

A Thesis
entitled

A CRITICAL EVALUATION OF THE ANALYTICAL
METHODS USED FOR THE SEPARATION AND
ESTIMATION OF COPPER AND NICKEL.

by
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CONTENTS.

	<u>Page.</u>
Introduction	1
<u>Part I. THEORETICAL.</u>	
Methods for the determination of copper in which nickel does not interfere.	6
Methods for the determination of copper in which nickel interferes.	41
Methods for the determination of nickel in which copper does not interfere.	52
Methods for the determination of nickel in which copper interferes.	56
The Statistical Treatment.	76
<u>Part II. PRACTICAL.</u>	
The preparation of Standards.	79
The separation and estimation of copper and nickel with salicylaldehyde.	89
The iodometric estimation of copper.	93

	<u>Page.</u>
The separation and determination of copper with sodium thiosulphate and the determination of nickel with diethylglyoxime.	108
The separation and determination of copper with potassium thiocyanate and the asymmetric estimation of nickel.	117
The estimation of copper by the iodate method and the determination of nickel with oxime.	127
The estimation of nickel in the presence of copper with diethylglyoxime and the estimation of copper with oxime.	130
The separation of copper by a more electropositive element and the estimation of nickel by Parr and Lindgren's method.	147.
A comparison of the procedures for the determination of copper and nickel.	156
Discussion.	159
Summary.	164
References.	167

INTRODUCTION

This thesis deals with the determination of copper and nickel both separately and in each other's presence. The work is divided into two sections, one of which treats the subject from the theoretical side while the other contains an account of the practical work performed by the author.

In the theoretical section an attempt is made to summarize the better-known methods for the determination of copper and nickel, and at the same time to incorporate such improvements, criticisms and variations as have appeared in the literature. The subject is so vast that its summary in so short a space must necessarily be incomplete; Yee and Sarver (1), for example, quote 111 references on the subject of the nickel-diethylglyoxime reaction, and a further 43 concerning the reaction of diethylglyoxime with other ions. Only a fraction of the literature was available, and space permitted only a fraction of this to be abstracted in the following pages.

The predominant impression gained after reading a number of papers is the partisanship of their authors; each author states the case for his particular reagent or procedure, often minimizing, or omitting altogether, the concomitant disadvantages. Frequently either no figures at all, or insufficient to indicate accurately the value of the method, are given, and in no paper was there found a mathematical estimate, based on a large number of results, of the accuracy and precision of the procedure.

The first aim in the practical section, therefore, has been to

accumulate/....

accumulate, for each of the methods studied, sufficient results to allow of a statistical treatment. From the readings obtained in each case has been calculated the precision and accuracy of the method. A comparative table of these statistical terms has finally been compiled so that the relative and absolute accuracy of any method can be seen at a glance.

The second aim has been to standardise the optimum conditions for each particular estimation. Even the best-known methods are variously described by different authors. In some cases the different procedures lead to results of the same accuracy and precision; in others, however, certain of the procedures are superior to the variations. In the following pages the variations for each particular method chosen for study have been investigated, and the conditions defined which have been found to give the best results.

Thirdly, the convenience of a method is an important factor in its choice for a particular estimation. In general, the choice between methods of equal accuracy will be determined by the following factors:-

- (i) The cost of the reagent(s).
- (ii) The time in which the estimation can be completed.
- (iii) The presence of interfering elements.

The final choice will depend on a combination of these factors with the accuracy required. It has been attempted, then, to determine and define the above conditions, so that the complete value of any method can be assessed by a combination of the statistical tables with the text.

To summarise, the theoretical section summarises the details of the better-known analytical procedures, while the practical section

shows/....

shows:- The best experimental conditions for carrying out any particular estimation, the accuracy and precision that may be expected under these conditions, and the disadvantages and advantages which the method offers.

Obviously there are too many methods to be studied in the space and time available, and it has been necessary to choose selectively from the various possibilities. A list of the methods studied in the practical section is given below.

- (1) The separation and determination of copper and nickel by salicylaldehyde. A recently devised cyanide procedure for the separation of nickel from other ions is also discussed, and is used in a modified form.
- (2) The separation of copper as the sulphide by the use of sodium thiosulphate, and its subsequent determination iodometrically. The nickel is determined in the filtrate with dimethylglyoxime. The direct iodometric titration of copper in the presence of nickel is also discussed.
- (3) The separation and determination of copper with potassium thiocyanate, and the estimation of nickel in the filtrate by a cyanometric titration.
- (4) The separation and determination of copper with potassium thiocyanate, and the estimation of nickel in the filtrate with oxine.
- (5) The separation and determination of nickel with dimethylglyoxime, following the suggestion of Ranade (2), and the estimation of copper in the filtrate with oxine. The copper is also precipitated as the/....

as the sulphide and determined iodometrically.

- (8) The separation of copper by means of a more electropositive element, and the subsequent determination of nickel by Parr and Lindgren's method.

The factors which have decided this choice are as follows:-

- (i) The standard methods are chosen to enable a comparison of their value to be made, and also to provide criteria by which the lesser-known methods can be judged.
- (ii) To investigate some of the lesser-known reagents and compare their value with that of standard procedures.
- (iii) To investigate and develop some procedures about which little but the barest information is available, e.g. the Ramsdo procedure, Parr and Lindgren's method.
- (iv) The separation of copper by means of a more electro-positive element is out of the usual line of analytical procedures, and was investigated to find how it compared with others.
- (v) The cyanide procedure for nickel separation is new, and because of the ease with which, it is claimed, it can separate nickel from other ions, it seemed desirable that it should be included.

PART I

THEORETICAL.

In the first part of this thesis it is proposed to deal as comprehensively as space permits, with the various analytical procedures for the quantitative determination of copper and nickel. Since this work is concerned with the separation as well as the determination of the two metals, the methods have been classified, for convenience, under the following headings:-

1. Methods For the Determination Of Copper.

- (a) Methods in which nickel does not interfere.
- (b) Methods in which nickel interferes.

2. Methods For The Determination Of Nickel.

- (a) Methods in which copper does not interfere.
- (b) Methods in which copper interferes.

Thus the separation and analysis of a copper-nickel mixture involves either the selection of a method from 1 (a) and the subsequent estimation of the nickel by a method selected either from 2 (a) or 2(b), or the separation of the nickel by a method chosen from 2 (a) and the estimation of the copper by a suitable method from 1 (a) or 1 (b), the selection being governed by the following factors:-

- (i) The degree of accuracy required, and the time consumed by the operations involved.
- (ii) The presence of interfering elements.
- (iii) The cost and availability of the reagents required.

(iv)/....

- (iv) The suitability of the method in relation to the quantity and concentration of the copper (or nickel) to be determined.

1. Methods for the Determination of Copper.

(a) Methods In Which Nickel Does Not Interfere.

The majority of analytical procedures for the determination of copper, including almost all the more important ones, fall into this section. In general, in the analysis of a copper-nickel mixture, the copper is first separated and estimated by one of the methods to be outlined in this section, and the nickel is subsequently determined in the filtrate by one of the methods to be given in the section dealing with nickel. Most of the more important procedures for the determination of nickel alone cannot be used without modification when copper is also present.

(1) The Iodometric Method For Determining Copper.

The Iodometric method for estimating copper is one of the oldest methods, and is the most useful and accurate analytical procedures. The first reference that has been found to it was in 1854 (3), while the first English reference that has been noticed was in 1896 (4). The method is very widely used on account of its accuracy and speed, and it has the additional advantage that few ions interfere with the reaction. The chief substances which interfere are oxides of nitrogen, trivalent arsenic and antimony, trivalent iron, hexivalent molybdenum or selenium, mineral acids in large concentrations, and excessive amounts of ammonium acetate.

The method/....

The method depends on the fact that when a cupric salt in a weakly acid medium is treated with an excess of a soluble iodide, cuprous iodide is precipitated and free iodine liberated, the amount liberated being proportional to the quantity of copper present. The amount of free iodine is estimated by titration with a standard solution of sodium thiosulphate, the iodine itself acting as indicator until the end-point has nearly been reached, when starch solution is used to determine the end-point exactly. From the amount of iodine present the copper content can be determined.



Thus,



Or, 1 ml. N $\text{Na}_2\text{S}_2\text{O}_3 \equiv 0.00354 \text{ g. Cu.}^{++}$

A copper estimation performed in this way is not, however, accurate for two reasons. Firstly, iodine is adsorbed by cuprous iodide, so that the amount of iodine actually determined by the titration with thiosulphate is the stoicheometric quantity less the amount adsorbed by the cuprous iodide. Secondly, the reaction on which the reaction depends, viz.,



is reversible, and does not go to completion due to the fact that cuprous iodide is not extremely insoluble. To minimise this error as far as possible the sodium thiosulphate solution may be standardised against a standard copper sample, reproducing as nearly as possible the conditions used in the actual estimation. Even so, this method is not particularly accurate, its popularity being chiefly due to its speed and convenience.

An improvement/...

An improvement in this method was claimed in 1919 by Bruins (5,6).

In this modification, potassium thiocyanate is added along with the iodide, with the result that the more insoluble cuprous thiocyanate is precipitated instead of cuprous iodide.



The greater insolubility of the cuprous thiocyanate makes for more complete reaction.

Bruins used two procedures for the titration of a copper salt slightly acidified with sulphuric acid.

- (i) Potassium iodide is added to the copper solution in the usual way, and the mixture titrated with a solution containing, per litre, 24.6 g. sodium thiosulphate, and 25-30 g. Potassium thiocyanate.
- (ii) The copper solution is titrated with a solution containing, per litre, 24.6 g. sodium thiosulphate and 8 g. potassium iodide.

The Bruins modification has been shown by Kruger and Tschirch (7) and others to be inaccurate because of the occurrence of side reactions; particularly, iodine and thiocyanogen are both liberated and react with one another.

Another attempt to improve the end-point was made by A.H. Low (8), who found that the end-point can be made sharper by the addition of about 1 mg. silver nitrate. The yellow colour of the silver iodide neutralises the purplish tinge of the cuprous iodide.

The procedure at present favoured has developed from Bruins' method, improved by Foote and Vance (9,10,11,12). They have shown the advantage of the Bruins method to lie in the formation of the more insoluble cuprous thiocyanate, which, giving a smaller concentration of cuprous ions, makes

the reaction/...

the reaction go more nearly to completion. Further, they have found that the iodine at low concentrations is not adsorbed by the cuprous thiocyanate, which becomes white as the free iodine is removed by titration, the end-point in the presence of starch being exceedingly sharp. Their modification involves adding the thiocyanate just before the end-point, so that, while all the advantages of the Bruhn method are included, the undesirable side reactions are eliminated. They state that when the thiocyanate is added as they suggest, an additional amount of iodine corresponding to about 0.15 ml. of decinormal thiosulphate is liberated.

This method was claimed by the authors, who quote the following figures, to be extremely accurate:- Using a volume burette, the error in determining 3.22 g. copper amounted to 0.0023 g. or 1 part in 1400; with a weight burette the error on 5.69 g. copper was 0.0031 g. or 1 part in 1800. The smaller error obtained when using the weight burette they attributed to the larger weights of copper used.

Their work also showed:-

- (i) Dilution before titrating does not affect the final result. Titrations performed on the same quantity of copper in volumes of 200 ml. and 20 ml. do not differ appreciably.
- (ii) Small amounts of nitric acid do not affect the final result. This is particularly important as it means that it is not necessary to remove completely by evaporation any nitric acid that may have been used to dissolve the sample.

Foote and Vance (11) have shown that this method can be used with modifications to determine copper in the presence of pentavalent arsenic

and antimony/....

and antimony, and ferric iron, the only elements commonly associated with copper that liberate iodine from iodides. They support the statement, first made by Mott (13) and later corroborated by Park (14), that the addition of a soluble fluoride eliminates all the difficulty arising from the presence of iron. This is converted to a complex fluoride ion (FeF_6^{3-}) insufficiently dissociated into Fe^{+++} ions to cause iodine to be liberated from potassium iodide. They showed further that by controlling the pH at about 3.7, copper may be determined accurately in the presence of pentavalent antimony and arsenic. Selenium does not interfere under these conditions. The interference of iron and manganese reported by Park (14) is denied by them; the high results he obtained when these elements were present are attributed by them to the fact that the solutions were allowed to become ammoniacal. Repeating his experiments taking care that the solutions never became ammoniacal, they observed no interference.

Effect of pH.

The effect of variations in pH on the results has been studied by Whitehead and Miller (15), who studied the results obtained after adding different volumes of acids. (They used the old iodide method: i.e. they did not add thiocyanate). Their work shows that volumes up to 5 ml. of 8 N hydrochloric, nitric, or sulphuric acids have a negligible effect on the results, but that volumes greater than this make the results high. They found, however, that the presence of acetic and tartaric acids (each 8 N) did not affect the results. No support was found for the statement by Moser (16) that the addition of 5%, by volume, of sulphuric acid to

the/....

the copper solution before titration improves the determination. They criticize as being too conservative the statement of Gooch and Heath (17) that not more than 5% of hydrochloric, nitric or sulphuric acids should be present.

Park (14), also using the old method, has shown that small amounts of ammonium acetate may be present, but that large amounts cause the reaction to be slow and the end-point uncertain.

