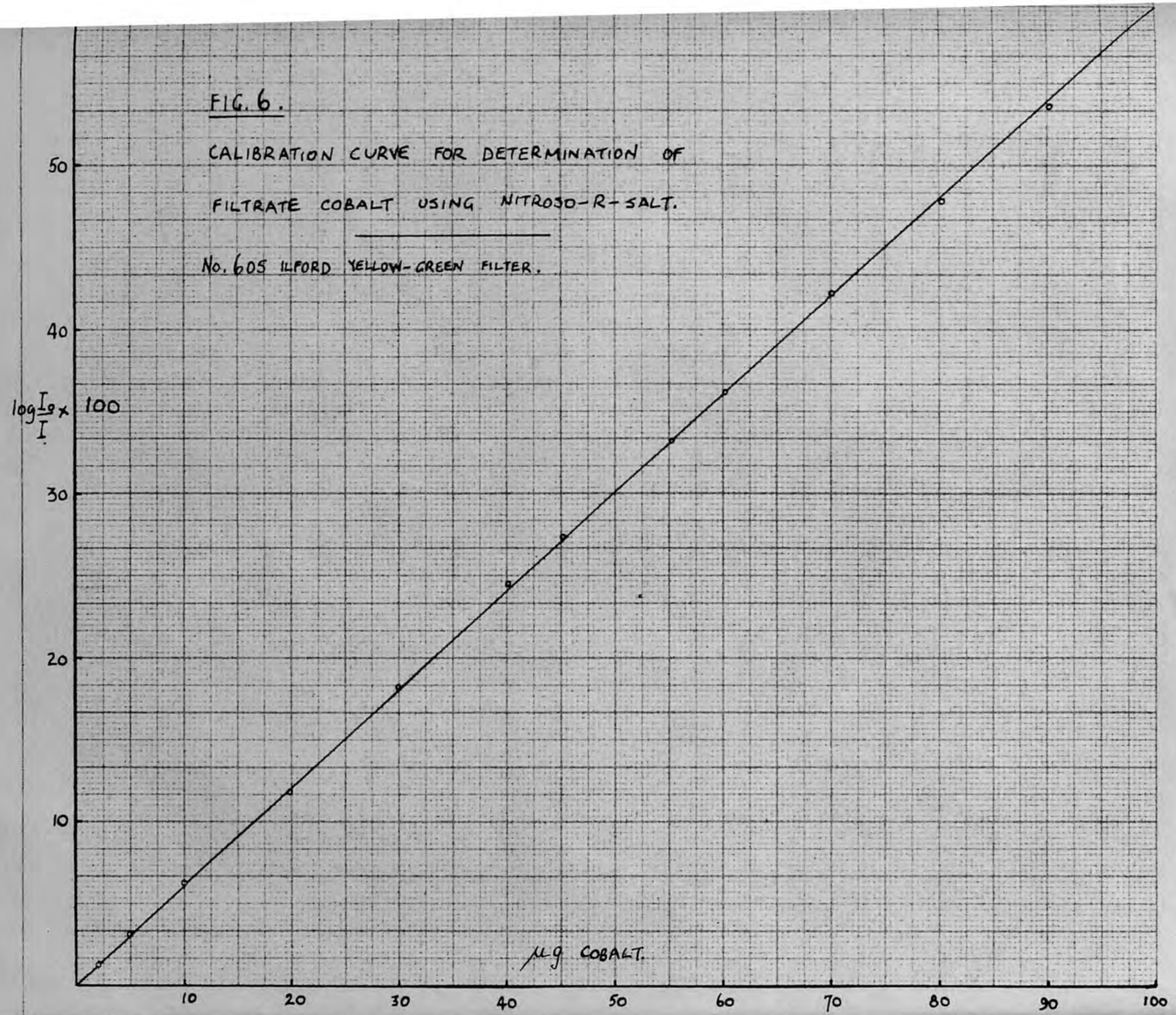

FIG. 6.

CALIBRATION CURVE FOR DETERMINATION OF FILTRATE COBALT USING NITROSO-R-SALT.

No. 605 ILFORD YELLOW-GREEN FILTER.

affect the results, even in relatively large amounts.

There is some contradiction in the literature on the best wavelength for measuring the absorption. Claassen and Westerveld(142) gave the transmission minimum for the cobalt - Nitroso-R-Salt complex at 415 $m\mu$, but recommended measurement at 550 $m\mu$ since at this wavelength the reagent itself absorbed least. For this reason the yellow-green filter was used.

Two typical results, to indicate the amount of cobalt in the filtrate, are given below. They are taken from the phosphate analysis of primary standards, one from Series I, the other from Series II.

Standard being examined.	Co taken mg.	Phosphate method used.	Co found as $Co_2P_2O_7$ mg.	Filtrate Co by N.R.S. mg.	Total cobalt mg.
$[Co(NH_3)_6]Cl_3$	100.1	As in Series I	100.1	0.4	100.5
$[Co(NH_3)_5Cl]Cl_2$	100.4	As in Series II	98.9	1.6	100.5

The filtrate cobalt will be dealt with more fully in Chapter 6.

4. The Phosphate Method.

The first procedure tried out was based on the standard zinc method(60), and consisted of adding 10% ammonium phosphate to a cobaltous solution buffered with ammonium chloride and sodium acetate. It is the method used in Series I of the primary standard analyses, and appears on page 78. Results were very consistent but always high on the basis of $[Co(NH_3)_5Cl]Cl_2$ as primary standard. The precipitate was rather fine, and easy to transfer, but it had a tendency to make washing and filtering difficult by becoming tightly packed under suction.

Typical results.

Co taken mg.	Co as $Co_2P_2O_7$ mg.	Co in filtrate mg.	Total Co mg.	Relative error %
100.1	99.9	0.8	100.7	+0.6
"	99.8	1.0	100.8	+0.7
"	100.0	0.7	100.7	+0.6
"	100.1	0.6	100.6	+0.6

It will be noted that the filtrate cobalt is ignored, the results on the basis of cobalt pyrophosphate would appear to be good.

In order to determine whether under different conditions of pH (1) the filtrate cobalt might be less, or even zero,

(2) the composition of the precipitate might

be different and lead to more accurate results, the pH was adjusted with N. NaOH or N HCl.

Method To the cobaltous solution, 5 gm. of ammonium chloride and 10 ml. 2N. sodium acetate were added and the total volume made up to about 120 ml. Using N. NaOH or N. HCl the pH was adjusted so that for the series, the values were distributed between pH 6 and pH 8.5.

Each solution was heated on a water bath; when hot, 12 ml. 10% ammonium phosphate solution was added. After a change in colour of the precipitate to violet, the beaker was removed from the bath and left standing for 1 hour. The precipitate was filtered off (X4 sintered crucible) and its pH measured. After washing with 1% ammonium phosphate and finally with 5 ml. of 50% alcohol it was dried for a short time at 110° and then ignited for 1 hour at 730°. Filtrate cobalt was determined using Nitroso-R-salt as described earlier.

It was not found possible to treat this series in a similar manner. Those of higher pH value took about 3 hours heating on the water bath to turn violet. The resulting loss of ammonia over this period resulted in a large drop in pH, so that the pH range for the series was rather narrow.

Results

No.	Co taken mg.	Co found as $Co_2P_2O_7$ mg.	Filtrate Co mg.	Total Co mg.	Relative error %	Final pH
1	99.9	100.2	0.3	100.5	+0.6	7.05
2	99.9	100.1	0.3	100.4	+0.5	6.55
3	99.9	99.5	0.9	100.4	+0.5	6.15
4	98.8	97.3	2.2	99.5	+0.7	5.80
5	99.8	98.0	2.4	100.4	+0.6	5.73
6	98.8	96.6	2.8	99.4	+0.6	5.60

Nos. 4 and 6 were not adjusted initially. Instead they were boiled gently for 10-15 minutes after precipitation in order to reduce the pH.

From the results it will be seen that the relative error does not depend on the pH, in the procedure used.

Matsuo(74) in investigating the effect of pH on the precipitation of cobalt ammonium phosphate, adjusted the pH after precipitation. He used the following method:-

A quantity of NH_4Cl was added to the cobalt solution to give the $Co^{++}:NH_4^+$ molar ratio required, (there appears to be no reason for the values selected), taking into account the ammonium phosphate solution to be added later as precipitant. Then, ten times the equivalent of ammonium phosphate was added in solution.

After heating on a water bath for a few minutes,

N. NH_4OH was added to adjust the pH. The total volume in each case was 100 ml. The solutions were then left to stand overnight, the precipitates filtered off, washed with water, and ignited for 30 minutes at 500°. The pH of the filtrate was measured and its cobalt content determined colorimetrically using αnitroso β naphthol. Matsuo's results are given in Fig. 4. This work, with slight modification, was repeated, using $[Co(NH_3)_5Cl]Cl_2$ as primary standard.

__Method:__ Sufficient NH_4Cl was added to the cobalt solution to give, with the 23 ml. of 10% ammonium phosphate solution added later, a 1:50 $Co^{++}:NH_4^+$ molar ratio. The total volume was adjusted to 100 ml. After heating on a water bath for a few minutes, 23 ml. 10% ammonium phosphate solution was added (10 times the equivalent of cobalt present) and the pH was adjusted using N. NH_4OH. The precipitate was left to stand overnight.

It was then filtered (X4 sintered crucible), washed with water followed by a little alcohol, and after drying at 100° for a short time, ignited for 30 minutes at 500°.

The pH of each filtrate was measured, and the filtrate cobalt determined using Nitroso-R-salt.

All the precipitates turned pink within a few minutes of adding the precipitant, and before the pH adjustment. Although fine in texture, they were easy to transfer and filter.

Results

Co taken mg.	Co found as $Co_2P_2O_7$ mg.	Filtrate Co mg.	Total Co mg.	Final pH filtrate
99.5	100.6	0.6	101.2	8.36
"	100.3	0.5	100.8	8.04
"	100.0	0.6	100.6	7.92
"	99.8	0.8	100.6	7.09
"	99.6	0.8	100.4	6.74
"	99.3	1.0	100.3	6.40
"	99.2	0.9	100.1	6.28
"	98.8	1.2	100.0	5.63

These results are shown graphically in Fig. 7.