No systematic work has been done on the influence of pH in the modified Foote and Vance method. Only three references to this have been noted, all in papers by these authors. In discussing the determination of copper in the presence of interfering elements, they write (11) "This mixture ... has a pH of approximately 5.7 as determined by the hydrogen electrode ... An acetate solution of this pH practically cannot be used in the usual iodometric determination of copper. In the presence of a thiocyanate, however, the reaction is rapid and the end-point exceedingly sharp." Later in the same paper they continue, "This series of determinations was carried out in order to show definitely that this method was reliable at the rather higher pH necessary to prevent the oxidation of iodides by arsenic acid. The highest pH of the solutions in the authors' previous work was 2.0". The only other observation on this point is in their original paper (9), where they say that the presence of nitric acid in small amounts (1 cc. of concentrated acid in 20 ml.) does not affect the final result, but they make no mention of any upper limit to the amount of nitric acid permissible, and no attempt to generalize/....

to generalize in terms of pH. Experiments by the writer on this aspect of the method are described later, in the experimental section of this thesis.

Precautions Necessary In The Preparation Of The Reagents.

Sodium Thiosulphate.

Kolthoff (18) states that sunlight hastens the decomposition of thiosulphate solution, that 0.01 N solutions decompose more rapidly than those of 0.1 N strength, that the sulphur deposit from decomposed thiosulphate solutions accelerates the decomposition, and that small amounts of mercuric iodide or of certain alkaline substances greatly retard it. He suggests that the decomposition may be caused by certain sulphur-consuming organisms. Kilpatrick and Kilpatrick (19) have proved this, finding that the action is caused by bacteria, identified as *thiobacillus thioparus*, whose characteristic reaction is the transformation of thiosulphate into sulphate and sulphur. Also, if the water is acid because of dissolved carbon dioxide there is a small tendency for the following reaction to occur:-



In practice carbon dioxide has very little effect on the stability of the solution as has been shown by Kolthoff (18), and Kilpatrick and Kilpatrick (19), and others.

Thiosulphate solutions, then, for stability, should be made up in freshly redistilled water and made sterile. This latter may be accomplished by adding 0.1 g. sodium carbonate per litre, or, according to Yoshida (20),

by adding/....

by adding either 0.05 molar borax solution, 0.1 N disodium hydrogen phosphate (Na_2HPO_4) solution, or water saturated with carbon disulphide. Kilpatrick and Kilpatrick (19) found that a solution prepared according to these specifications ^{had} changed only from 0.014065 N to 0.014016 N after eight months.

Starch Solution.

Starch is a very sensitive reagent for iodine, and is generally employed in the form of 1% aqueous solution to detect the end-point in iodometric titrations. A solution of soluble starch in water decays rapidly and is only effective when freshly prepared. The most common method of preservation is to add 0.5 g. pure salicylic acid which preserves the starch solution almost indefinitely.

Among other methods of preparing starch solutions may be mentioned:-

- (1) Stokes' Method (21). 5 gm. starch are mixed to a paste in a little cold water, poured slowly with stirring into a litre of boiling water, and boiled for two minutes. The mixture is cooled in cold water, allowed to stand overnight, and filtered into small 50 ml. medical bottles. These are immersed to the neck in a water bath and heated for two hours. The bottles are then stoppered with soft corks that have been sterilized by being drawn slowly through a flame. Solutions prepared and preserved in this way keep almost indefinitely without mould formation. A test solution kept for eighteen months in this way remained perfectly clear and as sensitive as when first made. On opening the bottle mould formation started within a week.
- (11) Chaplin's Method (22). In this method the starch solution is boiled for two hours instead of two minutes as in Stokes' method. Towards the end of the boiling 30 g. boric acid are added. Boric acid is effective against moulds but not against salivary enzymes. If protected from the latter, solutions that have been used intermittently during several months and kept in containers closed only by an inverted beaker appear indistinguishable from freshly prepared solutions.

- (iii) N. Kano (25) recommends the addition of 0.5 ml. of 2 N hydrochloric acid per 50 ml. of starch solution if it is to be used in acid solutions, or of a few drops of carbon disulphide if it is to be used in alkaline solutions.

These methods, however, are only necessary when the starch solution is prepared in bulk for use over a considerable period. For ordinary work 1 g. soluble starch is made to a paste in cold water, and this paste stirred into 100 ml. boiling water; the solution is filtered and cooled, and 0.5 g. succinic acid added.

Titration with starch should be carried out at a temperature of about 25°C. The sensitiveness of the end-point is less at 30°C., and the colour disappears altogether on raising the temperature. In ice-cold solutions the reactions are too slow to be of any practical use.

The disappearance of the starch-iodide colour should be more or less permanent. Its reappearance after the solution has stood for some time is probably due to one or more of four factors:-

- (i) The use of too little potassium iodide.
- (ii) Allowing insufficient time for the cupric ion to react with the iodide.
- (iii) The incomplete removal of oxides of nitrogen.
- (iv) The presence of some other oxidising agent.

(ii) The Use Of Thiocyanate in Determining Copper.

After the iodide method for determining copper, the thiocyanate method, either in its gravimetric or volumetric modifications, is probably the best and most widely used. The method was first recommended by

Rivot/.....

Rivot (24), and was further developed by Parr (25), Van Ness (26) and Demerout (27). The method depends on the fact that in a weakly acid medium, containing sulphurous acid as reducing agent, insoluble cuprous thiocyanate is precipitated from copper solutions by the addition of a soluble thiocyanate.



After the copper has been precipitated as the thiocyanate, there are a number of possible variations by which the copper may be estimated. The most important of these are:-

- (i) The cuprous thiocyanate is weighed as such.
- (ii) The cuprous thiocyanate is converted to metallic copper and weighed.
- (iii) The precipitate is redissolved and the copper determined by one of the standard procedures, such as the iodometric or electrolytic methods.
- (iv) It may be determined by one of a number of other volumetric procedures.

The chief interfering elements are lead, mercury, the precious metals, selenium, and tellurium, which all contaminate the precipitate. By precipitation with thiocyanate copper may be separated from iron, nickel, cobalt, zinc, cadmium, antimony, tin, manganese and bismuth. When much arsenic is present, precipitation should be carried out in a solution in which hydrochloric is the only free acid. When sulphuric acid is the only free acid, the addition of ferrous sulphate is recommended (28) to accelerate the conversion of cupric to cuprous thiocyanate.

Kelthoff/....

Kolthoff and v.d. Meer (29) have shown that for complete precipitation of copper as cuprous thiocyanate the acidity of the solution should not exceed 0.5 N, and the excess of thiocyanate added should be less than that required to render the filtrate 0.05 N with respect to this salt. A greater excess results in the formation of soluble complexes, thus giving rise to low values for copper.

In the ordinary method of estimation as cuprous thiocyanate, the copper salt, in very slightly acid solution, is treated either with gaseous sulphur dioxide or with a solution of sulphurous acid or of an alkaline bisulphite or metabisulphite, slightly in excess of the amount required to reduce all the copper present. Potassium thiocyanate is then added in slight excess to either the hot solution (25, 30, 31), or to the cold solution (28, 32, 33). The solution is allowed to stand until the supernatant liquid is quite clear, and the precipitate a pure white. The precipitate, after separation by filtration through a sintered glass crucible, is washed thoroughly with a solution of potassium thiocyanate and an alkaline bisulphite or metabisulphite, and finally with 80% alcohol, after which it is dried and weighed as Cu(CN)_2 .

An alternative gravimetric procedure is that recommended by Swonger and Nichols (35). In this variation the cuprous thiocyanate is precipitated as above, filtered on a tight paper lined with filter paper pulp, and washed as before. The paper and precipitate are placed in a porcelain crucible and dried at 110°C . A Rose lid is put on top of the crucible and the air displaced with a current of hydrogen. With the current of hydrogen still flowing the crucible is heated over a low flame until the

cuprous/....

cuprous thiocyanate has been changed to the oxide. The lid is then removed and the carbon burnt off. When the crucible has cooled, the lid is replaced and the air again displaced with hydrogen, after which the crucible is heated until the oxide has finally been reduced completely to metallic copper, which is cooled in hydrogen and weighed. This method has nothing to recommend it in preference to the direct weighing of the cuprous thiocyanate precipitate, since it is both longer and less accurate. It is little used.

There are a number of volumetric methods for estimating copper after it has been separated as cuprous thiocyanate, of which the following are the more important:-

(a) The Iodate Method.

The method of titrating a number of oxidisable substances such as free iodine, iodides, arsenites and antimonites, is due originally to Andrews (34). When an iodide is titrated with chlorine water in a neutral solution, the reaction is:-



If a large excess of free hydrochloric acid is present during the titration, the following reaction takes place:-



Andrews shows that, similarly, if potassium iodate is used instead of chlorine water, the stage at which the reaction stops is also dependent on the hydrochloric acid concentration. If the concentration is low the reaction stops at the stage at which free iodine is liberated:-



In the/....

In the presence of a large excess of hydrochloric acid, however, the reaction is:-



Now both iodine and iodine ^{mono}/chloride are brownish yellow in aqueous solution, but in some organic solvents, such as chloroform or carbon tetrachloride, iodine is purple while iodine ^{mono}/chloride is yellow. Thus such organic solvents can be used as indicators to show the completion of reaction (2).

This method is applied by Jamieson, Levy, and Wells (50) to the determination of copper. They showed that when iodate is added to a strong hydrochloric acid solution of cuprous thiocyanate, the latter is oxidized and iodine is set free. When the oxidation is complete, further addition of iodate converts the iodine to iodine monochloride, and the end-point is indicated by the disappearance of the iodine colour from a small quantity of, say, chloroform shaken with the mixture. The series of reactions when completed has the form:-



The detailed procedure for the estimation of copper by the iodate method is as follows:- Cuprous thiocyanate precipitated as above, is filtered through close quantitative filter paper, and washed as before. The precipitate and filter are transferred to a stoppered flask, containing chloroform (or carbon tetrachloride), excess of hydrochloric acid and a little water. This mixture is titrated with a standard solution of potassium iodate, the flask being stoppered and shaken vigorously after each addition. There appears in the chloroform layer a violet colour

which/....

which first increases and then decreases in intensity until it finally disappears. The end-point is very sharp, the colour disappearing over one drop.

The filter paper does not interfere in any way with the titration, and the authors state (*loc.cit.*), 'In order to make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds to three-quarters of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make to about 50 cc. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly coloured with iodine as soon as the cuprous thiocyanate is added, but this makes no difference with the results of the titration'.

A series of six results recorded by one of the authors (Jamieson) gives an average error of 1 in 350. Applications of the method to ores are outlined. Lead and antimony interfere and must be removed as sulphate or basic sulphate after evaporation with sulphuric acid; silver also interferes but can be removed as the chloride.

The iodate method is the most accurate volumetric method for estimating copper after it has been precipitated as cuprous thiocyanate. It has the advantage that potassium iodate is inexpensive and can be obtained sufficiently pure to allow of the preparation of standards by weighing. The solution keeps indefinitely. On the other hand the authors do not stress the importance of washing the precipitate free from thiocyanate, a process which is very laborious because of the large number of washings necessary and the fineness of the filter paper needed to retain the precipitate; the

final/....

final washings with 80% alcohol, in particular, are extraordinarily slow. It is absolutely necessary, before transferring the precipitate, to wash it particularly well so as to avoid error due to excess CN^- .

(b) The Permanganate Method.

The permanganate method for the estimation of copper is due to Furr (25), and involves the following stages.

(i) The copper is precipitated as cuprous thiocyanate.

(ii) The cuprous thiocyanate is decomposed with sodium hydroxide to give cuprous hydroxide. $\text{CuCN} + \text{NaOH} \rightarrow \text{CuOH} + \text{NaCN}$. (1)

(iii) The cuprous hydroxide is oxidised to cupric hydroxide by titrating with potassium permanganate.



(iv) Dilute acid is added to convert the sodium thiocyanate to thiocyanic acid.

(v) The titration with permanganate is continued to oxidise the thiocyanic acid, the end-point being the persistence of normal permanganate pink colour.



The copper is precipitated as the thiocyanate in the usual way, this being filtered through asbestos. The precipitate is washed with hot water, the washing being complete when the filtrate, after having been made acid, will not decolorise a drop of permanganate. The asbestos pulp and precipitate are returned to the beaker, 2-3 ml. 10% sodium hydroxide solution added, and the temperature raised to 60 - 70°C. The solution is now ready for titration with the standard permanganate, the object being

first to/....

first to add to the alkaline solution sufficient permanganate to oxidise the cuprous hydroxide formed from the addition of the alkali (stages 1 and 2), then to acidify and proceed with the rest of the titration to oxidise the thiocyanic acid. (stage 3). The progress of the reaction can be followed by the colour changes taking place, the yellow of the cuprous hydroxide changing to the dark brown of the cuprous hydroxide. When the yellow tint can no longer be detected the copper has all been oxidized and the reaction between the alkaline thiocyanate and the permanganate begins, resulting in the formation of the green manganate, thus:-



It is essential that this stage be reached before the addition of the acid, otherwise cuprous thiocyanate will be precipitated. Thus, when the yellow colour has finally disappeared and the green tint appears, dilute sulphuric acid is added slowly with stirring. After the solution has become clear, it is warmed to 60 - 70°C., and the titration with permanganate continued in the usual way to the normal pink end-point. It is essential that dilute acid be used, since concentrated acid has a tendency to produce carbon oxysulphide. The whole reaction is represented by the equation:-



This equation makes it apparent that much sulphuric acid is needed in the reaction, and also emphasises an advantage of the method, viz. that in proportion to the amount of copper present a considerable quantity of permanganate is required.

On the effect of other metals Farr (25) comments, "Removal of other

metals/.....

metals is not necessary, even silver does not interfere because it is unaffected by the treatment with caustic alkali, and the insoluble silver thiocyanate acts so very slowly on permanganate solution, as not to vary the end-reaction appreciably".

He also states that dilution affects the result, commenting, rather naively, "A solution of 1.5 g. ammonium thiocyanate to a litre of water has a strength very nearly corresponding to N/10 permanganate solution. Now up to this point of dilution the thiocyanate seems to react regularly and in accordance with the above reactions. If, however, the thiocyanate is largely diluted beyond this point, the amount of permanganate used is appreciably less than the same quantity of thiocyanate would use, if undiluted. For example, a measured quantity of say, 10 cc. thiocyanate, if diluted 200 times, will titrate approximately 0.1 cc. of N/10 permanganate less than the same solution would use if undiluted".

A set of 8 readings included in the paper gives an average error of 1 in 300. A disadvantage of this procedure is that the reactions, particularly the oxidation, do not go to completion, and it is necessary to establish and use an empirical factor. The permanganate method compares unfavourably with the iodate method both in simplicity and in accuracy.

(c) Denorest's Method.

A similar volumetric variation is that due to Denorest (27), a description of which is included in Scott's "Standard Methods of Chemical Analysis" (35). In this method, the cuprous thiocyanate is precipitated from a nearly boiling solution containing ammonium sulphate, about 5 g.

ammonium/....

ammonium tartrate and 1 ml. free sulphuric acid. A 5% solution of sodium sulphite is first added, and then slowly, with stirring, a 5% solution of potassium thiocyanate. The solution is filtered hot through asbestos and the precipitate washed thoroughly. It is decomposed in the crucible by pouring hot 10% sodium hydroxide onto it. The cuprous hydroxide in the crucible is washed well.

The alkaline filtrate now contains sodium thiocyanate, and from here the procedure is identical with that in the permanganate method. (see p.10 (iv) and (v), and p.21).

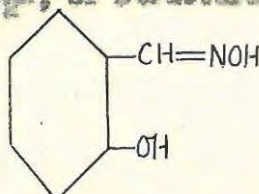
The advantage of this method over the permanganate method is that an empirical factor is not required, the theoretical factor being correct. It is, however, rather more time consuming, owing to the extra washing of the precipitate that is involved, though this is to a certain extent compensated for by the more rapid titration. It represents an improvement on the original permanganate method, but it is still neither as convenient nor as accurate as the iodate method. In particular, the end-point in the iodate titration is much sharper.

(iv) Garrigue's Method.

This modification is described in Scott's "Standard Methods Of Chemical Analysis" (35) but the original reference is not quoted, and could not be found in any journals or abstracts. In this method the cuprous thiocyanate is decomposed with excess hot sodium hydroxide, the cuprous hydroxide formed being filtered off and washed. The excess sodium hydroxide is then estimated by back titration with standard hydrochloric acid. This method is evidently not one of the better volumetric methods.

(111) The Determination Of Copper With Salicylaldehyde.

Salicylaldehyde, $C_7H_6O_2$, of structural formula



is an excellent reagent for the determination of copper and nickel. It is particularly useful for nickel, being almost as sensitive and accurate a reagent as is diethylglyoxime, than which it is more convenient to use, since the precipitate coagulates in the cold on stirring, and requires little washing.

Though both nickel and copper precipitate with salicylaldehyde, a separation can readily be effected by a suitable adjustment of the pH. Nickel starts to precipitate only at a pH greater than 5, while copper is completely precipitated at a pH of 2.6. Thus salicylaldehyde is not only an excellent reagent for the separation of copper from nickel, and its subsequent estimation but, if the filtrate contains sufficient salicylaldehyde, it is also possible to precipitate the nickel quantitatively merely by a suitable alteration of the pH.

The use of salicylaldehyde for estimating copper was developed by Ephraim (36), who precipitated the copper from a buffer solution of pH 2.6 by the addition of an alcoholic solution of salicylaldehyde. The chief disadvantage attending its use is the high cost of the reagent, but Astin and Riley (37) have shown that the reagent can be prepared at a relatively low cost from salicylaldehyde and hydroxylamine hydrochloride, by mixing the two in equivalent quantities. They have also shown that it is unnecessary to isolate the aldoxime prepared in this manner before using/....

using it in an estimation. A set of six readings using the reagent thus prepared gave an average error of 1 in 400, and the results showed that the formation of the salicylaldoxime had occurred to an extent about 90% of the theoretical.

The copper starts to precipitate at a pH of less than 1 and is completely thrown down at pH's of 2 and over. If the reagent is prepared by dissolving salicylaldoxime in alcohol, no difficulty is experienced in controlling the pH. The reagent as prepared by the Austin and Riley method (37), however, has itself a pH of 1.5, so that as the reagent is added, the pH of the solution will gradually decrease, and there is a danger that the pH may fall to a value where precipitation of the copper is no longer quantitative. To eliminate the possibility of this occurring, Biefeld and Howe (38) recommend the addition of about 0.5 ml. 2 N sodium hydroxide.

The literature is rather vague on the subject of interfering elements. Riley (39) states that "many of the common elements e.g. iron, silver, mercury, zinc, do not give precipitates with the reagent. Cobalt, however, gives a precipitate with the reagent in neutral solution." Vogel (40) states that "silver, mercuric, arsenious, ferric, nickel, cobalt and zinc do not interfere provided the solution contains sufficient acid; the copper complex alone is insoluble in acetic acid. In neutral or in faintly acid solutions nickel and cobalt are precipitated, but other ions remain in solution". Biefeld and Howe (38) state that salicylaldoxime has been used for the analysis of copper-cadmium mixtures, and for the determination of lead, nickel, zinc and palladium. They also state that the
procedure/....

procedure has to be modified for mixtures containing iron, because the complex formed by this metal with the reagent is occluded from the solution by the copper precipitate. They have shown that this occlusion is quite considerable. When plotted against the concentration over the range investigated, the occlusion values did not give an adsorption isotherm type of curve. From this the authors infer, "the probable conclusion is that the carrying down of the iron complex is not due to adsorption alone". The occlusion of the nickel complex by the copper, however, they showed to be negligible, even when the nickel concentration was 20 times that of the copper.

Salicylaldoxime is an excellent reagent for separating copper from nickel, and for the determination of both copper and nickel. The question of interfering ions, about which the literature is indecisive, has been studied experimentally and is dealt with in Part 2.

(iv) The Determination Of Copper With α -Benzoinoxime.

α -Benzoinoxime is $C_{14}H_{15}O_2N$. With copper it gives an addition complex of formula $Cu(C_{14}H_{11}O_2N)$.



Its use as a specific reagent for copper was first proposed by Feigl (41) but it was soon afterwards shown by Assalin (42) that the reagent was not suitable for the determination of copper by direct weighing, for three reasons:-

(1) The reagent is very insoluble in water, but soluble in alcohol. When

an/....

an alcoholic solution is added to an aqueous copper solution, the excess reagent is precipitated along with the copper complex, and is very difficult to wash away.

(ii) In ignition procedures, only slow and careful ignition will remove all the carbon.

(iii) The precipitated complex is very susceptible to contamination in the presence of other elements. Vanadium, molybdenum and tungsten are the chief interfering ions, but a large number of others contaminate the precipitate to a greater or lesser degree.

An example of the use of α -benzoinoxime in the gravimetric determination of copper is its use by Har (48) in estimating copper in copper-molybdenum steels. The copper and molybdenum are precipitated as sulphides by hydrogen sulphide and sodium thiosulphate. The mixed sulphides are ignited to the oxides, which are dissolved in nitric acid. The solution is made ammoniacal and a 2% alcoholic solution of α -benzoinoxime added. The precipitate which forms is coagulated, filtered off by ashless paper and washed with very dilute ammonium hydroxide. It is ignited in a silica crucible and weighed as cupric oxide. The author claims that this method is superior, both in accuracy and speed, to the ordinary method of precipitating the copper as the sulphide, igniting to the oxide, dissolving in acid and determining the copper electrolytically. This claim, however, is scarcely substantiated by the set of 10 readings he quotes, which on the average, are 7% higher than the theoretical value. In fact, it would seem that the author himself assumes this inaccuracy, for he states that, after the final weighing of the cupric oxide, one

should/....

should "multiply the results by 80 and divide by the number of grams of the sample, to get the copper content" an approximation which, differing as it does by 0.5% from the theoretical factor, could hardly be justifiable except in a fairly inaccurate method.

A more useful application of the reagent is given by Silverman (44) in a study of the rapid determination of copper in ferromolybdenum, calcium tungstate and ferrotungsten. In this method the sample is dissolved, and the copper precipitated with α -benzoinoxime in alkaline solutions as before, except that the solution is not heated but is allowed to stand for 15 minutes after the reagent has been added. The precipitate is washed with warm ammonium hydroxide and is then dissolved in a mixture of nitric and perchloric acids. The solution is heated until the nitric acid has been driven off, after which it is cooled, diluted with water and again heated to boil out the chlorine. The copper in this solution may then be estimated either iodometrically or electrolytically.

Silverman differs from Kar in performing the precipitation in the cold. He states (44) "precipitation should take place at room temperature. When precipitation was made hot, the results were low and inconsistent. It is conceivable that some of the oxime was hydrolyzed into ketone and hydroxylamine, which might reduce some cupric ions to the cuprous stage and be held in solution by ammonia and ammonium salts. Feigl stated that there should be no ammonium salts present".

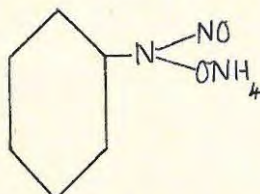
The use of α -benzoinoxime in estimating copper is not very extensive, because of the contamination of the precipitate by excess of the reagent. Its main application, when it is used, is in the separation of copper

from/....

from cadmium, zinc, cobalt and nickel, since these are not precipitated by the reagent in ammoniacal solution. Other ions which are precipitated by ammonium hydroxide are kept in solution by the addition of sodium potassium tartrate. The copper content is finally determined either by an electrolytic or by an iodometric procedure in neither of which methods does excess reagent interfere.

(v) The Determination Of Copper With Cupferron.

Cupferron is the ammonium salt of nitrosophenylhydroxylamine, $C_6H_9O_2N_3$. Its use in quantitative analysis was first proposed in 1909 by Baudisch (45)



for the separation of copper from iron. In weakly acid solution precipitation with cupferron effects complete separation of elements such as iron, vanadium, zirconium, titanium, tin, columbium and tantalum from others such as aluminium, beryllium, phosphorus, boron, manganese, nickel and hexivalent uranium.

The reagent gives good results when used in the determination of iron, titanium, zirconium and vanadium, but the results obtained in copper estimations are less satisfactory. It is therefore seldom used to determine copper. Among the interfering elements are lead, silver, mercury, bismuth, cerium, thorium and tungsten, and in certain cases, when present in excessive amounts, silica, phosphorus, alkaline earth and alkali salts.

The precipitation is performed in an ice-cold solution containing free mineral or organic acids. A cool 6% solution of the reagent is added

slowly/...

slowly with stirring, until an excess is indicated by the temporary flash of a fine white precipitate which redissolves, as contrasted with the flocculent and insoluble copper-cupferron precipitate. The precipitate is filtered off through quantitative filter paper, and washed with dilute solutions of either hydrochloric or sulphuric acid containing a little cupferron. The precipitate cannot be weighed as such, but must be ignited to the oxide which is weighed. In the presence of iron, which is also precipitated by cupferron, separation can be effected by dissolving the copper precipitate in ammonium hydroxide, in which the iron complex is insoluble. The copper can then be determined by a separate estimation on the filtrate.

A companion reagent to cupferron is neocupferron, which is α -nitroso-naphthyl-hydroxylamine. Its particular advantage over cupferron, as has been shown by Baudisch(46), is that it can be used to estimate very small quantities of iron and copper without first concentrating the solutions. To precipitate copper (and iron), the reagent is added to the acidified ice-cold copper solution in a 10:1 excess and the flask allowed to stand in ice for at least an hour. The precipitate is filtered off and washed first with ice-cold water, then with N hydrochloric acid, and is finally treated with ammonium hydroxide (5N) which dissolved the complex. The copper in this solution is estimated by comparing the colour with that of standard copper solutions which have undergone similar treatment.

(vi) The Separation And Determination Of Copper As Sulphide.

Hydrogen sulphide is widely used in quantitative analysis to

precipitate/....

precipitate and separate certain ions. The governing factor, which determines in each case whether or not a particular ion will precipitate, is the pH of the solution. By variations in the pH a number of group separations are possible.

In strong acid solutions ($\text{pH} < 1$), hydrogen sulphide precipitates members of the copper and arsenic groups. The copper group includes copper, silver, mercury, lead, bismuth, cadmium, rhodium, ruthenium, palladium and osmium. The arsenic group includes arsenic, gold, platinum, tin, antimony, iridium, germanium, selenium, tellurium and molybdenum. Thallium, indium and gallium may also be precipitated in the copper group, while vanadium and tungsten, in the absence of tartaric acid, precipitate partially in the arsenic group. There is also a possibility that elements, other than those so far mentioned, may be carried down through the formation of mixed sulphides. For example, zinc sulphide is carried down by copper, cadmium, or mercury sulphides; thallium by copper, arsenic and antimony, and nickel and cobalt by quadrivalent tin. Mixed sulphides are also formed by certain members of the group, for example, mercury with cadmium, tin or copper.

Papers on the analyses of ores have frequently quoted the use of hydrogen sulphide to effect an initial separation of the copper. For example, in a procedure described in the booklet "Standard Methods of Analysis of Pure Copper" (47), the copper is determined by precipitation as the sulphide, which is filtered off, washed and ignited to the oxide. In a method of analysing brass and bronze due to Von Kollrepp (48), hydrogen sulphide is used to separate, but not to determine, the copper

which/...

which is estimated by difference. Scott (49) lists precipitation with hydrogen sulphide as one of the standard methods for separating copper.