Fig. 7.

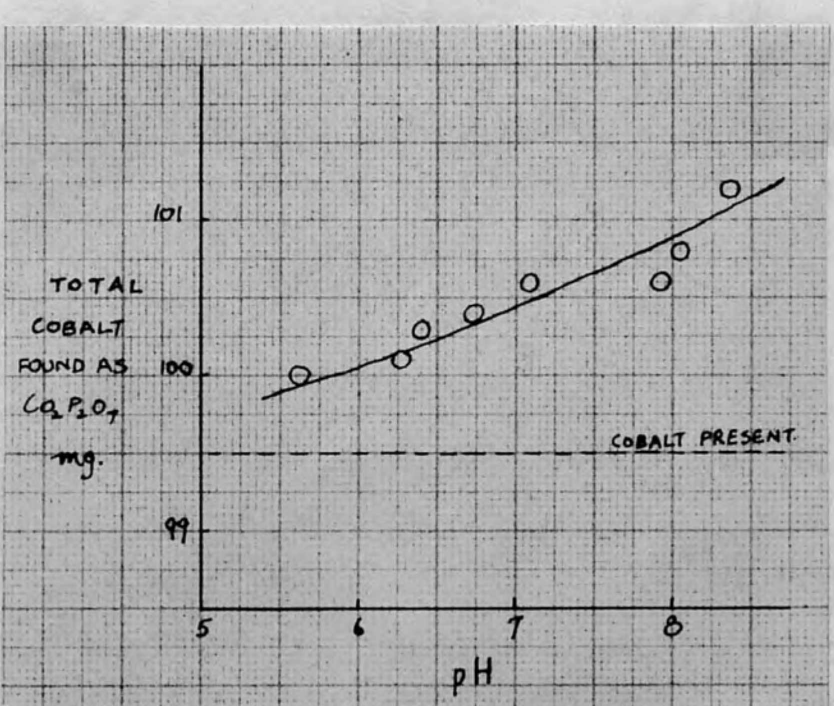

FIG. 7. EFFECT OF pH ON PRECIPITATION OF COBALT AMMONIUM PHOSPHATE USING MATSUO'S METHOD.

(TOTAL COBALT INCLUDES THE FILTRATE COBALT)

In contrast to the present work, Matsuo detected no filtrate cobalt at pH 8. He rejected the phosphate method on the grounds that it failed to produce a precipitate of definite composition. He did not specify the primary standard used.

The present work confirms that under the above conditions of analysis, the total cobalt found varies with the final pH of the solution. However, all the results are high, in contrast to Matsuo's, which were all low.

This form of the phosphate method was therefore rejected.

An investigation was then made of an alternative method of precipitating cobalt ammonium phosphate, that due to Clarke(64) and Hope(65), and later used by Schoeller(139). Schoeller determined the cobalt in the filtrate by saturating it with H_2S, filtering off the cobalt sulphide, and igniting to the oxide for weighing. The minor fraction obtained in that way was added to the major fraction as $Co_2P_2O_7$.

The method used by Schoeller, with filtrate cobalt determined by Nitroso-R-salt, was found to be very reproducible, and a modification of it was used in Series II of the primary standards experiments. Of these, the ones on $[Co(NH_3)_5Cl]Cl_2$, A to E on page 72 give a mean relative error of +0.17%. The precipitate in this form of the method is more difficult to handle than in the phosphate methods previously described. It has a slight tendency to stick to glassware, so that a "policeman" is necessary. However, owing to its granular nature, the precipitate is easily washed without becoming compressed by suction.

On using an equivalent amount of sulphuric acid instead of hydrochloric acid, the final results were found to be slightly lower by 0.1-0.2%. In view of the fact that in using hydrochloric acid the mean error was +0.17%, use of sulphuric acid would produce almost exact results. A large number of determinations has confirmed this; some will be given later.

In order to avoid measuring a very small volume of sulphuric acid it is recommended that 10ml. of 1:2 sulphuric acid is used in place of the 10 ml. of HCl. The only disadvantage of using sulphuric acid is that it retards the change from the blue amorphous precipitate formed initially, into the violet crystalline $CoNH_4PO_4.H_2O$. Whereas this change is complete in 20-30 minutes using HCl, about twice the time is required with H_2SO_4.

Further investigation of this form of the phosphate method will now be described. The influence of the following factors was determined:-

(a) excess of ammonium phosphate used,

(b) final pH,

(c) time of standing before filtration,

(d) washing the precipitate with various solutions,

(e) weighing as $CoNH_4PO_4.H_2O$ instead of as $Co_2P_2O_7$.

(a) excess of ammonium phosphate used.

Method: This was the same as the one used in Series II of the primary standard analyses (p. 72) except that 10 ml. 1:2 H_2SO_4 was used instead of HCl, the precipitate was washed with water instead of 1% ammonium phosphate solution, and the quantities of 10% ammonium phosphate solution used as reagent was as indicated below:-

Results

Co taken mg.	Equivalent of $(NH_4)_2HPO_4$ added	Total Co found mg.
99.4	2.5	99.4
99.4	4.3	99.4
99.4	10	99.6
99.4	25	99.9
99.4	50	100.3

The use of 10 ml. of 10% ammonium phosphate solution for 100 mg. cobalt which has been the case in previous work on the method, including the primary standard analyses, represents a total phosphate ion:Co^{++} molar ratio of 4.3. The NH_4^+:Co^{++} molar ratio is also affected by adding different amounts of ammonium phosphate, although here the variation is much less due to the 1:1 ammonia added to effect precipitation.

The results indicate that when the total phosphate ion:Co^{++} molar ratio is between 2.5 and 10, there is little variation in the final result. Later, it will be seen from a series of analyses in which the phosphate method is used on different amounts of cobalt, that very good results are obtained over the whole range.

(b) final pH.

On adding 1:1 ammonia to the heated acidified cobalt solution, a light blue precipitate appears. On further addition of ammonia the precipitate becomes slightly purple and partly dissolves. If slightly more ammonia is added the precipitate completely dissolves forming a soluble cobalt-ammine complex. At this stage the precipitate can be made to reappear by vigorous stirring, and the analysis continued. The filtrate cobalt however is much higher if the latter procedure is adopted, and as the Nitroso-R-salt method is only 1% accurate there is danger of slight error in the filtrate cobalt. For a series of analyses it was found that if the addition of ammonia was terminated at any stage between the precipitate turning slightly purple, and just completely dissolving, the results were almost identical. There was slightly less reproducibility where the precipitate had completely dissolved, probably for the reason mentioned.

For 100 mg. quantities of cobalt, if just sufficient ammonia is added for the precipitate to turn purple and partly dissolve, the filtrate cobalt is generally between 0.8 and 3.0 mg. The error in estimating this spectrophotometrically would be less than ± 0.03 mg.

(c) time standing before filtration.

In Schoeller's method (loc. cit.) on which the present method is based, the precipitate was filtered off within 10 minutes of turning violet. In the present work, it was found that filtering hot produced a filtrate containing over 10 mg. of cobalt. Furthermore, on cooling the filtrate and washings before making up to 500 ml. for the Nitroso-R-salt analysis, there was a tendency for slight re-precipitation of the cobalt ammonium phosphate.

As the possibility of error is less when the filtrate cobalt is low, the solution containing the precipitate was removed from the water bath when the colour change to violet was complete, and left to cool for 1-2 hours before filtration. Under these conditions the quantity of cobalt found was generally within the range given above.

The period of standing before filtration does not affect the final result, as shown by the following:-

Time between removal from bath and filtration.	Total cobalt found mg.
20 mins.	100.9
1 hour	100.9

/continued over

4 hours	100.8
6 hours	100.9

(d) washing the precipitate.

It was found that any differences in filtrate cobalt due to washing the precipitate with 1% ammonium phosphate solution instead of water, were superimposed on the general solubility of the precipitate under analytical conditions. In a number of parallel analyses, the filtrates where 1% ammonium phosphate solution had been used contained on average, 70% of the cobalt contained in filtrates where water had been used for washing. In view of this, washing with water followed by a little 50% alcohol is recommended.

(e) final weighing form.

Small changes in weight are not apparent in the published thermogravimetric curves of substances. In some cases additional quantitative information is given for regions where small but definite changes occur.

The method is used to prepare the substance under examination is seldom specified. In the majority of cases this is unimportant, but where one procedure leads to a contaminated substance, a knowledge of the preparative method would be very important when considering the thermogravimetric curve. Cobalt ammonium phosphate is a case in point. Duval's thermogravimetric curve is shown in Fig. 1; he does not describe the method used to prepare the specimen.

In view of the fact that the present work shows the cobalt ammonium phosphate prepared by different methods to be slightly different in composition, it was decided to compare the results by weighing as cobalt ammonium phosphate dried at 100° with those obtained by ignition to the pyrophosphate.

Results

Co. found as $CoNH_4PO_4.H_2O$ mg.	Co found as $Co_2P_2O_7$ mg.
148.1	147.4
147.8	147.6
77.6	77.3
77.5	77.2
77.4	77.2
77.2	77.1
77.3	77.0
102.9	106.0
106.2	106.1

In all cases except one, the cobalt found is less on the basis of $Co_2P_2O_7$ i.e. weighing as $CoNH_4PO_4.H_2O$ would lead to high results.

To find out whether results equivalent to those for $Co_2P_2O_7$ could be obtained by drying the ammonium phosphate at a higher temperature, samples were heated at intervals of 5° above 100° for one hour, cooled and re-weighed.

Results

No	Weight difference mg				Overall change in weight 100°-120° mg.
	105°	110°	115°	120°	
1	-0.7	+0.2	-0.1	+0.3	-0.2
2	-0.5	+0.3	-0.1	+0.3	0.0
3	-1.3	+0.5	-0.1	+0.4	-0.5
4	-1.3	+0.5	-0.1	+0.3	-0.6

The weight of $CoNH_4PO_4.H_2O$ in each case was about 0.24 gm. Weight differences in each case are in terms of the previous weight.

The behaviour can be seen to be erratic. Much the same behaviour was found in the case of $CoNH_4PO_4.H_2O$ prepared by adding ammonium phosphate to a neutral cobalt solution. As methods involving this procedure have been rejected, the results will not be given.