Despite the number of references to it in the literature, this method has several disadvantages, which, together with the development and refinement of better methods (in particular the iodometric and electrolytic procedures), have thrown it into virtual disuse. This statement is confirmed in a letter from the Australian Munitions Supply Board which accompanied the booklet (47) which has already been mentioned.

A first and obvious disadvantage is the large number of elements that interfere. Further, even if these are absent, or are easily removable, there is still the possibility that others may be occluded by the precipitate. There is also difficulty in the quantitative ignition of the sulphide to the oxide, because of the tendency for a certain amount of sulphate to be produced.

In particular, in the presence of nickel the method is unsatisfactory. Crookes (50), in 1905, wrote - "The ordinary process of separating copper from nickel, founded on the precipitation of copper by sulphuretted hydrogen, leaves much to be desired on account of the facility with which the copper sulphide after washing passes to the state of the sulphate; and also because copper during precipitation always carries down with it considerable quantities of nickel, which passes to the state of sulphide in the precipitate."

A recent variation is the precipitation of copper as the sulphide with sodium thiosulphate (51, 52). The copper is not weighed as the oxide, which instead is fused with potassium bisulphate, and the melt

dissolved/.....

dissolved in water. The solution is acidified with acetic acid and the copper determined iodometrically. This procedure is specifically applied (52) to the separation of copper and nickel in German silver. The filtrate is evaporated to dryness (to remove sulphuric acid), heated with bromine water (to remove colloidal sulphur), and the nickel estimated with dimethylglyoxime.

The papers mentioned confine themselves merely to outlining the procedure. No results are quoted nor is there any discussion of the effect of interfering elements.

(vii) Separation of Copper in the Metallic Form By Precipitation
By A More Electropositive Element.

One of the standard procedures (53) for separating copper from other ions is the displacement of copper from an acidified solution of one of its salts by means of a more electropositive element (metallic zinc or aluminium are generally employed). A sheet of pure aluminium (or zinc) is bent up at the corners, so as to rest table-like on the bottom of the beaker, thus exposing the maximum surface area. A little sulphuric acid is added, and the solution is heated for some time. The copper is quantitatively precipitated in the form of spongy metallic copper. When the precipitation appears to be complete (this is tested for by adding small pieces of aluminium foil, until one of these remains untarnished), hydrogen sulphide water is added to precipitate any last traces of copper. The solution is decanted through a filter, and the copper rinsed out with a jet of hydrogen sulphide water, leaving the aluminium as clean as possible. The copper in the filter paper is

washed/....

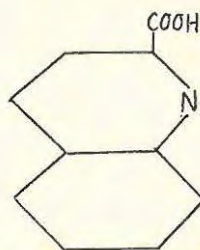
washed a number of times with hydrogen sulphide water. Finally, the copper may be estimated either iodometrically or electrolytically.

If it is to be estimated iodometrically, the filter paper and precipitated copper are transferred to a beaker and the copper dissolved in concentrated nitric acid, which has previously been warmed in the beaker containing the aluminum sheet to dissolve any traces of copper that may not have been transferred to the filter. If it is to be estimated electrolytically, a hole is punched in the bottom of the filter, and the copper is washed through with a jet of water into a beaker containing nitric acid. From either of these solutions the copper can be estimated by the normal electrolytic or iodometric procedures.

The method is convenient and accurate, and has the advantage that the interfering elements can be read off at a glance from the electro-negative series. The greatest potential source of error in this procedure is that the copper will be oxidized. To avoid this the metallic copper is not allowed to be exposed to the air, and hydrogen sulphide water is used for all the washings. Nickel does not interfere, and this procedure may be used to separate copper from it.

(viii) The Separation And Determination Of Copper with Quinaldinic Acid.

Quinaldinic acid is



and is quoted (54, 55) as being a particularly good reagent for copper, zinc, and cadmium. Sherran (56) has investigated the pH range over which

the/.....

the copper is quantitatively precipitated by this reagent, and has shown that precipitation is complete between pH 2.5 - 6.96. Attempts to extend the range beyond pH 7 resulted in the precipitation of cupric hydroxide.

In Shennan's method the copper solution is buffered with sodium acetate and acetic acid so as to be within the pH range quoted above. The solution is boiled and an aqueous solution of the reagent added slowly. After standing for 45 minutes the solution is filtered through a sintered glass crucible. The precipitate is washed well with water, dried at 125°C., and weighed. Shennan concludes that "while quinaldinic acid offers a convenient, rapid and highly accurate method of determining copper, zinc and cadmium separately, it is unsuited for separation of these metals from one another."

Shortly after Shennan's paper, Majumdar (57) investigated more fully the precipitation of copper and its separation from cadmium under the original conditions of Ray and Bose (54), in which the pH was fixed by the addition of 2N sulphuric acid, and not by an acetic acid-sodium acetate buffer solution. He includes a table showing the results of 10 estimations made on pure copper solutions, in which the pH varied between 1.22 and 2.01. The results are of exceptional accuracy, 7 of the 10 agreeing perfectly with the theoretical value (0.02118 g.) while the largest variation recorded is .00004 g. On the average over the 10 readings there is a variation of only 1 in 2000 from the theoretical. Further he shows that between these pH values the results are still quantitative in the presence of cadmium; a set of 4 results give an average deviation of only 1 in 1000 from the theoretical. The author

concludes/....

concludes, "Shennan's statement, that quinaldinic acid is unsuitable for the separation of copper from cadmium, is thus shown to be incorrect".

Ray and Dutt (58) and Ray and Sarier (59) have also published a procedure by means of which copper can be separated from zinc using quinaldinic acid and suitable pH control.

Majumdar (57) also showed that copper quinaldinate is appreciably soluble in acetic acid. A few determinations of copper in the presence of 55 ml. glacial acetic acid in the absence of sodium acetate gave results 0.6% low, and the filtrate when tested with rubenic acid showed copper to be present. This solubility, however, is reduced by the presence of sodium acetate; this is in direct opposition to Shennan's statement that "sodium acetate has a pronounced solubilising effect".

Quinaldinic acid, then, to judge from Majumdar's figures, is an outstanding reagent, not only for the direct estimation of copper, but also for its separation from cadmium, lead, manganese, nickel, cobalt and acids of phosphorus and arsenic, and its subsequent determination. Though some difference of opinion as to the best conditions for the precipitation has appeared in the literature, the work of Majumdar has established the original procedure of Ray and Bose, in which 2 ml. 2N sulphuric acid are added, as being the most suitable. Against all its obvious advantages, viz. accuracy, speed and convenience, the big disadvantage is its high cost (3/5 per gram-B.D.S. Catalogue, 1946), and it is this which presumably accounts for the little use that has been made of it in analytical chemistry.

(12) The/....

(ix) The Determination Of Copper With Potassium Ethyl Xanthate.

The use of potassium ethyl xanthate to separate copper from nickel is described in a recent paper (80). The principle of this method is that copper, in a feebly ammoniacal solution, is precipitated as cupric xanthate, while nickel remains in solution as a complex ammine.

The detailed procedure (which is a microchemical one) is as follows: A few drops of ammonia are added to the copper-nickel solution. A 2% aqueous solution of potassium ethyl xanthate is added all at once, and the solution stirred until the precipitate coagulates. If the precipitate is not a bright golden-yellow a few drops of ammonia must be added.

The mixture is allowed to stand for fifteen minutes, and is then filtered through a filter-stick. Concentrated nitric acid is added and the solution evaporated to dryness. After the elimination of the nitric acid, the evaporation is repeated with water. The dry residue is finally dissolved in water. Any residue is filtered off using a filtering stick. The pH is adjusted with sodium acetate (using Morck's Indicator) to about 5, and the copper determined with salicylaldehyde in the usual way.

The nickel may be determined by dimethylglyoxime (or other standard reagent) in the filtrate from the potassium ethyl xanthate separation.

The authors include three results, which show an average error of 1 in 400. The reagent would appear to be convenient to use, and also has the advantage of being inexpensive. It was originally intended to develop the use on a macro-scale of this reagent in the separation and determination of copper and nickel. This was prevented, however, by an inability to obtain supplies of the reagent.

(x)/....

(x) Other Reagents For Determining Copper.

The nine sections above include the more important methods by which copper can be separated from nickel and subsequently determined. It is proposed to conclude with a short list of organic precipitants which may be used to estimate copper in the presence of nickel. In most cases the original papers were not available, so that it is not possible to give more than a superficial account of their use and applicability. The information is, in the main, taken from textbooks on organic analytical reagents by Yoe and Sarver (61), Mellan (62) and Von Stein (63).

(1) Ethylenediamine.

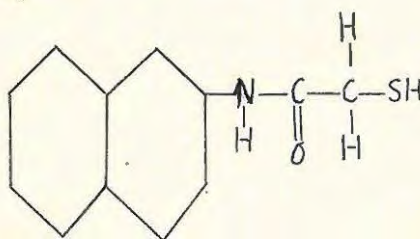
Spacu and Macarovici (64) have shown that when this reagent is added to a neutral or faintly acid copper solution, a blue complex cation is produced, which, upon heating and treatment with an iodo-mercurate, precipitates a complex suitable for the gravimetric determination of the metal. To the neutral or faintly acid copper solution ethylenediamine is added dropwise until a blue colour is obtained. A slight excess of the reagent is added, followed by 1-2 g. ammonium thiocyanate and 2 g. potassium iodide. The solution is heated to boiling and a hot potassium iodide-mercury solution added until precipitation is complete. When the mixture has cooled, the precipitate is filtered off and washed with a wash liquid containing mercuric chloride, potassium iodide, ammonium thiocyanate and ethylenediamine. It is then washed with ethyl alcohol and finally with ethyl ether. After drying in a vacuum for ten minutes, it is weighed as $(\text{CuNH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{HgI}_4$.

The/....

The factor for converting the weight of the precipitate to the weight of copper is .8713. On account of the small copper content of the precipitate, the reagent is used mainly in the determination of small quantities of copper.

(44) Thionalide.

Thionalide is the p-aminonaphthalide of thioglycolic acid, $C_{10}H_7NHCOCH_2SH$, of structure,

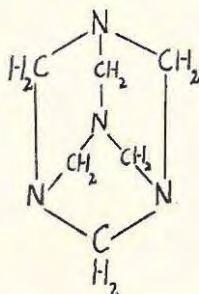


It is a reducing agent and forms complexes with the metals which form slightly soluble sulphides. Its application to copper has been described by Berg and Roebeling (65), and by Mayr and Gebauer (66). In acetic acid it precipitates most of the metals of the hydrogen sulphide and ammonium sulphide groups. In sodium hydroxide-tartrate solution, the following ions are precipitated :- cadmium, copper, iron (ferrous) gold, manganese, mercury and thallium. In potassium cyanide-tartrate solution the following ions are precipitated:- antimony, bismuth, gold, lead, thallium, and tin. In the presence of sodium hydroxide, thionalide precipitates bismuth, lead, mercury, and thallium. If the solution contains mineral acid, copper, as well as arsenic, bismuth, mercury and silver, is precipitated quantitatively, and can be separated from calcium, barium, iron, magnesium, thorium, zinc, cadmium, manganese, cobalt, nickel, chromium, lead and aluminium.

(44)/....

(iii) Hexamethylenetetramine.

Hexamethylenetetramine is $(CH_2)_6N_4$ and can give crystalline precipitates with the following :- Cadmium, antimony, tin, bismuth, magnesium, silver, mercury, gold, iridium, palladium, platinum, lead, lithium, cobalt, nickel, calcium, manganese, molybdenum and copper.



The only reference to its application to the determination of copper that could be found was in von Stein's, 'Organic Reagents In Inorganic Analysis' (65) where a paper by Dick (67) is quoted. Von Stein writes, 'The ... solution, containing ... copper, is boiled with ... the reagent and an excess of formic acid. The boiling is continued until all of the formic acid is driven off and the precipitate formed is filtered^{off} and washed. The residue is ignited to a constant weight and calculated as cupric oxide. Precipitations of copper with this reagent allows of the separation of the metal from alkalies, alkaline earths, manganese, magnesium, cadmium, nickel and cobalt. It is difficult to obtain a quantitative precipitation of copper in the presence of arsenic or zinc.'

(iv) Glucose.

Greaves (68) quotes a method involving glucose for the separation of copper from nickel. The method was originally evolved as an

improvement/....

improvement on the hydrogen sulphide separation. Potassium hydrogen tartrate is added to the solution. A solution of caustic potash in alcohol is next added, giving a blue solution of copper and nickel tartrates. This is cooled, treated with a solution of pure glucose, and boiled for one or two minutes. The copper is precipitated as the suboxide, which is washed, dried, ignited and weighed. The method is now completely out-of-date; no reference to it has been found in any literature since 1900. No figures are quoted by Crookes, so that no estimate of its merit can be made.

2(b) Analytical Methods For Copper In Which Nickel Interferes.

The methods outlined in this section are, on the whole, not as important as those included in the previous section. In most there is some disadvantage which limits its applicability.

(1) The Determination Of Copper With 8-Hydroxyquinoline.

8-Hydroxyquinoline (8-quinolinol, oxine) is C_9H_6N-OH , having the structure



The hydrogen of the hydroxyl group may be replaced by a large number of metallic ions, which co-ordinate with the nitrogen as shown. Oxine was first mentioned in 1881 by Skraup (69) who used some of its reactions for qualitative identifications. Its use in quantitative analysis has been developed largely by R. Berg (70) (71) (72) (73) (74) (75) (76) since 1927.

Oxine/.....

Oxine is a light buff coloured, crystalline powder, soluble in acids, acetone, ethyl alcohol, but almost insoluble in water. It is one of the most valuable organic precipitants known, precipitating in general the same ions as are precipitated by ammonia. The ions which are precipitated are determined by the pH of the solution, as is shown in the following table (77):-

Metal	Lowest pH at which precipitation takes place.	Minimum pH for perfect precipitation.	pH above which no precipitation takes place.
Aluminium	2.8	4.2	12.3
Zinc	2.8	4.4	
Cadmium	4.0	5.4	
Nickel	2.8	4.6	Above 13.2
Manganese	4.3	5.9	Above 12.3
Cobalt	2.8	4.2	
Titanium	3.8	4.8	12.0
Uranium	3.1	4.1	12.1
Thallium	3.7	4.4	12.5
Lead	4.8	5.4	
Calcium	6.1	9.2	
Magnesium	6.7	8.2	
Iron	2.4	2.8	
Copper	2.2	2.7	
Bismuth	3.5	4.8	12.9

In an ammoniacal solution, oxine will precipitate:- Beryllium, barium, calcium, cobalt, columbium, iron (ferric and ferrous), lead, magnesium, mercury (mercuric), molybdenum, nickel, strontium, tin, tantalum, titanium, tungsten, uranium, vanadium (vanadic and vanadous) and zirconium.

In a dilute acetic acid solution, oxine will precipitate:- Aluminium, antimony, cobalt, columbium, iron (ferric and ferrous), lead, manganese, mercury, (mercuric), nickel, silver, tantalum, titanium, uranium, vanadium, (vanadic and vanadous) and zirconium.

In/....

In an acetic acid solution buffered with an acetate, oxine precipitates:- Aluminium, bismuth, cadmium, copper, cobalt, iron (ferrie) indium, nickel, manganese, thorium, titanium and zinc.

In an ammoniacal solution buffered with a tartrate oxine will precipitate:- Cadmium, copper, magnesium, and zinc.

It is evident from the above that while oxine can be used to precipitate a very large number of ions, the universality of its reaction may be a decided disadvantage when separations have to be considered.

The most important analytical applications of oxine are to the determination of copper, bismuth, aluminium, zinc, nickel, magnesium and cadmium. Fleck and Ward (78) have shown that the following metals can be completely precipitated with oxine in acid and alkaline media, buffered with ammonia and sodium acetates, within the pH range shown.

Metal	pH
Cobalt	4.25 - 14.55
Molybdenum	3.70 - 7.40
Copper	5.56 - 14.50
Nickel	4.48 - 7.40
Magnesium	9.50 - 12.67
Zinc	4.7 - 15.55

Estimations with oxine may be performed either gravimetrically or volumetrically. In the former, the precipitated oximates are dried and weighed as such (the more common procedure), while in the latter they are redissolved and titrated either iodometrically or bromometrically. Ignition to the oxide is seldom employed, because of the high volatility of the compounds, though loss from this cause can sometimes be prevented by the addition of oxalic or sulphuric acid before ignition.

The/...

The Determination of copper with oxine is described by Berg (70), from whose paper the following details are taken. He uses two procedures; in one the precipitation is carried out in acid solution while in the other the medium is alkaline. In the first method, a slight excess of a 2% solution of oxine in alcohol is added to the warm solution, buffered with acetic acid-sodium acetate, and the temperature gradually increased. The precipitate which forms is filtered off, washed with hot water and either weighed or titrated iodometrically after having been dissolved in 5% hydrochloric or sulphuric acids.

In the second method the solution containing tartaric acid is treated with an excess of sodium hydroxide. As before, a 2% solution of oxine in alcohol is added, the solution warmed to 60-70°C, and the precipitate filtered from the cold solution. It is washed first with 1% sodium tartrate solution containing sodium hydroxide, and finally with distilled water. As before, the estimation can be completed either gravimetrically or volumetrically.

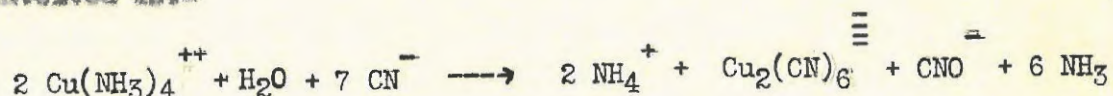
Berg (70) gives sets of figures illustrating the results of applying both procedures, the copper being estimated either by weighing or by an iodometric titration. They are sufficient to show the value of the method; the results tend to be slightly low, but no estimate of the accuracy is possible from his figures because, ^{firstly} there are insufficient results, and secondly, the weights he uses are so small that a considerable error is likely on that account, apart from any inherent in the method itself. For example, for three of the readings the copper content is 0.0025 g., which either (a) gives
a /....

a precipitate weighing 0.0719 g. (i.e. an error of 1 mg. in weighing at once vitiates the result by nearly 1%), or (b) requires on titration 0.80 ml. sodium thiosulphate (i.e. an error of only half a drop in the titration vitiates the result by over 3%). Of the thirteen titration volumes quoted, only two are over 25 ml., three are between 20 and 15 ml., one between 10 and 15 ml., five between 10 and 1 ml., and two less than 1 ml.

Oxine is seen to be a useful reagent for copper both in acid and alkaline solutions, though there are insufficient results available to allow of an exact comparison with other methods. One of the advantages of oxine is that it allows of the separation of copper from certain elements, such as arsenic and antimony, which interfere in the iodometric estimation. The main disadvantage attending its use is in the large number of interfering elements.

(11) The Estimation Of Copper By The Cyanide Process.

The cyanide process (79) for estimating copper is not as important as the cyanide process for nickel, and is used mainly as a routine method when no great accuracy is required. The reaction involved is:-



The copper solution is neutralised with sodium carbonate or hydroxide, the reagent being added until a slight precipitate forms. One ml. ammonium hydroxide is now added and the solution titrated with standard potassium cyanide. The blue colour changes to a pale

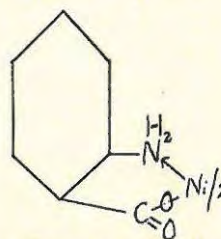
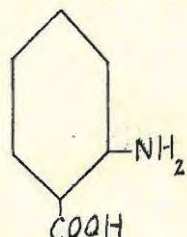
pink/....

pink, and finally the solution goes colourless. The potassium cyanide is standardised against pure copper.

Silver, zinc, nickel, cobalt and cadmium interfere. Large amounts of iron also interfere and must be removed, but the titration can be made in the presence of small amounts of iron. The chief appeal of the method lies in the simplicity and rapidity with which determinations can be made. The end-point, however, is very difficult to determine accurately, and with the more convenient iodide method available, the method has little to recommend it.

(iii) The Determination Of Copper With Anthranilic Acid.

Anthranilic acid (o-amino benzoic acid), $C_7H_7O_2N$,



in hot neutral solution forms addition complexes of the type shown, with copper, cobalt and nickel. Funk and Ditt (124), using the sodium salt, have described methods for the gravimetric determination of zinc, cadmium, cobalt, copper and nickel from neutral solutions of their salts.

Sherman, Smith and Ward (80) have investigated the effect of acetate buffers on the determination, and have shown that copper anthranilate, unlike zinc, cadmium, cobalt and nickel anthranilates, is not affected by the presence of acetate ions. They have also shown that precipitation of copper is complete over the range

pH/....

pH 5.3 - 7.3. They conclude 'that the conditions can be extended but little beyond the conditions specified by Funk and Ditt, who ... carried out precipitations from neutral solutions'.

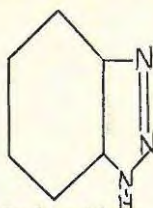
The reagent is relatively very cheap (4/10 per 100 g. - B.D.H. catalogue, 1946), is soluble in ethyl alcohol, ethyl ether, and boiling water, and 'all the precipitates are beautifully crystalline and very easy to handle, and except in the case of nickel we find the determinations under the conditions specified to be highly accurate; the range of separations which can be effected is, however, very limited' (80).

(iv) The Precipitation Of Copper With Sodium Hydroxide.

The precipitation of copper by sodium hydroxide is suggested (81) for its separation from elements such as molybdenum, vanadium, arsenic and tungsten. This procedure has a number of disadvantages:- organic compounds must be absent; the precipitate, except in small amounts, is inconvenient to work with; it is almost impossible to avoid contamination of the oxide with alkali. Its use today is very rare.

(v) The Estimation Of Copper With 1,2,3-Benzotriazole.

Benzotriazole is $C_6H_5N_3$, of structure -



Its use in the precipitation of copper has only recently been developed (82). With copper in ammoniacal solutions it gives a blue-green precipitate of composition $(C_6H_4N_3)_2Cu$. In the absence

of/....

of nickel, silver, ferrous iron, cadmium, zinc and cobalt, the copper may be estimated by direct weighing of the precipitate. If these ions are present, the precipitate must be redissolved and titrated iodometrically. On the other hand, copper can be precipitated from a solution containing arsenic, antimony, molybdenum and tin, which are coprecipitated with copper by hydrogen sulphide, and which interfere in subsequent iodometric titrations.

The precipitation is performed in tartaric acid-acetic acid solutions at a pH between 7.0 - 8.5. Below pH 5.0 no precipitation occurs, while at a pH 8.8 the precipitate begins to dissolve. Curtis showed (62) that variations in temperature between 25° and 100°, in the duration of the digestion, and in the volumes of the solution, do not affect the degree of completeness of precipitation of the copper. He also showed that as little as 0.2 mg. of copper in 200 ml. solution are determinable.

The author outlines a procedure for estimating copper in irons and steels. In these, interfering elements are usually present, so that the precipitation is only preliminary, and the estimation must be completed by ignition of the precipitate to the oxide, which is dissolved in acid and titrated iodometrically.

A table is included showing a comparison of analyses of copper ores by electrolysis and by benzotriazole. The results are excellent. Of the six results, four agree perfectly, the other two differ by 0.3% from the theoretical value.

As the use of this reagent is little known, it is considered

useful/....

useful to include, in full, a summary of its advantages and disadvantages, quoted from the original paper (82) :-

"The benzotriazole separation in the determination of copper in cast iron and steels possesses the following advantages over the hydrogen sulphide-iodide-thiosulphate method:

"It permits a more rapid dissolution of the sample than is possible in the other procedures, wherein a nonoxidising acid attack is advisable.

"It permits a more complete dissolution of the sample. This is most helpful in the analysing of certain cast irons which are not sufficiently decomposed by nonoxidising acids to yield a sulphide precipitation free from iron.

"It affords a clean separation from Mo^{++++} , Se^{+++} , Te^{+++} , Sb^{++++} , and As^{++++} , which may interfere in the iodide titration.

"The copper-triazole precipitate may be ignited more rapidly than the copper sulphide precipitate with less danger of fusion.

"The disadvantages attending the benzotriazole separation are:

"The reagent is expensive, 100 grams costing approximately \$25, and about 1 gram is used per determination.

"The conditions for precipitation are comparatively narrow (pH 7.0 to 8.5), whereas extreme latitude is permitted in the sulphide precipitation.

"The separation by benzotriazole is not practical for materials containing large amounts of nickel, cobalt, silver, cadmium and zinc because these metals also precipitate, and a large bulk of

precipitate/...

precipitate difficult to filter and ignite results."

(vi) Other Reagents For Estimating Copper.

This section is concluded, as was the previous, with a short list of organic precipitants which may be used to determine copper.

(1) 5,7-Dibromo-8-hydroxyquinoline.

This reagent forms slightly soluble compounds with copper, molybdenum, tungstate and trivalent vanadium. It has been used (83, 84) mainly to estimate very small quantities of copper such as might be found in industrial water. A 0.5% solution of the reagent in 5N hydrochloric acid, or a saturated solution (about 0.5%) in acetone, is added to the copper solution, which is digested for 30 minutes on a water bath. The precipitate is filtered off, dried at 105°C and weighed as $C_{12}H_7Br_2N_4Cu$.

(ii) Acetylene.

Copper may be determined by precipitation as the acetylide, and titration of the latter with potassium cyanide solution, according to the equation:-



Iron and zinc interfere, but this may be avoided by the addition of sodium phosphate. No references were available to the writer but Yoe and Sarver (61) quote a number:- (85) (86) (87) (88) (89).

(iii) Pyridine/...

(iii) Pyridine.

A neutral or faintly acid solution of a copper salt on treatment with ammonium thiocyanate and pyridine precipitates quantitatively dipyridine copper dithiocyanate, $\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_2$. The precipitate is filtered off and washed first with an aqueous solution of pyridine and ammonium thiocyanate, then with pyridine and ammonium thiocyanate in alcohol, next with pyridine in ethyl alcohol, and finally with pyridine in ether. It is dried in a vacuum desiccator and weighed. Chalk (90) has shown that aluminium, antimony, bismuth, cadmium, chromium, lead, manganese, mercury (mercuric), tin (stannic and stannous), titanium, uranium and zinc do not interfere. Cobalt, mercury (mercurous), nickel and silver interfere. The advantage of this method is the speed with which an estimation can be performed; a determination is said to take from one to one and a half hours. Further information is contained in references (91) (92) (93).

(iv) The Determination of Copper With Salicylimine.

In a recent paper (94) a description is given of the use of salicylimine to determine copper and nickel. Both copper and nickel are quantitatively precipitated between pH's 7-11. The procedure for the determination of both is identical. 5% of sodium tartrate is added to the solution, followed by an excess of ammonia and salicylimine solution (prepared by dissolving salicylaldehyde in ammonium hydroxide). The precipitate is filtered off and washed. After drying to constant weight at

100°C./....