From the above work, and in view of the consistent results obtained by the phosphate method via $Co_2P_2O_7$, this appears to be the better weighing form. $730^{\circ} \pm 10$ was adhered to for consistency in igniting to the pyrophosphate. Duval's work indicates a much wider range. For the few samples ignited at various temperatures between 650° and 900°, the weight of pyrophosphate was found to remain constant, confirming this.

Final form of phosphate method.

To the approximately neutral cobalt solution, add 10 ml. 1:2 sulphuric acid, and 10 ml. 10% ammonium phosphate aolution. Adjust the volume to 150 ml.

Heat on a water bath; when hot, add sufficient 1:1 ammonia to cause the precipitate formed to turn slightly purple and partly dissolve. (approx. 25mls. required). Remove the beaker from the bath when the precipitate is violet and stand in a cool place for at least one hour.

Filter through a X4 sintered crucible, and wash with cold water followed by 5 ml. 50% alcohol. Dry the cobalt ammonium phosphate for 15 minutes at 100^o and then ignite at about 730^o for one hour. Cool for two hours and weigh as $Co_2P_2O_7$.

Make up the filtrate plus washings to 500 ml. in a volumetric flask. Withdraw 10 or 25 ml. and analyse in the following way:-

To the aliquot in a total volume of 40 ml. add one drop of phenolphthalein, and neutralize with 1:50 HCl. Add a few ml. excess of the acid, then boil gently on a hot plate. Add 4 ml. 50% sodium acetate solution, continue boiling, and then add 4 ml. 0.2% Nitroso-R-salt. Allow the colour to develop fully (about 2 minutes), add 2 ml. conc. nitric acid and boil for a further minute. Cool rapidly and make up to 100 ml. in a volumetric flask.

Treat a blank solution similarly.

Measure the optical density using a 4 cm. cell and 545 mμ filter.

From a previously constructed calibration curve, determine the total filtrate cobalt and add this to the cobalt found via the pyrophosphate.

The following results illustrate the accuracy of the method when used to estimate various amounts of cobalt.

Results

No.	Co taken mg.	Co found mg.	Relative error %
1.	——	120.5	——
2.	——	120.5	——
3.	241.0	240.9	0.0%
4.	241.0	241.3	+0.1
5.	48.2	48.2	0.0
6.	48.2	48.1	-0.2
7.	24.2	24.2	0.0
8.	24.2	24.2	0.0

The relative errors are in terms of Nos. 1 and 2. In these analyses 10 ml. 10% ammonium phosphate was used in each case.

The results indicate that the high accuracy is maintained over a considerable range of cobalt concentration.

Behaviour of $CoNH_4PO_4.H_2O$ and water.

For both $ZnNH_4PO_4$ and $MgNH_4PO_4$ solubility measurements have been made and the solubility products evaluated. In the case of $MgNH_4PO_4$, Titan Yellow was used to determine the solubility spectrophotometrically.

An attempt was made to measure the solubility of $CoNH_4PO_4.H_2O$ in water using Nitroso-R-salt.

Experiment 1: About 4 gm. $CoNH_4PO_4.H_2O$ was agitated with distilled water in a thermostat at 25°. After various intervals of time, a portion was filtered (X4 sintered glass filter) and the cobalt content of the clear solution determined using Nitroso-R-salt.

Earlier work gave erratic results. Further investigation indicated that the soluble cobalt concentration was a function of time. The general pattern of behaviour is shown in Fig. 8. It will be seen that:-

(a) in all cases the soluble cobalt concentration decreases to zero or nearly to zero eventually.

(b) the time taken for this to happen, and the maximum amount of cobalt passing into solution appears to depend on the history of the $CoNH_4PO_4.H_2O$ used.

(c) It is not possible to obtain a value for the molar solubility of $CoNH_4PO_4.H_2O$.

Somewhat similar behaviour was found even on shaking a clear saturated solution of $CoNH_4PO_4.H_2O$.

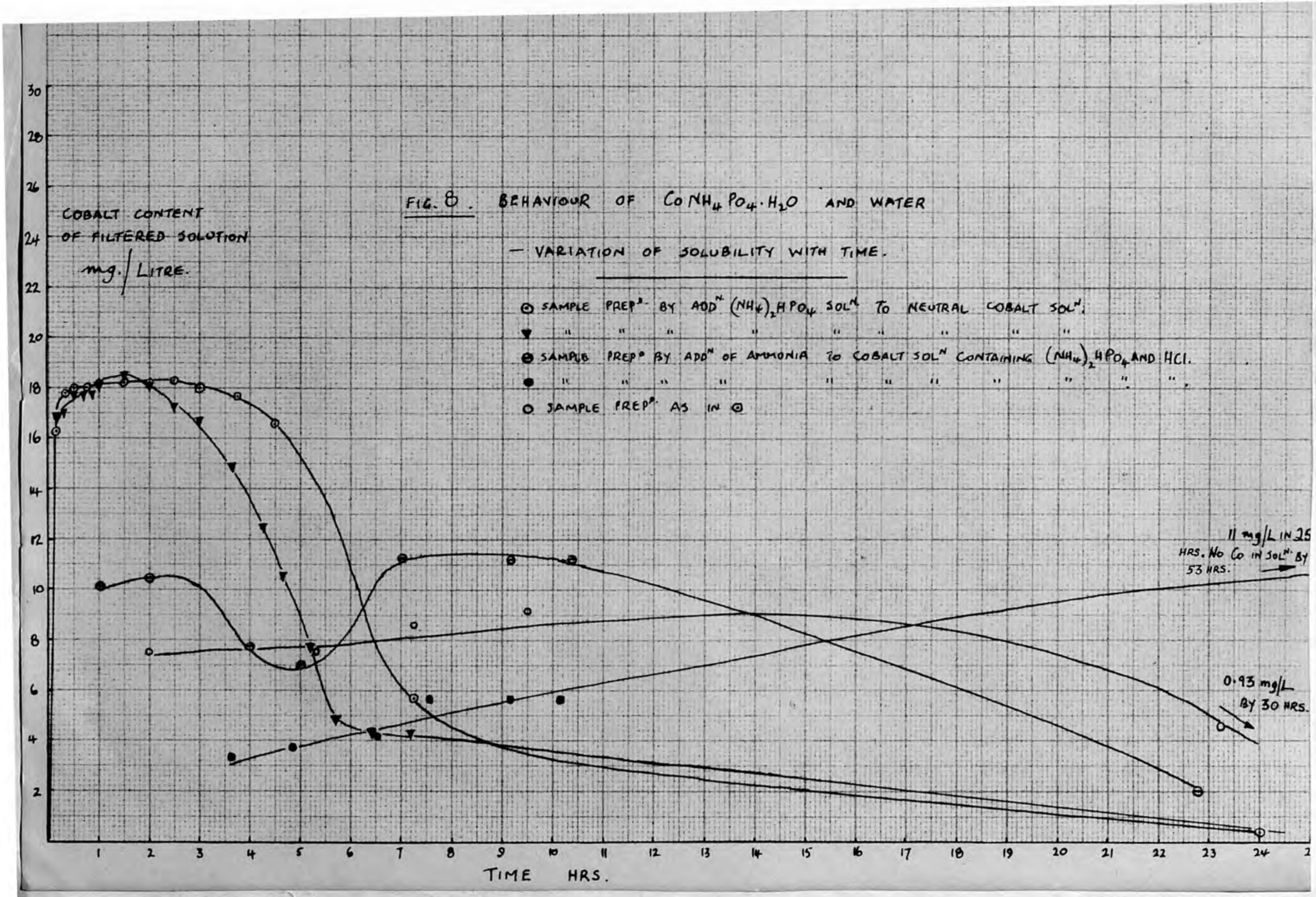

FIG. 8. BEHAVIOUR OF $CoNH_4PO_4 \cdot H_2O$ AND WATER

— VARIATION OF SOLUBILITY WITH TIME.

<u>Experiment 2</u>: About 2 gm. $CoNH_4PO_4.H_2O$ was shaken with distilled water for one hour, filtered, and the cobalt content of the clear solution determined. The clear solution was transferred to a clean flask, stoppered, and again shaken up, this time in a thermostat at 25°. After various intervals of time, aliquot portions were withdrawn and analysed for cobalt. The result is shown in Fig. 8a.

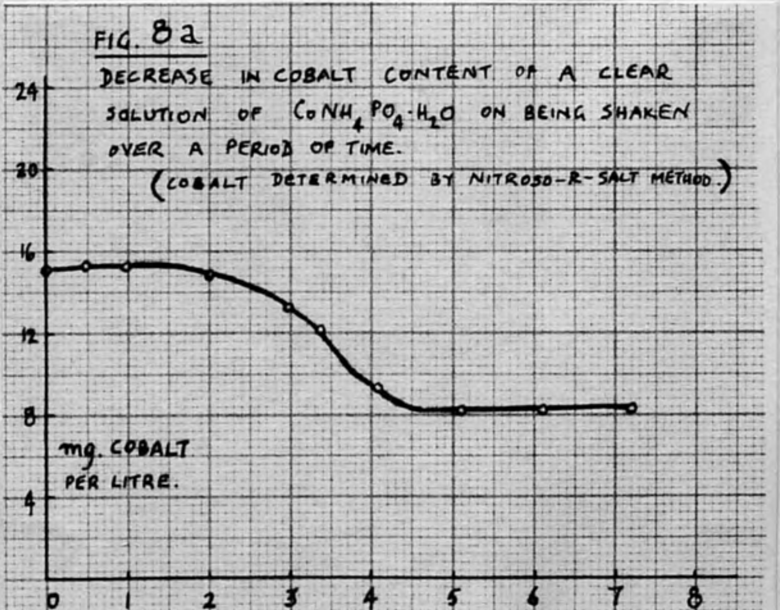

FIG. 8a

DECREASE IN COBALT CONTENT OF A CLEAR SOLUTION OF $CoNH_4PO_4 \cdot H_2O$ ON BEING SHAKEN OVER A PERIOD OF TIME.
(COBALT DETERMINED BY NITROSO-R-SALT METHOD.)