100°C., it is weighed. A set of 6 results for copper determinations shows a deviation of only 1 in 600 from the theoretical. The chief interfering ions are iron (ferric and ferrous), vanadium and palladium. The original paper is extremely sketchy about details, but the results show that the application of salicylimine is, at least, worthy of further study.

2. Analytical Method For The Determination Of Nickel.

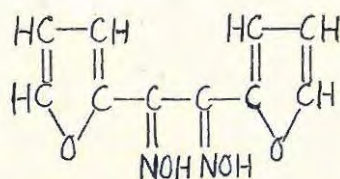
(a) Methods In Which Copper Does Not Interfere.

The analytical procedures discussed in this section contrast with those outlined above, in that the majority are not specific for nickel in the presence of copper, whereas most copper estimations may be performed in the presence of nickel. There are, in fact, only two methods of any importance in which copper does not interfere. These two methods are discussed below.

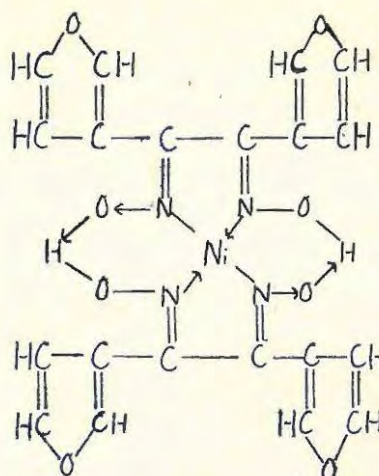
(1) The Determination Of Nickel With α -Furildioxime.

The use of α -furildioxime for determining nickel has been proposed by Soule (95), who studied it in the hope of finding a reagent superior to dimethylglyoxime and α -benzildioxime.

His first step was to show that it could be synthesised fairly cheaply. He started with commercial furfural, which he first converted into furoin, and this in turn into furil by Emil Fischer's method, slightly modified. The furil was refluxed with hydroxylamine hydrochloride in the presence of methanol giving α -furildioxime.



α -furildioxime



α -furildioxime - nickel complex

The product obtained was found to be sufficiently pure for the analytical investigations.

He then showed that the reagent provides a considerably more delicate test for nickel than either dimethylglyoxime or α -benzildioxime, and quotes the following comparison:-

<u>Reagent</u>	<u>Ratio</u>	<u>Sensitivity (Mg. per cc.)</u>	
Dimethylglyoxime	1:400,000	0.0025	(96)
α -benzildioxime	1:2,000,000	0.0005	(97)
α -furildioxime	1:6,000,000	0.00017	

Only one reagent more sensitive to nickel could be found from a search of the literature, viz. potassium dithio-oxalate (98), which gives a magenta colour easily visible in a test-tube, when 1 part of nickel is present in 8,000,000 of solution.

Tests showed that very few ions precipitated with the reagent. The only common one was ferrous iron; palladium and platinum also gave precipitates. In ammonia solution silver, copper, zinc, iron (feric), chromium, aluminium, cobalt and manganese gave no precipitates with α -furildioxime. Ferrous iron, however, gave a greenish colour/....

colour in an ammoniacal solution containing less than 1 part in 3,000,000. On increasing the concentration the colour darkened through blue to purple, until finally a purple precipitate formed. It was found, however, that if the α -furildioxime was not purified, several ions, particularly copper and cobalt, gave tests with it.

The method of analysis adopted was as follows:- The nickel solutions was diluted to 100 ml., ammonia added until the solution smelt slightly of it and an excess of the dioxime reagent added slowly with stirring. The precipitate coagulated rapidly, and the nickel was then determined by one of a number of methods. It could be determined directly by filtering off the precipitate through a Gooch crucible, washing with warm water, and weighing.

Alternatively, filter paper was used to separate the precipitate, which was then redissolved in nitric acid. The paper pulp was removed by filtration, and the filtrate evaporated after addition of concentrated sulphuric acid. This eliminated excess nitric acid and organic matter. The nickel was deposited electrolytically from this solution after it had been made ammoniacal.

At first, care was taken to remove the last traces of organic matter and to secure an electrolyte having the characteristic colour of an ammoniacal solution. 'It was discovered, however, that this was unnecessary. Solutions varying from dark red through yellow to violet, are electrolysed with no apparent difficulty or difference to results'. (95).

A third procedure used by Soule was 'collecting the dioxime

precipitate/...

precipitate on a filter paper, drying at 120° - 130°C . and weighing (presumably using counterpoised filter papers), and then, as a check, igniting to nickelous oxide in a covered crucible. After the oxide had been weighed, it was converted to the sulphate. This was dissolved in water and the nickel determined by electrolytic deposition.

Finally, the nickel could be determined cyanometrically. The precipitate and filter paper were transferred to a beaker containing nitric acid. On heating, the precipitate dissolved and most of the organic matter was destroyed. The solution was filtered, and ammonium persulphate added to the filtrate, which was then heated to destroy the last traces of organic matter. The nickel in this solution was then determined by a cyanide titration (q.v.).

α -furildioxime may be used to separate nickel from zinc, manganese or cobalt, but offers no particular advantage over dimethylglyoxime. Ferric iron also does not interfere as long as tartaric or citric acid, or their sodium salts, are added. Citrates and tartrates, however, have a tendency to reduce ferric ions to ferrous ions particularly in the presence of sunlight, and, as ferrous ion interferes, there is a danger that the nickel precipitate may be contaminated with ferrous furildioxime. Soule has shown that this can be avoided by the addition of sodium pyrophosphate, or simply by filtering within half an hour of precipitation.

The results quoted in Soule's paper are insufficient to

allow/....

allow of an estimate of the accuracy of this method, though they do show that it is probably of the same order as that obtained using dimethylglyoxime. The factor for the nickel-furildioxime precipitate is .1181, compared with .2031 for nickel dimethylglyoximate; this means that a particular weight of nickel gives nearly twice the weight of precipitate with α -furildioxime that it would with dimethylglyoxime. This, together with its greater sensitivity and the fact that the nickel-furildioxime complex is less soluble in alcohol than the nickel-dimethylglyoxime precipitate, makes it especially valuable in the determination of small quantities of nickel. A further point in its favour is, of course, the small number of interfering ions. Against all these advantages, however, is the great disadvantage of its price, viz. 5/- per gram (B.D.H. Catalogue, 1948) - the cost of 25 g. AnalaR dimethylglyoxime - which militates against its use in any but specialised work.

(11) The Separation Of Nickel From Other Elements By A Cyanide Process.

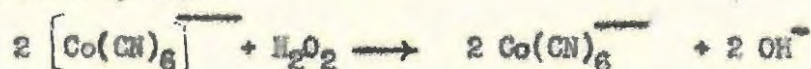
An extremely useful method, using cyanide, which enables nickel to be separated from aluminium, beryllium, columbium, chromium, cobalt, copper, iron, manganese, molybdenum, tantalum, silicon, titanium, vanadium, tungsten and zirconium has recently been published (101). The solution is treated with excess potassium cyanide so that the precipitate which at first forms is redissolved.

The/...

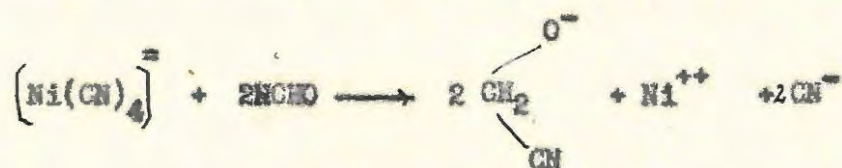
The cyanide forms addition compounds with the metals thus -



Hydrogen peroxide is added and the solution boiled. The nickel addition complex is unchanged, but the other complexes are oxidised, e.g.



Excess peroxide is removed by boiling, and formaldehyde and solid dimethylglyoxime added. The formaldehyde selectively decomposes the nickelous complex, leaving the other complexes unaffected.



The nickel is then precipitated by the dimethylglyoxime. Alternatively the nickel may be determined electrolytically or cyanometrically. Iron and chromium interfere; iron is extracted with iso-propyl ether, and chromium is converted to chromate with perchloric acid, the chromium being volatilised off by heating with hydrochloric acid.

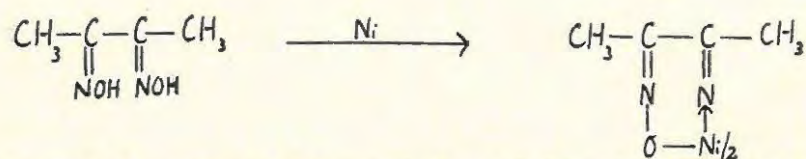
A set of readings for five alloys shows excellent results, the average error being 1 in 350.

2.(b) Analytical Methods For Nickel In Which Copper Interferes.

Almost all the more important procedures for nickel, including of course, the dimethylglyoxime method, fall into this section. Several of the reagents described here have already been discussed in the sections dealing with copper; in these cases the only additions are data specifically related to the use of these reagents in the determination of nickel.

(i) The Determination Of Nickel With Dimethylglyoxime.

Dimethylglyoxime is $C_4H_8O_2N_2$,



and is a white crystalline solid, soluble in ethanol and ether, but insoluble in water. It is one of the best, and certainly the most widely known of the organic precipitants, reacting principally with nickel and palladium. Use was first made of it for the qualitative precipitation of nickel by Kraut (99), and in (100) 1907 Brunck used it to estimate nickel. Its introduction was a landmark in the study of organic reagents in inorganic analysis.

With nickel, dimethylglyoxime gives a stable, crystalline, brilliant red salt of definite composition, of a high degree of purity and extremely low solubility. It is insoluble in dilute ammonium hydroxide, in solutions of ammonium salts, in excess of the reagent and in dilute solutions of acetic acid containing sodium acetate. It is soluble in free mineral acids (thus the precipitation/...

precipitation is incomplete in neutral solutions of nickel chloride, sulphate or nitrate; if, however, the free acid formed is neutralised with sodium, potassium or ammonium hydroxide or by the addition of acetate salts of these bases, nickel is completely precipitated), in cyanide solution, in alcoholic solutions containing not more than 50% of alcohol by volume, and in concentrated solutions of cobalt.

Its great advantage is that it will precipitate nickel quantitatively in the presence of cobalt, and in general there are few interfering ions. A disadvantage is its insolubility in water, so that there is a tendency for excess of the reagent to precipitate; this danger is all the greater if cobalt is present as well, when excess reagent must be added to combine with the cobalt. Further, too much alcohol increases the solubility of the precipitate (100).

Very few ions interfere with the precipitation. Palladium, however, is precipitated in weakly acid or weakly ammoniacal solutions. As a general rule it is better to eliminate members of the hydrogen sulphide group before the precipitation of the nickel. The literature, however, tends to be rather vague on the extent of their interference, and the statements are generally expressed qualitatively, e.g., 'moderate amounts of copper, arsenic, molybdenum and probably several others of the group do not interfere', (102). The details about copper, in particular, are vague. In small concentrations it gives a very delicate colour reaction

with/...

with dimethylglyoxime, which will actually detect 1 part in 10,000,000 but does not precipitate. In fact, Reif (103) actually uses dimethylglyoxime to separate nickel from copper on a micro-scale, the copper being estimated in the filtrate with salicylaldoxime. However, when 'much copper is present it must be removed, as should most of the other members of the hydrogen sulphide group' (104). No quantitative qualifications to the 'moderate' and 'much' could, however, be found. Further discussion on the effect of the presence of copper will be found in the practical section of this work.

Besides palladium, gold and platinum also contaminate the precipitate. Silicon and tungsten in amounts up to a few milligrams do not interfere; in greater amounts they must be removed. If much ferrous iron is present the results tend to be high. If this is the case the iron should be oxidised to the ferric state, and tartaric acid added, producing a complex tartrate which does not form the hydroxide with ammonium hydroxide.

If iron, aluminium, cobalt, manganese or zinc are present, tartaric or citric acids are added before the solution is made ammoniacal. When much cobalt is present, precipitation is more complete and the precipitate formed purer, if an excess of sodium acetate instead of ammonium hydroxide is added to the weakly acid solution. The general procedure in the presence of some cobalt, manganese or zinc is as follows:- Any iron present is oxidized, excess oxidising agent removed, and tartaric acid added. The
solution/...

solution is diluted and boiled. After the solution has cooled the pH is adjusted with ammonia to 7.5 - 8.1 using an indicator. If a precipitate forms it is dissolved with tartaric acid, ammonia then being added until the solution is slightly alkaline. This is repeated until the solution is clear when in an alkaline state, when the solution is acidified with hydrochloric acid and heated to 70°C. Dimethylglyoxime is added, followed by ammonia, until precipitation is complete. The solution is heated to coagulate the precipitate, which is filtered off, washed and weighed.

The dimethylglyoxime, in the form of a 1% alcoholic solution, is generally added to a warm weakly acid solution of the nickel salt, and ammonia then added. This procedure gives a precipitate which is more easily filtered.