In order to determine whether contact with water for long periods would affect its subsequent solubility, the following was carried out on a sample of $CoNH_4PO_4.H_2O$:-

Experiment 3: 2 gm. $CoNH_4PO_4.H_2O$ which had been agitated with distilled water for three days (peak soluble cobalt content was 18mg/L) was filtered off, washed with distilled water, and again agitated with fresh distilled water. After one hour, the soluble cobalt content was found to be 4.4 mg/L, considerably less than the original 18mg/L.

After 18 hours of further shaking, the cobalt content had decreased to zero as in other cases.

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7. The Electrolytic Method.

In view of the large number of variable factors that might influence results obtained by the electrolytic method, the present work was restricted mainly to:-

(a) an examination and comparison of some existing electrolytic procedures,

(b) an assessment of electrolytic cobalt as a primary standard in cobalt analysis.

General Method.

A Griffin and Tatlock electrochemical analysis apparatus with provision for heating and stirring the electrolyte, was used. Platinum gauze cylindrical electrodes of the usual type were employed for all analyses. They were cleaned, dried and weighed in the usual way. An enclosed ammeter recorded the current passing; the potential between the electrodes was measured using an Avometer. The beaker holding the electrolyte was about half an inch greater in diameter than the outside electrode, and was covered with a split watch glass.

Experiment 1: The solution, containing about 100 mg. cobalt was set in position and electrolysed for a measured length of time. A high rate of stirring was maintained. The average current passing and the potential difference between the electrodes were noted.

At the end of the electrolysis, the beaker was lowered from the electrodes with the current still passing, and replaced by a larger clean beaker. The electrodes were now washed, and the washings poured into 500 ml. volumetric flask. The original spent electrolyte in the small beaker was also added, and the volume made up to the mark. After being shaken, 10 or 25 ml. were withdrawn and analysed for cobalt using the Nitroso-R-salt method.

Blank tests carried out on the reagents other than cobalt indicated no interference with the method. The washed electrodes were dried at 100° for 30 minutes, cooled in a desiccator, and weighed.

The usual assumption was made that all platinum lost from the anode would have been deposited on the cathode; the relevant correction for this was made.

Results: Some representative results are shown in the following table:-

No.	Composition of electrode	Cobalt* taken mg.	Time electrolysed mins.	C.D.	Temperature electrolyte	Change in weight anode mg.	Residual cobalt (by N.R.S) mg.	Total cobalt found	Relative error
1.	($CoSO_4$ (NH_4Cl (NH_4OH ($NaHSO_3$	98.6	30	2A 3.25v	room	-0.5	6.5	99.9	+1.3
2.	as in 1.	99.0	45	2A 3.25v	room	-0.8	0.4	100.5	+1.5
3.	as in 1, but without $NaHSO_3$	98.6	30	2A 3.25v	room	-0.9	3.3	98.9	+0.3
4.	as in 3.	98.6	30	2A 3.50v	room	-0.5	2.9	99.1	+0.5
5.	($CoSO_4$ ($(NH_4)_2SO_4$ (NH_4OH (Hydrazine SO_4	98.7	45	3A 2.25v	room	-0.3	4.1	100.1	+1.4
6.	as in 5.	98.7	120	1.5A	room	0	0.2	100.3	+1.6
7.	as in 5.	98.7	45	3A 2.25v	60°	-1.6	5.3	100.1	+1.4
8.	as in 5.	98.7	45	3A 2.25v	75°	-1.0	0.8	100.3	+1.3

<u>Notes</u> * (a) for this series a stock solution standardised by the phosphate method was used.
(b) C.D. - current density.
(c) in all electrolyses a high rate of stirring was maintained.
(d) all materials used except $NaHSO_3$ were AnalaR.

It will be seen that all results are high, suggesting a contaminated cathode deposit. Also, there is residual cobalt in each case, even when electrolysis has been carried out for two hours.

<u>Experiment 2:</u> An attempt was made to quantitatively deposit cobalt from the bicarbonate-hydrogen peroxide complex. 10 gm. A.R. sodium bicarbonate and 10 ml. 30% A.R. H_2O_2 were added to the cobaltous solution. When the effervescence had ceased the sides of the beaker were washed down with distilled water and the solution electrolysed at room temperature in the manner described above.

Results

No.	COBALT TAKEN mg.	TIME ELECTRO-LYSED mins	CURRENT DENSITY.	CHANGE IN WEIGHT ANODE mg.	RESIDUAL COBALT (NRS) mg.	TOTAL COBALT FOUND mg.	RELATIVE ERROR. %
1.	98.7	120	1.5A 3.5V	0	0.4	100.3	+1.6
2.	96.2	65	2.0A 4.5V	+0.2	0.1	97.8	+1.6
3.	96.2	60	2.0A 4.5V	-0.5	0.5	97.1	+0.9

No. 1 contained $CoSO_4$ solution.

Nos. 2 and 3 contained $CoCl_2$ solution.

In each case the phosphate method was used to standardise. Again each result is high. A blank test was again made to ensure that under the conditions, there was no interference with the Nitroso-R-salt method used to analyse the spent electrolyte.

The anode loss can be seen to be much less under the above conditions; a slight gain in anode weight was found in No. 2.

This set indicates that a contaminated cathode is not entirely due to sulphur. Nos. 2 and 3 contain no sulphur, but results are still high indicating a contaminated deposit. Hitherto it has been assumed that the contamination is due to sulphur or carbon; a recent procedure(22) recommends dissolving up the deposit, estimating the sulphur as $BaSO_4$, and applying the relevant correction.

In order to determine what would happen in the absence of both sulphur and carbon, a standard cobalt chloride solution was electrolysed in the presence of NH_4Cl, NH_4OH, and a little hydrazine hydrochloride. The result was 0.7% high; in this case the contamination must have been due to something other than sulphur or carbon.

<u>Experiment 3:</u> The evidence suggesting that the cobalt deposit is contaminated, is indirect. A typical electrolytic deposit has been shown to be impure by direct analysis in the following way: 50 ml. of a cobalt solution was analysed using the phosphate method with nitric acid instead of the sulphuric, (because the subsequent cobalt deposit was dissolved up in nitric acid, and NO_3^- affects the phosphate

analysis giving low results). Another 50 ml. portion was electrolysed in the presence of $(NH_4)_2SO_4$, NH_4OH and Hydrazine sulphate. The weighed deposit was dissolved up in nitric acid, and the solution analysed using the phosphate method.

The quantity of nitric acid used in dissolving the deposit was similar to that used in the first analysis.

Result;

Cobalt content of 50 ml. solution by
phosphate method using nitric acid..........98.7 mg.
Weight deposit..............................100.1 mg.
Residual cobalt in spent electrolyte......... 0.3 mg.
$\therefore$ Deposit should contain 98.7 - 0.3 = 98.4 mg. cobalt
Cobalt actually found in deposit............ 98.6 mg.

This confirms that the deposit contained about 1.6% impurity, i.e. that it was about 98.4% cobalt.

A C.I.O.S. report (143) claims that 99.8-99.9% pure cobalt was obtained by electrolysing a solution of cobalt carbonate in formic acid at room temperature and at pH 5.8-6.0. Attempts to carry this out were unsuccessful.

In all the above work the cathode deposit was weighed after drying at 100°. The effect of drying at a higher temperature was investigated. No change in weight was found on drying at temperatures up to 140°.

Some procedures in the literature recommend continuing the electolysis until a spot test using Nitroso-R-salt shows absence of cobalt. A few drops of the electolyte are withdrawn and several drops of 50% sodium acetate solution are added followed by a little nitric acid and several drops of 0.5% Nitroso-R-salt solution. A red colouration indicates the presence of cobalt.

This test was carried out on solutions containing known amounts of cobalt. The results are given below:-

Strength cobalt solution	Colour produced.
1 mg. Co/125 ml.	Definite reddish colouration
0.5 " " " "	Very slight orange-yellow.
0.25" " " "	No difference detected between these and a blank.
0.1 " " " "	

The volume containing the various quantities of cobalt (125 ml.) is the normal volume used in analysis by the electrolytic method.

The result indicates that small amounts of cobalt may remain in solution even when this method indicated that all the cobalt has been deposited.

8. The Anthranilate Method.

Preparation of reagent:

Batches of 5-8 gm. B.D.H. Anthranilic acid were re-crystallised three times from boiling water, using animal charcoal. The product was filtered off and dried in a vacuum desiccator over P_2O_5. It was very faintly yellowish with m.pt.144°. It was stored in a dark bottle.

3% sodium anthranilate solution was prepared in the following way. Slightly less than 7.5 gm. of anthranilic acid was shaken up with 55 ml. N. NaOH diluted to 100 ml. with distilled water. One drop of phenolphthalein was added, and the solution made slightly acid by adding a saturated aqueous solution of anthranilic acid.

The total volume was made up to 250 ml. with distilled water. The reagent was stored in a dark bottle in a cool place; for washing the precipitate, a 0.15% solution of sodium anthranilate solution was made by dilution, and stored in the same manner.

$[Co(NH_3)_5Cl]Cl_2$ was used as primary standard for all work on the anthranilate method.

Procedure:-

The volume of the cobalt solution was adjusted to 200 ml. Normal sodium carbonate solution was added until a slight cloudiness appeared. This was just cleared by the addition of 1:200 HCl. The solution was heated on a hot plate until it gently boiled. While being heated, it was kept just clear by the dropwise addition of the 1:200 HCl.

The required excess of 3% sodium anthranilate solution was added slowly from a burette while stirring the solution. After 5 minutes of very gentle boiling, the beaker was removed from the hot plate and left to stand for about an hour. The precipitate was filtered off (X4 sintered glass filter), and washed with cold 0.15% sodium anthranilate followed by 5 ml. alcohol. After drying for one hour at 115° the precipitate was cooled and weighed.

Previous examination of filtrates from the anthranilate method had shown small amounts of cobalt to be present. Therefore all filtrates and washings were made up to 500 ml. as in the phosphate method, and analysed for cobalt using the Nitroso-R-salt method. As the pH values of the filtrates was approximately 7.0, no adjustment with acid was necessary before adding the 50% sodium acetate solution.

Generally 25 ml. of the made-up filtrate was analysed.

Notes.

(a) Sodium anthranilate solution is affected by sunlight, turning brown. Therefore, filtrates were analysed as soon as possible, or if this was not possible, they were stored overnight in a dark place.