When copper, cobalt and manganese are present, extra amounts of the reagent must be added, as these ions react with it, and extra time must be allowed for precipitation. As much as two days may be required for the complete precipitation of very small amounts of nickel from solutions containing cobalt salts. Apart from the usual method of dissolving it in alcohol, several other ways for preparing the reagent have been suggested. Hillebrand and Lundell (105) suggest its dissolution in ammonium hydroxide; Kasey (106) has recommended that it be dissolved in hot water containing 0.7% sodium hydroxide. Recently, Raithel (107) has claimed to have improved the method by using 1 g. of the reagent dissolved/...

dissolved in 100 ml. water containing 1 g. sodium peroxide. The solution thus prepared is claimed to have the advantages of eliminating the slight solubility of the nickel dimethylglyoxime in alcohol, and being less expensive. He published the following table to justify his claim:

<u>Aqueous Dimethylglyoxime.</u>	<u>Alcoholic Dimethylglyoxime.</u>
3.28%	3.25%
3.26%	3.27%
3.29%	3.26%
3.29%	3.25%
Theoretical Nickel 3.23	

Very shortly afterwards, however, it was shown (108) that this method has little to recommend it. In the first place, unless the sodium peroxide and dimethylglyoxime are dissolved in not less than 50 ml. water, the reaction is dangerously violent. Further, 'it would seem that the sodium peroxide used by Raithel was not fresh, but sodium hydroxide ... Our determinations of nickel with the reagent prepared in this manner were unsatisfactory, giving results 0.3 to 0.4% too high, owing to contamination of the nickel dimethylglyoxime precipitate by ferric hydroxide. Satisfactory results were obtained after the reagent solution had been allowed to stand for three weeks at which time little, if any, peroxide remained in the solution. It was also shown that in as much as dimethylglyoxime is a mild reducing agent, it was gradually destroyed by oxidation by the peroxide, considerably more rapidly than in sodium hydroxide solution'. (108).

A/...

A short paper (109) published in 1934 proposed that the contamination of the nickel dimethylglyoxime precipitate with copper could be prevented by the preliminary addition of sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) to the solution. The author of this paper, Renedo, is vague about quantitative details and does not state any relation between the amount of copper present and the amount of hydrosulphite to be added. He gives no theoretical explanation, and quotes only one result - the analysis of a copper-nickel alloy, which gave good results. These points are discussed in Part 2.

Dimethylglyoxime, then, is the standard reagent for nickel. Although not as sensitive as some (e.g. α -furildioxime) nor as convenient as others (e.g. salicylaldoxime), it has the great advantage of being relatively cheap (4/11d. per 25 g. AnalaR-B.D.H. Catalogue 1946).

(11) The Determination Of Nickel With α -Benzildioxime.

α -benzildioxime, the third of the dioxime trio for estimating nickel, was first applied to the determination of nickel by Atack in 1913 (110). He showed that its use provides an extremely delicate test for nickel, capable of detecting 1 part in 2,000,000. The test is more delicate for nickel in the presence of cobalt than that using dimethylglyoxime; 1 part of nickel in 1,000,000 in the presence of 100 times the amount of cobalt is readily detected by α -benzildioxime. Ferrous salts, which produce an intense pink colour with dimethylglyoxime, do not mask the reaction between nickel and α -benzildioxime.

Quantitatively/...

Quantitatively it is an excellent reagent for estimating nickel, particularly in small amounts. Its application is restricted to the determination of small amounts of nickel for two reasons, firstly because the extremely low solubility of the reagent (a 0.02% alcoholic solution is used), makes the volumes involved, except in the determination of very small amounts of nickel, impracticably large; secondly, because the factor is only .1093 and a small amount of nickel produces a large quantity of precipitate. As a result it is general to estimate less than .025 g. nickel.

A 0.02% alcoholic solution of the reagent is added to the ammoniacal nickel solution, and the precipitated coagulated by heating the whole for a few minutes on a water-bath. An advantage of the procedure compared with that involving the use of dimethylglyoxime is that precipitation is complete within a few minutes, instead of the longer time (generally about an hour) needed completely to precipitate and coagulate the nickel dimethylglyoximate. The precipitate is filtered off through a Gooch, washed with warm 50% alcohol and hot water, and is finally dried at 110°C. The final estimation is gravimetric, the precipitate being weighed. No volumetric variations are mentioned in the paper (110). Ignition to the oxide gives unsatisfactory results, due 'possibly ... to the retention of small amounts of carbon, even though ammonium nitrate was added before the final ignition'.

The/...

The results obtained using this procedure are excellent. Atack (110) quotes a set of 6 results, which give on the average a deviation of 1 in 400 from the theoretical values.

The method gives satisfactory results for the determination of nickel in the presence of cobalt. Owing to the formation of a soluble cobalt salt of the dioxime, excess of the reagent must be added, the precipitate being washed until the filtrate is colourless. A set of four results for the determination of nickel in the presence of cobalt is included, in Atack's paper, giving an average deviation of 1 in 250 from the theoretical values.

In the presence of iron, sodium citrate is added to prevent the iron from precipitating in ammoniacal solution. The results of three estimations reported by Atack and performed on iron-nickel mixtures differed on the average by 1 in 250 from the theoretical values.

In the presence of manganese, precipitation is effected by the addition of a fairly large excess of an alcoholic solution of α -benzildioxime in slightly acid (acetic acid) solution. 'Satisfactory results were obtained' (110). No figures are quoted.

Zinc or magnesium are kept in solution by the addition of a large amount of ammonium chloride, precipitation being performed in an ammoniacal solution. Under these conditions neither element interferes.

In the/....

In the presence of chromium, the precipitation is carried out in dilute ammoniacal solution, containing tartrate. The nickel precipitates quantitatively.

Nitrates interfere and must first be removed by evaporation to fuming with sulphuric acid. Copper also interferes and must be removed either by hydrogen sulphide or by some other suitable method.

A disadvantage of the reagent is its cost, viz. 14/6 per 25 g. (B.D.H. Catalogue, 1946), though it can be synthesised very cheaply from benzil and hydroxylamine hydrochloride. The two are boiled together in methyl alcohol for three hours. The precipitate formed is filtered off, washed with hot water and a small amount of 50% alcohol. On drying it should consist of pure α -benzildioxime (m.pt 237°C). The method using this reagent is not subject to much interference from other ions and such interference as does occur can be fairly easily guarded against. A big disadvantage of the reagent is its very slight solubility, which not only necessitates the use of large quantities of alcohol in the preparation of the reagent but also makes the volumes involved very cumbersome. On the whole the results obtained by the use of this reagent are about the same in accuracy as those obtained using dimethylglyoxime, though

α -benzildioxime is superior for the estimation of small quantities of nickel. Its disadvantages, however, outweigh its advantages, and it is not extensively used.

(111)/....

(iii) The Estimation of Nickel By Titration With Potassium Cyanide.

Of volumetric procedures for determining nickel, the cyanide method is the one most commonly used. It is not a good method for an occasional estimation where a high degree of accuracy is required. Its particular use is in the routine determination of nickel in alloys and ores, where the accuracy required is not too high. The main trouble attending its use is the indefiniteness of the final disappearance of the turbidity which makes the exact determination of the end-point difficult. The accuracy attainable depends to quite a considerable extent on the experience of the experimenter in assessing the end-point of the titration. Once he has standardised his own procedure results of good accuracy can be obtained.

The theory of the method depends on the reaction in the ammoniacal solution between hexamine nickel ions and cyanide ions to give the more stable cyanide complex ion.



If potassium cyanide is added to a solution containing the nickel-hexamine complex with some silver iodide in suspension, the cyanide will react preferentially with the complex until the above reaction has gone to completion, whereupon any excess cyanide will react with the silver iodide.



i.e. the insoluble silver iodide forms a soluble complex and the

turbidity/...

turbidity of the solution will disappear.

Thus, if a solution containing nickel ions, ammonia and silver iodide is titrated with potassium cyanide, the presence of excess cyanide will be indicated by the disappearance of the turbidity. The silver iodide acts as an indicator for the presence of excess cyanide.

The potassium cyanide solution can be standardised similarly by direct titration with a standard silver nitrate solution, which reacts with potassium cyanide to form the complex $KAg(CN)_2$; if a solution containing iodide and cyanide is titrated with silver nitrate no precipitate forms until the silver present is more than equivalent to the cyanide present.

The estimation of nickel by this method, then, involves the following steps:-

1. The cyanide solution is first standardised by direct titration with a standard solution of silver nitrate in the presence of potassium iodide as indicator.
2. Potassium iodide and a known volume of silver nitrate (of known normality) are added to the solution, which is then titrated with the standardised potassium cyanide solution.

Iron, manganese, chromium, vanadium, molybdenum and tungsten do not interfere; copper, cobalt and zinc do and must therefore be removed if present.

The procedure followed is quite standard, the only variation being the use of silver nitrate solutions of different volumes

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and strengths. Vogel (111) and Clowes and Coleman (112) recommend the addition of 0.5 ml. of a 0.1 N solution of silver nitrate. Silverman and Gates (113) and Silverman, Goodman and Walter (114) use a 0.02 N solution of which 5 ml. is added. Scott (115) recommends a decinormal solution of which 5 ml. are added. In practice, there is little to choose between them.

The silver nitrate solution should not, however, be stronger than decinormal, as there is a danger of the silver iodide settling out as a curdy precipitate. A large excess of ammonia should be avoided as silver iodide is soluble in excess.

To sum up:- The cyanide titration is a valuable routine method for nickel analysis, being rapid and convenient. By a subjective standardisation of the procedure results of good accuracy can be obtained.

(iv) The Determination Of Nickel With Salicylaldoxime.

Salicylaldoxime and its use in the separation and determination of copper have already been described (p.24), and it has been mentioned that since both copper and nickel are quantitatively precipitated by the reagent, and since copper is completely separated at a pH lower than that at which nickel starts to precipitate, salicylaldoxime can be used not only to separate and estimate copper, but also to determine the nickel in the filtrate by a suitable adjustment of the pH. At a pH of about 7 the nickel is precipitated completely and may be determined by filtering off and weighing the precipitate.

IT/....

It only remains to mention one additional point, viz. the question of the optimum pH for the precipitation of the nickel, about which there is some divergence of opinion. Riley (87) recommends the precipitation of nickel from a solution which is just acid. Pearson (116) states that in mixtures containing zinc and low concentrations of ammonium salts, the precipitation must be carried out at a pH of exactly 6.5. On the other hand workers at Hopkin and Williams, Ltd., (117) specify a pH of from 7 to 8 as necessary for complete precipitation of the nickel. Chambers (118) also separated the nickel from an alkaline solution. Diefeld and Howe (38) state that the quantitative precipitation of nickel starts at pH 7, and that determinations performed on solutions having a pH as high as 9.9 give satisfactory results, but that at a pH less than 7 results are low. They suggest, 'perhaps the presence of other salts affect the solubility of the nickel complex as in the case of zinc', but do not carry the matter any further.

Salicylaldehyde is an accurate and precise reagent for nickel. Six results, each in duplicate, given by Riley (87) in a determination of the nickel in the filtrate from a copper separation, show a mean deviation of only 1 in 450 from the theoretical values. It is also an extremely convenient reagent to work with. On the debit side is the interference of cobalt. Also its cost is high, viz. £4/6 per 25 g. (B.D.H. Catalogue, 1946), though it can be easily synthesised from salicylaldehyde (27/6 per/...

per 500 g.) and hydroxylamine hydrochloride (34/7 per 500 g.). By mixing the two in equivalent quantities and heating, a yield 90% of the theoretical is obtained, which can be used without any crystallisation or purification. Salicylaloxime decomposes slowly in solution, and the decomposition products are removed with difficulty. For this reason the reagent should always be prepared fresh, and no reagent more than 3 days old should be used.

(v) The Determination Of Nickel With 8-Hydroxyquinoline.

The use of oxine as a precipitant, and the question of pH and of interfering elements have been described previously (p.41). Its application to the determination of nickel is due to Berg (119) and follows the same form as that for copper. The nickel is precipitated in an acetic acid-sodium acetate solution of pH about 5. The precipitate may either be dried at 105°C. and weighed as $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2 \text{H}_2\text{O}$, or it may be dried at 140°C. and weighed as the anhydride. No preference is stated by the author who gives a few results. These show that the method is fairly accurate, but they do not allow any more definite opinion to be stated.

(vi) The Estimation Of Nickel By Farr and Lindgren's Method.

Farr and Lindgren's Method (120) is a volumetric modification of the dimethylglyoxime method. The original paper, however, was not available, and the only reference that the writer could find was in Scott's 'Standard Methods Of Chemical Analysis' (121).

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The nickel is precipitated with dimethylglyoxime in the usual way, and the precipitate is filtered off through a quantitative filter. After washing, the precipitate, together with the filter, is transferred to a beaker, and dissolved in dilute sulphuric acid. The excess sulphuric acid is diluted and titrated back with standard sodium hydroxide. The interfering elements are the same as those in the dimethylglyoxime method. The procedure has been developed in Part 2 of this thesis.

(vii) The Precipitation Of Nickel As The Hydroxide.

The use of alkali hydroxides in analytical chemistry has already been outlined in the section dealing with copper. Nickel can be precipitated from a boiling solution by the addition of an alkali hydroxide if the solution is free from ammonium hydroxide, and contains either alkali persulphate, peroxide, hypobromite or hypochlorite. The best method of precipitation is nearly ^{to} neutralise the solution with sodium hydroxide, and then to pour slowly with stirring into an excess of hot alkaline solution of alkali (not ammonium) persulphate. The hydroxide formed is filtered off and ignited to the oxide.

This procedure has little of advantage to offer. It is inaccurate because of the retention of the alkali by the precipitate, which is also contaminated with silicon. For any degree of accuracy it is necessary to perform a double precipitation, making the procedure very laborious.

(viii)/...

(viii) The Precipitation Of Nickel As The Sulphide.

This method, like the previous, is completely obsolete. Nickel can be precipitated with hydrogen sulphide either in acetic acid-sodium acetate solution or in ammonium sulphide solution. Both methods are unsatisfactory; in the former, precipitation is usually incomplete, and in the latter there is a tendency for the nickel to pass into solution. A large number of ions interfere.