(b) Nitroso-R-salt analysis of a blank solution containing a similar quantity of sodium anthranilate as that used in the cobalt analysis (including the wash solution) gave no reading on the Spekker.

(c) the pH values of all filtrates lay between 6.7 and 7.0.

Results. Some representative results are given in the following table:-

Series 1.

COBALT TAKEN mg.	EXCESS OF 3% SODIUM ANTHRANILATE USED %	COBALT FOUND AS ANTHRANILATE mg.	FILTRATE COBALT (NRS) mg.	TOTAL COBALT FOUND mg.	ERROR. mg.
120.3	10	120.6	0.1	120.7	+0.4
"	15	120.5	0.2	120.7	+0.4
"	20	120.2	0.5	120.7	+0.4
"	30	120.3	0.2	120.5	+0.2
"	30	120.3	0.2	120.5	+0.2
"	30	120.5	0.1	120.6	+0.3
"	30	120.5	0.1	120.6	+0.3
Mean error = +0.31 mg. ≡ +0.26%					

In carrying out the above procedure a drawback was encountered, which previous workers do not appear to have mentioned. The precipitate is very light, and even on the most gentle boiling, splashing occurs. This results in particles of the precipitate being deposited on the walls of the beaker and even on the underside of the covering watch glass. Much care is required to remove this quantitatively into the filter without loss. When the degree of heating was slightly misjudged in some earlier experiments, lower results were obtained, presumably due to loss in this way.

The precipitate itself was found to be easy to wash.

In an attempt to overcome the above difficulty, a series of experiments was made to find out whether heating on a water bath could replace the five minutes' boiling. The results are shown in the following table:-

Results

Series II.

COBALT TAKEN mg.	EXCESS OF 3% SODIUM ANTHRANILATE USED %	TIME HEATED ON BATH mins.	COBALT FOUND AS ANTHRANILATE mg.	FILTRATE COBALT (NRS) mg.	TOTAL COBALT FOUND mg.	ERROR. mg.
120.3	10	30	119.0	2.1	121.1	+0.8
"	15	"	120.1	1.1	121.2	+0.9
"	20	"	120.5	0.5	121.0	+0.7
"	30	"	120.5	0.3	120.8	+0.5
"	30	45	120.8	0.2	121.0	+0.7
"	40	"	121.2	0	121.2	+0.9
"	30	"	121.0	0.1	121.1	+0.8
Mean error = +0.76 mg. ≡ +0.63%						

Under these conditions the total cobalt found is higher and the relative error greater.

In his determination of the pH range for complete precipitation of cobalt, Goto(44) used an acetate buffer.

He did not detect the increased solubility of the precipitate in the presence of sodium acetate, which Shennan, Smith and Ward(46) found in later work. These investigators concluded that the range of separations which could be affected was very limited.

Owing to the ease with which the filtrate cobalt may be determined using the Nitroso-R-salt method, some cobalt analyses were made in acetate and tartrate buffers. Heating was carried out on a hot plate as in Series I.

COBALT TAKEN mg.	EXCESS OF 3% SOD. ANTH. USED. %	BUFFER PRESENT	COBALT AS ANTHRANILATE mg.	FILTRATE COBALT mg.	TOTAL COBALT mg.	ERROR mg.
120.3	30	3 gm. sod. acetate	118.4	0.2	118.6	-1.7
"	30	" " "	118.4	0.3	118.7	-1.6
"	30	3 gm. sod. tartrate	113.0	6.4	119.4	-0.9

It will be seen that in the presence of acetate ions, the filtrate cobalt is the normal amount, but the total cobalt is low. In contrast, the presence of tartrate ions leads to an abnormally high filtrate cobalt but a lower negative error for total cobalt. The method, therefore, cannot be used in the presence of these ions.

In view of the fact that the nitrate ion interferes with many methods of cobalt analysis, the anthranilate method was carried out in the presence of 1 gm. KNO_3. The filtrate cobalt was normal and the total cobalt unaffected, showing no interference.

9. The Carbonato-Complex Method.

When hydrogen peroxide is added to a cobaltous solution containing an excess of sodium or potassium bicarbonate, a green soluble complex is formed in which the cobalt is trivalent. A green solid isolated from the solution has been called cobalt (III) triscarbonatocobaltiate, $Co[Co(CO_3)_3]$.

H_2O_2 is oxidised by Co(III), but as the former is also an oxidising agent, a cycle of reactions is possible involving the reduced oxidant. In such circumstances, self-oxidation-reduction of the H_2O_2 is induced i.e. catalytic decomposition.

Analytical procedures have been proposed based on the initial formation of the complex. They have been described on p. 40 et seq. As a preliminary to quantitative reduction of the complex, it is important that all excess H_2O_2 is decomposed. In view of the instability of the complex itself, especially on heating or in the presence of insufficient bicarbonate, much care is needed.

Previous work in this laboratory(144) on the catalytic decomposition of H_2O_2 by the complex indicated that it took place within a short time even at room temperature. For example, it was found that 1 millimole of the complex in 250 ml. $\frac{N}{10}$ H_2O_2 destroys 99.4% of the peroxide in 7 minutes.

i) The iodometric procedure.

In 1951, Laitinen and Burdett(93) described an iodometric procedure for estimating cobalt based on the initial formation of the complex. High accuracy was claimed. Their method has been carefully examined using $[Co(NH_3)_5Cl]Cl_2$ as the primary standard.

(a) Standard sodium thiosulphate: An approximately decinormal solution of A.R. sodium thiosulphate was standardised in the following way:-

(1) a decinormal solution was made from A.R. KIO_3 which had been dried at 130° for two hours. To 25 ml. of this solution, 10 ml. N. HCl was added and 2gm. KI (iodate-free). The thiosulphate solution was run in until pale yellow, when 2 ml. starch solution was added. The titration was continued until the solution was colourless.

(2) A.R. potassium dichromate was twice recrystallised from water, ground up, and dried at 180° for one hour. A decinormal solution was made up. 25 ml. of this was diluted to 40 ml., and 2 gm KI (iodate-free) was added, followed by 8 ml. conc. HCl. The thiosulphate solution was added until the colour changed to yellowish-green, 2 ml. starch solution was added, and the titration continued until the colour changed sharply from blue to light green.

The values for the strength of the thiosulphate solution agreed within 0.1%.

Method: A.R. materials were used throughout.

To 25 ml. of the cobaltous solution, 5 gm. sodium bicarbonate was added, followed by 5 ml. 30% H_2O_2. When the effervescence had more or less subsided, the flask walls were washed down to return any cobalt or peroxide solution ejected as spray. After heating gently * with the occasional addition of 0.5 gm. portions of sodium bicarbonate, the solution was cooled, diluted to 100 ml., and 5 gm. KI added. Then 1:1 HCl was carefully added dropwise while swirling the solution, until it was neutralized, and 10 ml. added in excess. The liberated iodine was titrated with the standard thiosulphate.

*(They did not specify the temperature. In the present work the complex was heated to between 35°-40°.)

Results: The following is a typical set of results:-

Cobalt taken 100.3 mg.
Cobalt found (1) 100.7 mg.
(2) 100.3 "
(3) 100.9 "
(4) 103.0 "
(5) 100.8 "
(6) 101.0 "
(7) 100.2 mg.
(8) 100.1 "
(9) 100.9 "
(10) 99.7 "
(11) 100.5 "

Both the precision and the accuracy are poor. Experiment (4) has a relative error of +2.7%.

The exact end-point was difficult to detect, the colour change being from dark blue, through dark brown and light brown to pink. It was found that the change from light brown to pink could be brought about by prolonged shaking, and without further addition of thiosulphate. Both starch and sodium starch glycollate produced the same sluggish end-point.

Other analyses carried out using different amounts of cobalt gave similar results.

Another bad feature of the method, and probably a source of error, is the neutralisation of the bicarbonate, during which the iodine is liberated. Apart from possible loss of free iodine, there is danger of localised destruction of the complex by the acid without corresponding liberation of iodine.

The iodometric procedure was finally rejected, and an attempt made to use alternative reductants.

If an acidified standard ferrous solution were added to the complex, and a back titration with standard dichromate envisaged, the following difficulties would be encountered:-

(1) if the ferrous solution were added before the acid, or in the presence of too little acid, the ferrous iron would be spontaneously oxidised in the alkaline solution. High results would be obtained.

(2) if the ferrous solution were too acid, the complex would be broken down before all the standard ferrous solution were added, owing to the instability of the cobaltic ion in acid solution.

The first of these difficulties was encountered in the perborate method (96-97) and elaborate precautions were taken in order to add the standard ferrous solution without air being introduced.

(ii) Direct titration of standard ferrous iron with the carbonato-complex.

Attempts to titrate a standard ferrous iron solution with the carbonato-complex immediately gave encouraging results.

(a) Standard potassium dichromate solution: This was used as a primary standard for standardising the ferrous solution. Batches of A.R. potassium dichromate were powdered and dried at 180° for one hour, and $\frac{N}{20}$ solutions made up.

(b) Standard ferrous solution: This was made using A.R. $FeSO_4.7H_2O$ and was approximately $\frac{N}{10}$. It was 0.7 N in H_2SO_4.

(c) Standardisation of ferrous solution: 25 ml. of the ferrous solution was diluted to 50 ml. with distilled water and 8 ml. 20% A.R. H_2SO_4 added to make the solution approximately normal in acid.

5 ml. A.R. phosphoric acid was added and the dichromate solution was run in, swirling the solution, until within 5 ml. of the end-point. Three drops of 0.2% sodium diphenylamine sulphonate were added, and the titration continued, with continual swirling, to a faint violet colouration. The end-point was found to be extremely sensitive; successive titres generally agreed to within 0.02 ml.

Results using re-crystallised A.R. potassium dichromate did not differ from those using the ordinary A.R. material.

<u>Method:</u> To the cobalt solution in a 500 ml. volumetric flask, a warmed solution of A.R. $KHCO_3$ containing 10 gm. of the salt was added, followed immediately by 5 ml. 30% A.R. H_2O_2. The spray was washed down from time to time. After half an hour, a further 20 gm. $KHCO_3$ was added, and the total volume made up to 500 ml. It was gently mixed, the stopper carefully released, and the complex poured into a burette.

25 ml. of the standard ferrous solution was diluted to about 60 ml., adjusted to approximately 1 N using 20% A.R. sulphuric acid, and 5 ml. A.R. phosphoric acid added. The complex was run in with constant swirling of the ferrous solution, until three drops of 0.2% sodium diphenylamine sulphonate added just before the end-point produced a colour change from pink to mauve. This was sharp and easily detected.

Results:

Cobalt taken:- 241.0 mg.
Cobalt found:- 241.2 mg. (+0.1%)
240.9 mg. (<0.1%)
240.7 mg. (-0.1%)
241.5 mg. (+0.2%)

Although giving very good results, the method in this particular form was unsatisfactory. In the above series the titres were about 72 mls., even for the large amount of cobalt present. Were the original cobalt solution weaker, an even larger titre would have resulted.

Therefore an indirect procedure was attempted whereby the whole of the complex was run into an excess of standard ferrous solution, and a back titration with standard dichromate made after adjusting the acidity and with phosphoric acid present. The ferrous solution was standardised as in the previous series.

All results were consistently low.

At this stage, the strengths of both the complex and the ferrous solution were varied in turn, in an attempt to improve the results. For example, the complex was diluted before the addition, so that the concentration of Co^{+++} would be less to minimise the loss of free oxygen by interaction with water. (This was thought to be a possible cause of the low results.)

A check on the ferrous-dichromate titration with 30 gm. $KHCO_3$ present indicated no interference due to this.

Further work showed that the rate of adding the complex must be very slow for the oxidation to take place quantitatively. When this and other precautions were taken, consistently accurate results were obtained.

(iii) Final Method Adopted.

Previous work in this laboratory on the catalytic decomposition of H_2O_2 by the cobaltic ion (loc.cit.) had indicated that the rate diminished with increase in concentration of bicarbonate. In the earlier work on the method, 10 gm. $KHCO_3$ was added initially; subsequently it was found that 5 gm. was sufficient to prevent decomposition of the complex, even when heated to 40^o or more, and this quantity was therefore used.

In order to increase the stability of the complex on dilution or transfer from one vessel to another, an additional quantity, usually 10 gm., was added just before these operations. Also, a 1:10 $KHCO_3$ solution was used for washing down any spray, making up to the required volume, and in transferring to complex, to prevent decomposition by localised dilution of the bicarbonate.

The analytical method finally adopted is the following. All materials used were A.R.

Method: To the cobalt solution in not more than 25 ml., add 5 gm $KHCO_3$ as a saturated solution (about 20 ml.), followed immediately by 5 ml. 30% H_2O_2. When the effervescence has subsided, wash down the spray with 1:10 $KHCO_3$ solution, heat the complex to 40^o for 10 minutes, and then stand for 20 minutes, occasionally washing down any spray.

Add an additional 5 gm. $KHCO_3$ as a saturated solution, and make up the total volume to about 100 ml. with 1:10 bicarbonate solution.

Cool the complex, and using a funnel with a drawn-out stem, run it very slowly into excess of a standard ferrous solution in a conical flask, and containing at least sufficient H_2SO_4 to neutralise all the bicarbonate. During the whole time, gently swirl the flask containing the ferrous solution, to ensure complete mixing.

Adjust the acidity to 1 N with 20% H_2SO_4, add 5 ml. phosphoric acid, and back titrate the ferrous solution with standard dichromate, adding three drops of 0.2% sodium diphenylamine sulphonate just before the end-point, which is indicated by a colour change from pink to mauve.

Results: In the following series all except Nos. 7 and 8 were carried out using $[Co(NH_3)_5Cl]Cl_2$ as primary standard. Nos. 7 and 8 were carried out on a stock solution standardised by the phosphate method.

No.	Co taken mg.	Co found mg.	Relative error %
1.	51.80	51.85	+0.1
2.	"	51.69	-0.2
3.	129.7	129.6	-0.1
4.	"	129.6	-0.1
5.	"	129.8	+0.1
6.	"	129.6	-0.1
7.	120.5	120.3	-0.2
8.	241.0	240.5	+0.2

<u>Notes</u> (1) In some analyses, the complex was transferred to a 250 ml. volumetric flask, made up to the mark, and after gently mixing, aliquot portions were run into excess standard ferrous solution. The back titration was carried out as in the above. 1:10 $KHCO_3$ solution was used in transferring to the volumetric flask and for diluting to the mark.

The results were of the same accuracy as the above set.

(2) It was found convenient in practice to allow the slow addition of the complex to the ferrous solution to proceed as the latter was being gently agitated by a mechanical shaker.

10. Other Methods.

The α nitroso β naphthol, ferricyanide, cyanide, E.D.T.A., and perborate - $SnCl_2$ methods have been investigated to varying degrees. As they were not found capable of giving a high degree of accuracy, they will only be reported briefly.

(1) The α nitroso β naphthol method

In view of its extensive use, and in order to compare it with other methods, the α nitroso β naphthol method was tried out.

(a) Reagent: B.D.H. α nitroso β naphthol was recrystallised twice from ligroin. 2 gm. of the purified material was shaken with 100 ml. A.R. glacial acetic acid, and 100 ml. of hot distilled water added. The solution was filtered and used immediately.

Method: All materials used were A.R.

A cobalt solution containing 5 ml. conc. HCl and in a total volume of 150 ml. was heated to about 80° and 200 ml. of the above reagent added. The solution was boiled for 5 minutes, and then left to stand for 2-3 hours.

The precipitate was filtered through No. 42 papers (it was found necessary to employ two filter papers as the precipitate was so bulky), washed with hot (80°) 1:2 HCl, and then washed free of acid with hot water. The filter papers were transferred to a crucible and dried for one hour at

100°-110°. They were just covered with oxalic acid, and ignited gently until the organic matter had burned off, then after cooling and moistening with a few drops of nitric acid, the residue was ignited at 800° for one hour.

After cooling and weighing, the cobalt was calculated on the basis of the oxide being Co_3O_4.

A Rose attachment was fitted to the crucible and the oxide heated in a stream of hydrogen for 45 minutes. The metallic cobalt was allowed to cool almost to room temperature with the hydrogen still passing, and after a further period of cooling, it was weighed.

Results:

No.	Cobalt taken mg.	Co found as Co_3O_4mg.	Cobalt found as metal, mg.
1.	48.15	48.29 (+0.3%)	48.00 (-0.3%)
2.	48.15	49.03 (+1.8%)	48.47 (+0.6%)
3.	24.08	——	24.13 (+0.2%)
4.	"	——	24.17 (+0.4%)
5.	"	24.10 (+0.1%)	24.18 (+0.4%)
6.	"	24.31 (+1.0%)	24.22 (+0.6%)

In Nos. 5 and 6 ordinary grade αnitrosoβ naphthol was used, without further purification.

The method was found to be unsuitable for the estimation of macro amounts of cobalt. The procedure was difficult to carry out, especially washing the precipitate.

Even when only 24 mg. of cobalt was present, the precipitate was too bulky for comfortable handling.

(2) The ferricyanide method.

Preliminary titrations of an approximately decinormal potassium ferricyanide solution against a decinormal cobalt solution potentiometrically, gave sharp reproducible end-points as the following titres indicate:-

25 ml. potassium ferricyanide took 29.43 ml. cobalt sol'n.
29.40 " " "
29.43 " " "

The potential curves were not plotted; instead, the cobalt solution was added 0.1 ml. at a time near the end-point, and the exact volume calculated from the change in potential per unit volume.(42)

In view of the doubts expressed by Bagshaw and Hobson(53) as to whether the 'kick' coincided with the equivalence point, standard potassium ferricyanide and cobalt solutions were titrated in order to compare the theoretical and experimental titres.

(a) Standard potassium ferricyanide. A.R. potassium ferricyanide was twice re-crystallised from water and dried at 80°. 32.9005 gm. was dissolved in water and made up to 1L.

(b) Standard Cobalt solution. This was prepared from $\left[Co(NH_3)_5Cl\right]Cl_2$ in the usual way. It was 0.033784 N.

(c) Potentiometer. A Pye potentiometer was used.

(d) Electrodes. A saturated calomel dip type electrode as supplied with the Cambridge pH meter, and a platinum electrode were used.

Procedure: 25 ml. of the ferricyanide solution was diluted with 100 ml. of 5 N ammonia containing 5 gm. citric acid. The electrodes were inserted and the solution covered with about 25 ml. of light petroleum. (This serves to exclude air, shield the operator from the strongly ammoniacal vapour, and minimise the formation of encrustation on the burette tip.) The cobalt solution was slowly added. When within 1.0 ml. of the end-point, it was run in 0.1 ml. at a time, and the change in potential for each addition noted. In practice, the end-point almost coincided with the reversal of polarity.

The actual volume was determined by the method given above.

Results: Volume of cobalt solution theoretically required for 25 ml. ferricyanide solution.....74.06 ml.

No.	cobalt solution titre ml.	Relative error %
1.	73.82	-0.29
2.	73.60	-0.61
3.	74.14	+0.11
4.	73.73	-0.44
5.	73.62	-0.59
6.	73.90	-0.21

All titres except No 3 are low indicating that the maximum value of $\frac{dE}{dV}$ does not coincide with the equivalence point. Further the precision is not very good. No further work was done on this method.

(3) The Cyanide Method.

The method, developed by Evans$^{(83)}$ was assessed using $[Co(NH_3)_5Cl]Cl_2$ as primary standard. Evans did not specify the standard he used.

Reagents:

Potassium cyanide - 4.8 gm. A.R. KCN made up to 1L and containing 3 gm. A.R. NaOH.

Silver Nitrate - 5.792 gm. A.R. $AgNO_3$ made up to 1L.

All other reagents used were A.R.

Procedure: To the cobalt solution in 100 ml. volume, 20 ml. saturated borax solution and 10 ml. 4% KI solution were added. The cyanide solution was run in from a burette until the solution was only slightly turbid; if V ml. had been added at this stage, more cyanide solution was run in to make the total volume (1.3v + 5) ml.

10 ml. 10% Na_2CO_3 solution was added, and a rapid stream of air passed through the solution for 6 minutes exactly, after which 10 ml. 1:1 ammonia and 25 ml. 20% NH_4Cl solution were added. Any leakage from the cyanide burette was also washed in from a small beaker kept under it

for this purpose.

The $AgNO_3$ solution was then added until a permanent turbidity appeared, whereupon just sufficient of the cyanide solution was added to clear. The volumes of KCN and $AgNO_3$ solutions used were noted.

Both burettes were re-filled. A volume of cyanide solution 0.5 ml. less than previously used, was run into the solution. This was again titrated with $AgNO_3$ solution to a turbidity and back to clear again with cyanide until a volume of cyanide equal to that in the first titration was used.

1 ml. $AgNO_3$ solution ≡ 0.8037 mg. cobalt.

Results: One set of six results will be given. They reflect the general pattern of other results using the method.

Cobalt taken......44.34 mg.

Cobalt found......44.65 mg. (+0.6%)
44.36 " (-)
44.68 " (+0.7%)
44.38 " (+0.1%)
44.47 " (+0.3%)
44.78 " (+0.9%)

Maximum relative error = +0.9%

(4) The E.D.T.A. Method.

In order to judge the end-point of Harris and Sweet's method(107) cobalt solutions containing 20, 30, 40 and 50 mg. of cobalt were prepared. Excess of disodium ethylene diamine tetra-acetic acid solution was added, the pH adjusted to 10 with 1:1 ammonia, and sufficient 0.2% Eriochrome Black T indicator to impart a distinct blue colour.

An approximately decinormal zinc sulphate solution was added until the indicator turned red. The change in colour was not sharp for 20 and 30 mg. cobalt present, and became pregressively worse as the cobalt content increased.

It was concluded that the method was incapable of accurate results for macro quantities of cobalt.

(5) The perborate-stannous chloride method.

Willard and Hall's results with stannous chloride(17) and the recent revival of interest in this reagent, encouraged an attempt to develop a method based on sodium perborate oxidation of cobalt to $Co(OH)_3$, followed by reduction with excess standard stannous chloride solution and back titration with potassium dichromate potentiometrically.

Reagents:

Stannous chloride solution: To 80 ml. conc. HCl in a 1L storage bottle connected directly to a burette, several pieces of marble were added to expel oxygen. 12 gm. of crystalline A.R. stannous chloride was added, and when dissolved, the volume made up to 1L.

A carbon dioxide atmosphere was maintained over the solution even when in the burette.

Sodium perborate: To 31 gm. A.R. boric acid dissolved in 250 ml. water, 43 gm. Na_2O_2 was added with stirring, in small portions, the temperature not being allowed to exceed 30^o (ice). By the following day, 20 gm. of crystalline sodium perborate separated out. It was filtered off, washed with a little cold water, and dried.

Standardisation of stannous chloride solution: The tip of the stannous chloride burette was bent sideways and downwards into the centre opening of a three-necked round-bottomed flask. A stirrer was also arranged down through the same opening. One of the other openings supported a saturated calomel electrode; the third a platinum electrode. The usual potentiometer circuit was used. Standard decinormal potassium dichromate was introduced into the flask followed by 8 ml. conc. HCl and a few fragments of marble to displace the air. The stannous chloride solution was run in, and the end-point determined by the procedure described in the ferricyanide method.

Conscutive titres were in good agreement.

Method: The cobalt solution was introduced into the three-necked flask, followed by 1gm. sodium perborate and 3gm. A.R.

NaOH. The mixture was boiled gently for 10-15 minutes to decompose the excess perborate. On cooling, a stream of carbon dioxide was passed through the solution containing $Co(OH)_3$. A few fragments of marble were added, and then the acid stannous chloride solution (with stirring) until all the cobaltic hydroxide had dissolved. (This occurred rapidly when sufficient $SnCl_2$ was present.)

Excess of the standard potassium dichromate solution was then added, and a back titration made with the stannous chloride solution.

Care was taken that sufficient marble was present to ensure the CO_2 atmosphere required when using the stannous chloride.

The volume of standard $SnCl_2$ solution used in reducing the $Co(OH)_3$ was determined, and from it the cobalt present.

<u>Results</u>: All results were low, the best being

Cobalt taken.....98.6 mg.

Cobalt found.....96.8 mg (-1.8%)

C. DISCUSSION OF RESULTS.

Primary Standards.

The assumption that $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $K_3Co(CN)_6$ prepared by the methods described, contain the theoretical quantities of cobalt is supported by the following. In the first place, successive batches of each gave very similar results when analysed by the standard methods, and very close agreement with one another. The possibility of all three containing more, or less cobalt than theoretical, to exactly the same extent, is very small. Again, they contain no water of crystallisation, so that there is no uncertainty in this respect.

If the complex selected as standard has to be prepared and purified, $[Co(NH_3)_5Cl]Cl_2$ is probably the best of the three. The method used to decompose it is very satisfactory and can be recommended.

The cobalt sponge is quite unsuitable as a primary standard, and its description as 99.99% cobalt is misleading. It would be more accurate to state that of the elements examined for spectrographically, the total was estimated to be less than 0.01%. The low results obtained from the use of this sponge are consistent with the possibility that it contains unreduced oxide. From the results, sponge I would have contained 99.86% cobalt, and sponge II 99.39% cobalt.

The cobalt wire examined was evidently a very pure specimen. The wire is manufactured from cobalt sponge, the purity of which has been shown to vary, so that it is possible that a particular wire made from a sponge containing more oxide than usual, might also be contaminated with oxide.

Co (II) sulphate and $CoSO_4.K_2SO_4.6H_2O$ as primary standards are clearly unsuitable. The same applies to electrolytic cobalt prepared by the usual methods.

The present work does not suggest that only the complexes mentioned would be suitable as primary standards. It is probable that many other cobalt compounds would give similar results to the complexes examined, for example carbonatotetrammine cobaltic nitrate which was used by Laitinen and Burdett. (loc. cit.)

However, it does appear that far too little attention has been given to primary standards in cobalt analysis; it is desirable that all authors should state clearly the standard used, or the methods used to standardise stock solutions. In the latter case, details of the methods would not be superfluous; use of the phosphate method under conditions which produce interference has already been mentioned.

The electrolytic method, and electrolytic cobalt as primary standard, without doubt, have caused errors. The present results indicate that if a typical electrolytic procedure is used in standardising a stock solution (with the estimation of residual cobalt in the spent electrolyte), the results can be 1.6% high. Such a deposit would only contain 98.4% cobalt.

Methods.

Electolytic: All modern forms of the electrolytic method for cobalt estimation recommend the inclusion of a reductant during the electrolysis. The present work shows that both in the presence and the absence of a reducing agent the results, using $\left[Co(NH_3)_5Cl\right]Cl_2$ as primary standard, are invariably high. The problem raised due to the last traces of cobalt not being deposited on the cathode is the least difficult to overcome; the Nitroso-R-salt method is both rapid and accurate for this purpose. There seems little prospect of improving the method in its present form, and no doubt, any accurate results claimed were due to compensation of errors. In this respect, there is the possibility of the high results being masked by the neglect of residual cobalt in the spent electrolyte. Not all the electrolytic procedures recommended have been examined. For example, very slow electrolysis over a long period (12 hours) has been suggested; this was not attempted in the present work.

As to the nature of the contaminants in the deposit, sulphur is almost certainly a contributary cause; in the absence of sulphur the positive error is less, and Kallman(22), assuming all the contamination to be sulphur, described a procedure for its estimation as $BaSO_4$, in a solution of the deposit after electrolytic analysis. The present work shows that 0.7% contamination is possible when both sulphur and carbon are absent. In the circumstances, it is difficult to avoid the conclusion that the cobalt is contaminated with oxide. In their recent study of the equilibrium-pH diagram for cobalt, Deltombe and Pourbaix(28) show how in the absence of complexing substances, a cobalt deposit contaminated with oxide is possible above pH 6.3. Until a knowledge of the system $Co-NH_3-H_2O$ is available, it will not be possible to discuss this possibility profitably, for the analytical conditions used.

An important point in connection with the above is that the values reported for the electrode potential of cobalt vary quite considerably. Like the nickel electrode, it appears to be impossible to obtain a satisfactory reversible cobalt - cobaltous potential. However, the varying degrees of impurity of the cobalt electrodes used, was probably a contributary factor in producing the divergent results. Haring and Westfall(145) in measuring the potential of the cell $Co \mid CoSO_4 \mid Hg_2SO_4 \mid Hg$ used an electrodeposited cobalt electrode which had been prepared from a typical plating solution. They found that the potential varied according to the procedure used in depositing the cobalt.

Anthranilate Method: The anthranilate method is difficult to carry out on account of the precipitate splashing. The results are invariably slightly high, probably due to contamination by the reagent itself; if heating is carried out on a water bath, the error is more than twice as much, making this procedure inadmissible.

If the filtrate cobalt is neglected, the results are very good. (For Series I the relative error would be +0.09%). It is doubtful whether the use of a factor would be justified in view of the small error involved and the more accurate results possible using the phosphate or carbonato-complex methods. Such a factor would, in any case, have to be based on the total cobalt, including the filtrate. Its value would be 0.997 from the results of Series I.

The estimations made in the presence of sodium acetate and sodium tartrate indicate that the behaviour is not simply a question of solubility of the precipitate. The total cobalt in each case is very low, so that estimation in the presence of these ions is not possible, even when accompanied by filtrate analysis.

On the whole the method is not satisfactory. Its only advantage appears to be the non-interference by the nitrate ion, this not being so in the phosphate method.

Phosphate Method: In the phosphate method, it is clear that variation in procedure can lead to different results, and this must be due to the various precipitates having different compositions. If this is considered in conjunction with errors due to faulty primary standards and neglect of filtrate cobalt, it is not difficult to realise why the method has not found acceptance previously. Both Dick(71) and Kraus(72) precipitated the cobalt by methods similar to the one which produces high results in the present work, and both neglect filtrate cobalt, so that compensation of errors probably took place. In all the phosphate analyses carried out, no filtrate was found with complete absence of cobalt. Usually, the amounts found were substantial, as the results show.

On the dependence of total cobalt on pH, there is much disparity between Matsuo's results (Fig. 4) and the present work using his procedure (Fig. 7). For example, at pH 8, his result for a 1:50 $Co^{++}:NH_4^+$ molar ratio is 0.4% low, whereas the present work, under similar conditions, indicates the total cobalt to be 1.4% high. It is possible that he used a poor primary standard in his work, although a difference of 1.8% is a great deal to be attributed to this.

Volumetric procedures based on initial precipitation as cobalt ammonium phosphate, followed by filtration and titration of the precipitate with standard acid e.g. Sutton(69), cannot account for all the cobalt in view of the loss of filtrate cobalt.

The contamination of the cobalt ammonium phosphate is relatively small, so that identification of the substance or substances causing it would be difficult. It is possible however, as has been done in the magnesium ammonium phosphate method, to investigate theoretically the possible contaminants. The substances precipitated will depend on the solubility products of the various possible compounds, and the concentrations of PO_4^{---}, HPO_4^{--}, $H_2PO_4^-$ and NH_4^+ in a particular solution. The proportions of total phosphoric acid and total ammonium in various forms at different pH values is shown in Fig. 9.

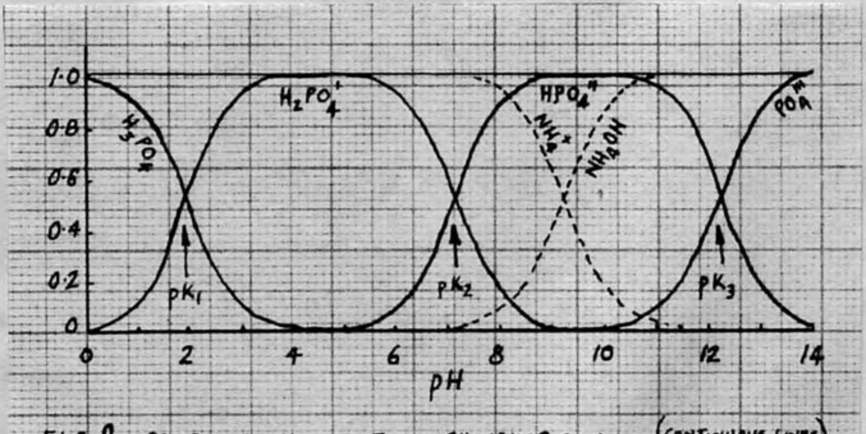

FIG. 9. PROPORTIONS OF TOTAL PHOSPHORIC ACID (CONTINUOUS LINES) AND TOTAL AMMONIUM (BROKEN LINES) IN VARIOUS FORMS.

Some possible contaminants are:-

$Co_3(PO_4)_2$

$CoHPO_4$

$CoNH_4PO_4 \cdot (NH_4)H_2PO_4 \cdot 4H_2O$

Basic cobalt phosphates.

H_3PO_4

$NH_4H_2PO_4$

$(NH_4)_2HPO_4$

$(NH_4)_2SO_4$

When other substances are present, e.g. sodium acetate, ammonium chloride, the number of possible contaminants is further increased.

For each possible contaminant, one can predict the probable direction of error due to its presence. For the final product to be $Co_2P_2O_7$, it is not essential that the violet precipitate at the point of filtration consists of $CoNH_4PO_4.H_2O$ only. For example, $CoHPO_4$ as contaminant, would revert to $Co_2P_2O_7$ after ignition at 730°. The probable direction of error will depend on the ignition product, and will not necessarily be the same after drying at 100° as after ignition at 730°.

The effect of pH on the contaminants will now be considered. In the phosphate method, which involves the addition of $(NH_4)_2HPO_4$ solution to a neutral cobalt solution (analagous to the zinc method), the final pH is about 6.6, and results are high. One might postulate co-precipitation by $CoNH_4PO_4(NH_4)H_2PO_4.4H_2O$ owing to the high proportion of total phosphoric acid being present in the form $H_2PO_4^-$ at this pH. On ignition at 730°, the products would probably

be $Co_2P_2O_7$ giving no error,
HPO_3 " a ⊕ve error
P_2O_5 " a ⊕ve error

(P_2O_5volatizes only on long continued ignition at 1000° to 1100°).

However if this were the only factor, the positive error would decrease if the analyses were carried out in progressively more alkaline solutions. This is not the case. The experimental results show increase in positive error with increase in pH (Fig. 7). On the other hand, in the final form of the accurate phosphate method in which 1:1 ammonia is added to an acid cobalt solution, the final pH is 9+, and results are lower than in the above method. Again, at this pH the proportion of NH_4^+ ion is less than in more acid solutions. This suggests that high results might be due to contamination by ammonium salts. The fact that as the $NH_4^+:Co^{++}$ molar ratio increases, the results are higher, is probably due to the greater tendency for contamination by ammonium phosphate.

From pH 5 to pH 9, a progressively higher proportion of total phosphoric acid is in the form of the hydrophosphate ion HPO_4^{--}, with the increased possibility of $CoHPO_4$ as contaminant. As mentioned above, the product of ignition at 730° would be $Co_2P_2O_7$ with no resulting error.

The matter is further complicated by the changes in composition between the initial formation of the light blue amorphous precipitate, and the final crystalline cobalt ammonium phosphate. This change is generally characterised by a deep royal blue phase. According to Bassett and Bedwell(146), the following compositional changes occur:-

$$Co_3(PO_4)_2 8H_2O \longrightarrow (CoNH_4PO_4)_2 \longrightarrow (CoNH_4PO_4 . H_2O)_4$$

initial precipitate. Royal blue phase Final violet form.
very unstable

In view of its speculative nature, this aspect of the phosphate method will not be discussed further.

$CoNH_4PO_4 . H_2O$ and water: The thermodynamic solubility product of $MgNH_4PO_4 6H_2O$ has been evaluated by a quantitative treatment of the ionisation - pH curves of phosphoric acid (147-148). The calculations involve a knowledge of the molar solubility of the compound in water, the value of which had been determined(149). Owing to the anomalous behaviour between cobalt ammonium phosphate and water, no value for its molar solubility is possible, and a similar calculation cannot be carried out.

As to what exactly happens between $CoNH_4PO_4H_2O$ and water, there are two possible explanations. In the first case ageing of the precipitate may be involved. If 'Ostwald ripening' is visualised, larger crystals with lower solubility would be expected to grow at the expense of smaller particles with a greater solubility. The progressive decrease in soluble cobalt would therefore be explained. If during an analysis, the precipitate is left overnight, the filtrate cobalt is not affected, so that a similar process does not occur in this case. If ageing of $CoNH_4PO_4 . H_2O$

took place during digestion on the water bath in the analysis, it would probably be very beneficial; the process generally results in a purification of the original precipitate. A second possibility is hydrolysis. It has been previously reported that the carbonate, halides, and normal phosphate of cobalt hydrolyse in water. Of these, the behaviour of $Co_3(PO_4)_2$ with water is interesting, and may be related to that of $CoNH_4PO_4.H_2O$. Hubicki and Grychowski(150) agitated 1 gm. of the normal phosphate with 150 ml. of water and determined the P_2O_5 in solution after various intervals of time. It was found that the P_2O_5 went into solution especially in the first 12 hours, but after 84 hours it ceased to do so. Similar behaviour was found in the normal phosphates of Cu(II), Ni, Pb(II), Ba, Zn, Fe(III), Ca and Al. These workers assumed that hydrolysis took place on the surfaces of these phosphates; the reactions were represented in the following manner:-

$$9\ AlPO_4 + 3H_2O \longrightarrow H_3PO_4 + Al_9(OH)_3(PO_4)_8$$

$$8\ FePO_4 + 3H_2O \longrightarrow H_3PO_4 + Fe_8(OH)_3(PO_4)_7$$

The present results show that the ability of $CoNH_4PO_4.H_2O$ to pass into solution is markedly less in a sample previously agitated with water for a long time. This would be explained by assuming that an insoluble basic phosphate, analogous to those proposed by Hubicki and Grychowski, were formed on the surface of the $CoNH_4PO_4.H_2O$. Such a deposit would almost certainly affect the results if it occurred under analytical conditions. The fact that under analytical conditions, the filtrate cobalt appears to be unaffected on leaving overnight, suggests that the interaction under these conditions is much less, if at all. Further investigation is needed.

From an analytical standpoint, the phosphate method developed gives extremely accurate results (± 0.1%), and its precision is high. If the filtrate cobalt was proportional to the weight of precipitate, the use of a factor might have been possible in order to eliminate the filtrate analysis. This is not the case. However, the method of filtrate analysis is quite rapid, and the 0.2% Nitroso-R-salt solution, if kept in a dark bottle and stored in a dark place, is stable for several months.

Carbonato-complex method: Although not quite as accurate as the phosphate method, the carbonato complex method has an accuracy of about ± 0.2%. The end-point is quite sharp and easy to observe. In their attempt to develop a method based on the initial formation of the carbonato complex, Willard and Hall(17) bubbled CO_2 through the complex to displace dissolved oxygen resulting from the decomposition of the excess peroxide. In the present work, the volume of complex has been kept small, so that possible error due to this is reduced. It is also minimised by the warming of the complex.

The titration of ferrous iron with dichromate in dilute solution is subject to an indicator error. In the present work the strengths of both are above the value for which an error is produced. Any such error, would, in any case be cancelled in the standardisation of the ferrous solution by the dichromate.

The most possible source of error in the present method appears to be the tendency for low results if the complex is added too rapidly to the ferrous solution. If the procedure recommended is used, results are accurate.

Other methods: As for the other methods,examined, none was found capable of accurate results. This does not mean that they are of no use. The ferricyanide method, for example, is subject to very little interference (only Mn). For this reason it is admirably suited to the estimation of cobalt in complex materials, and where a high degree of accuracy is not required.

In comparison with the dimethylglyoxime method for nickel, the α nitroso β naphthol method for cobalt is very inferior. The valuable feature of the reagent is its selectivity in separating cobalt. Its use purely for this purpose would be enhanced if the precipitate could be dissolved in acid for the subsequent accurate determination of cobalt by another method. Its bulkiness, and its strong resistance to acids seriously hampers development in this direction.

For accurate estimation of cobalt, the three most recommended methods have been the electrolytic, the sulphate, and the α nitroso β naphthol (weighing as metallic cobalt). The present work suggests that a much higher degree of accuracy and precision would be obtained if they were replaced by the phosphate and carbonato-complex methods.

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