(ix) The Determination Of Nickel With Anthranilic Acid.

Anthranilic acid is not as good a reagent for the determination of nickel as it is for that of copper. The original method of precipitation was to add the reagent to a boiling solution with constant stirring. The solution is boiled for several minutes to coagulate the precipitate, and cooled for 10 minutes. The precipitate is filtered off, washed first with a solution containing 5% of the reagent and then with alcohol, dried at 105°C. and weighed.

Shenman, Smith and Ward (122) studied the effects of buffers on the precipitation. They showed that in unbuffered solutions the results are 1% high; in sodium acetate over 1% low; in sodium tartrate rather high. The two results given for determinations in ammonium acetate solutions differ by only 1 in 500 from the theoretical. Considering the cheapness of the reagent, and the results quoted by Shenman, Smith and

Ward/...

Ward, this reagent would seem to offer a very convenient method for the estimation of nickel once the optimum pH conditions have been standardised.

(x) The Estimation Of Nickel With Pyridine.

Nickel precipitates with pyridine just as copper does, forming the complex $\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2$. The experimental conditions are the same as those described under copper.

Dobbins and Sanders (125) have described a volumetric variation of this method which they claim is as accurate as best volumetric methods, and more convenient. The nickel is precipitated with pyridine in the usual way, except that instead of adding 1 g. ammonium thiocyanate, an excess of a 0.1 N solution of ammonium thiocyanate is added. The precipitate is separated by filtration and from the filtrate a 100 ml. aliquot is drawn off. To this is added 1 ml. nitric acid and a measured excess of 0.1 N silver nitrate. The excess Silver nitrate is then titrated back with the 0.1 N ammonium thiocyanate using ferric alum as indicator. This method can be used for both cobalt and nickel; if both are present, the nickel and cobalt are determined together by this method and the nickel determined separately by dimethylglyoxime.

The authors give two sets of six readings to illustrate the application of the method to the determination of nickel. The first set gives a mean value of 0.0126 g. nickel compared with the dimethylglyoxime value of 0.0125 g.; the second set gives a mean of 0.05065 g. nickel compared with the dimethylglyoxime value/....

value of 0.0506 g.

To judge from the above-mentioned paper this would appear to be an excellent volumetric method. The results quoted are good, the method is quick (the estimation being performed on the filtrate avoids the necessity to drain and wash the precipitate), the reagents are cheap, and the end-point sensitive.

(xi) The Determination Of Nickel With Salicylimine.

The use of salicylimine in the determination of nickel is identical to that previously described for the determination of copper (see p. 51). The results obtained in nickel estimations seem to be less accurate than those obtained in copper determination. A set of six results included in the original paper (94) show an average deviation of 1 in 400 from the theoretical nickel content.

THE STATISTICAL TREATMENT.

The science of statistics may be roughly defined as the study and interpretation of chance variations. Statistical analysis has been applied in the past in such fields as biological and agronomic research, and to certain problems in chemical industry. In recent years there has been a growing tendency to use statistical methods in interpreting and comparing the results of analytical determinations. The figures obtained cannot, obviously, reveal anything that is not already implicit in the data; their function is to simplify and objectify the results. In fact the only reliable way to compare two or more methods is to analyse statistically a large number of results obtained by the use of the various procedures.

The present author has made extensive use of statistical analysis in the following pages both to show the types and magnitudes of the errors involved in any particular estimation, and also to allow a precise comparison of the various methods to be made. The following four quantities have been evaluated in each case.

The Standard Deviation (σ) is a measure of the precision or reproducibility of the results. It is defined as

$$\sigma = \frac{\sum d^2}{n - 1}$$

where d = Deviation of a reading from the mean value
 n = Number of readings.

The accuracy /..

The Accuracy (ϕ) is a measure of the actual correctness of the results. It is defined as

$$\phi = \frac{\sum d^2}{n - 1}$$

where d = Deviation of a reading from the theoretical value.
 n = Number of readings.

Ideally an analytical procedure should have a high degree of both accuracy and reproducibility, i.e., the values of σ and ϕ should be small.

The Probable Error is a quantity such that in any set of observations it will be equally probable that there will be the same number of errors less than it as there are greater than it.

$$\text{Probable Error} = \frac{2}{3} \times (\text{Standard Deviation}).$$

The Standard Error (ψ). The standard deviation calculated from a number of readings, say n , is liable to error, viz. error due to random sampling. Obviously, however, the larger n is, the more representative is the sample, and the more likely it is that the calculated standard deviation is ^{the} correct value. The standard error is the term used to connect the standard deviation with the number of readings used in its computation. It is defined as

$$\psi = \frac{\sigma}{n}$$

Thus, though the standard deviations for two cases may be identical, the standard errors will be the same only if the same number of/....

of readings were used in each case. If, however, the number of readings used was different, then that case for which there were more readings will have the smaller standard error, indicating the smaller chance of error resulting from more thorough sampling.

In the pages that follow each set of results is accompanied by another table in which the actual values of the above four quantities have been worked out for those results. For comparative purposes, however, these values are of no use, as they depend on the amount of substance present. For example, the two cases below are obviously of equal accuracy though the statistical terms evaluated as described above will be different:-

Theoretical.	Found.	Theoretical.	Found.
	.1001		.5005
.1000	.1001	.5000	.5005
	.1001		.5005

To reduce the accuracies, etc., to a comparative basis it is necessary to express the results as a percentage. A second table is therefore included in which all the quantities given in the first table are expressed as a percentage. The first table shows the absolute values of the different quantities for a particular weight of metal present, whereas the second reduces them to a common denominator and allows direct comparison between the various methods to be made.

PART 2. PRACTICAL.

The Preparation of Standards.

Copper.

Standard copper solutions were prepared from 'Kahlbaum pro analysis' copper sulphate, three times recrystallised. The solutions so prepared were standardised by electro-deposition determinations, which procedure, had itself previously been standardised against a standard sample of copper, 99.98% pure, supplied by the British Bureau of Standards. Different weights of the copper were dissolved in the minimum amount of dilute nitric acid, and when solution was complete sulphuric acid was added. Excess nitric acid was evaporated off. After dilution, 5 ml. dilute sulphuric acid and 1 ml. nitrous free nitric acid were added and the copper deposited electrolytically.

The results obtained from the standardised electrolytic method agreed to within 1 in 2000 with those calculated from the weight of copper sulphate present, and standard copper solutions were subsequently prepared by direct weighing. The recrystallised copper sulphate was checked monthly to test for any possible alteration in its composition. No change was found during the longest stretch for which one particular sample was used, viz. three months.

Nickel.

Standard nickel solutions were prepared from three-times recrystallised nickel ammonium sulphate, Merck grade, which had been shown to be cobalt free by tests described by Vogel (125).

These/....

These solutions were then standardised with dimethylglyoxime, the results agreeing to within 1 in 1200 with the results calculated from the weight of nickel ammonium sulphate present. Due to the slight solubility in alcohol of the nickel-dimethylglyoxime addition complex, the results with dimethylglyoxime were the lower of the two, and the direct calculation by weight was therefore taken as standard. The Nickel Ammonium Sulphate was found to remain unaltered over a period of two months.

In the cases of both copper and nickel the concentrations of the ions were known with certainty to within 1 in 1000, and almost certainly to within 1 in 2000.

1. The Separation And Estimation Of Copper And Nickel With Salicylaldoxime.

Salicylaldoxime is another of the well known oxime reagents such as dimethylglyoxime, α -furildioxime, α -benzildioxime, α -benzoinoxime, which are among the best organic precipitants. The work done on it and the information available is, in general, less than that on the others, and for that reason it is considered here in more detail than other reagents in later sections. Another reason for the fuller discussion is that it is a unique reagent in copper-nickel analysis, in that it is the only reagent that can be used not only to separate copper from nickel, but can also be used to determine both.

The main points to be investigated here are:-

- (1) A determination of the accuracy and precision of the method/....

method. From this it will be possible to establish its analytical merit and its comparative relation to the other more widely known procedures.

(ii). The standardisation of the optimum pH for precipitation and separation, and the investigation of the pH range within which these are complete, so that a decision may be made between the various different conditions described in the literature.

(iii). A more complete and comprehensive study of certain interfering elements about which the literature is vague, and an attempt to develop methods to eliminate their interference.

First is given a description of the reagent itself and of the procedure followed in its analytical application.

Preparation of Salicylaldoxime Reagent.

A 1% alcoholic solution of salicylaldoxime was used for the estimations. It was prepared, following Ephraim's procedure (36), by adding 1 g. salicylaldoxime in 5 ml. 95% alcohol to 95 ml. water and heating to 80°C. without stirring. The resulting solution was cooled, stirred and filtered.

An alternative method of preparation which was used was that of Austin and Riley (37), which has the advantage of cheapness. 2.22 g. salicylaldehyde were dissolved in 8 ml. 95% alcohol and added to 1.27 g. hydroxylamine hydrochloride dissolved in 2 ml. water. The resulting solution was diluted with 15 ml. 95% alcohol

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and stirred into 225 ml. water at 60°C. The reagent was filtered before use. This gave an approximately 1% solution of salicylaldoxime.

In the determinations below, salicylaldoxime, supplied by the Eastman-Kodak Company was used, and was found to be satisfactory without further purification. The reagent prepared according to the Austin and Riley method was also tested, and this was found to give results of identical accuracy. If the reagent was to be used regularly, it would always be prepared by this procedure, because of the much greater economy. The preparation is quick and easy, and gives a 90% yield of a product which can be used directly without purification or even crystallisation. It should be noted, however, that the reagent prepared in this way has a pH of 1.5, and if it is used in the separation of copper and nickel care must be taken that the pH does not fall below the level at which precipitation of copper is quantitative. This was found to occur where the copper or nickel present was considerable, i.e. when a large amount of reagent must be added. The effect was counteracted by adding 0.5 ml. 2 N sodium hydroxide (38). It was found advisable to add the hydroxide whenever the volume of reagent added exceeded 50% of the total volume of the solution.

Procedure.

The volume of the copper-nickel solution should be about 100 ml. 1 g. crystallised sodium acetate and 25 ml. glacial acetic acid were added to the solution, which was then stirred. A solution of pH 2.5 - 2.6 was thus obtained. A 1% alcoholic solution of

salicylaldoxime/...

salicylaldoxime (prepared as described above), in 25% excess of the volume required to precipitate both metals, was added dropwise from a burette with constant stirring. When the addition was complete, the solution was well stirred for 2 minutes and then allowed to stand for half an hour to allow the precipitate to coagulate. The mixture was filtered through a sintered glass crucible and the precipitate washed with cold water until the filtrate gave no colouration with ferric chloride solution. The complex was dried at 100°C. for an hour, and weighed as $\text{Cu}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$.

After the precipitate had been washed ten times and the washings allowed to drain into the suction flask, the filtrate and washings were transferred to a beaker. Ten washings were found sufficient to ensure complete removal of any nickel solution from the copper complex. The eleventh washing was tested with ferric chloride which generally gave no reaction.

The filtrate was then made alkaline by the dropwise addition of dilute ammonia, with stirring. When it was just alkaline it was stirred for two minutes and allowed to stand for 10 minutes. At the end of this time when the precipitate had coagulated, a drop of ammonia was added to the clear supernatant liquid to test for complete precipitation of nickel. If any cloudiness appeared the process was repeated, i.e. more ammonia was added, the solution was allowed to stand for ten minutes, and a drop of ammonia again added to the clear liquid.

When/...

When precipitation was finally complete, the mixture was filtered through a sintered glass crucible. The precipitate was washed with cold water until the filtrate gave no reaction with ferric chloride solution, dried for 1 hour at 100°C., and weighed as $\text{Ni}(\text{C}_7\text{H}_5\text{O}_2)_2$.

The Influence Of pH.

Copper was found to be quantitatively precipitated at a pH as low as 2.4, thus confirming Biefeld and Howe's results (58). Below this value precipitation was incomplete, falling off rapidly when the pH decreased below 2. At all pH's below 2.4 and 3.0 copper was completely thrown down without interference from the nickel. At pH's of over 3.1 the nickel started to precipitate.

The divergence of opinion as to the best pH for the nickel estimation (see p.70) was next investigated. It was found that the minimum safe pH for quantitative nickel precipitation is 7. At pH's below this, results were variable and unreproducible, though complete precipitation at these lower values sometimes occurred, in one case at a pH as low as 6.8.

For the upper limit it was found that at pH's above 9.5 results were irregular and unreproducible. This sets the upper limit a little below that of Biefeld and Howe (58), who state, 'Determinations of the metal in solutions having a pH as high as 9.9 gave satisfactory results'. At pH's above 10 the results fell off rapidly.

It is evident that the pH conditions involved are such as can

be/....

be easily and conveniently attained. Although the pH range for copper separation and estimation may appear small, in practice a buffer solution of acetic acid-sodium acetate readily gives a solution within this pH range. Further, the pH range for nickel estimation is sufficiently wide to make its adjustment a simple matter. It is completely unnecessary to fix the pH at about 7 within .1 pH unit. The range extending as it does above pH 9, it is quite sufficient to add ammonia dropwise until the solution retains a slight smell of it.

The Occlusion Of Nickel By The Copper Complex.

The amount of nickel occluded by the copper complex was found to be negligible and variations of the copper-nickel concentration ratio from 1/10 to 10 were found to have no effect on the accuracy. These results are shown below in Table 1.

Table 1.

<u>Theoretical Copper (g).</u>	<u>Weight of Precipitate</u>	<u>Copper Found.</u>	<u>Theoretical Nickel.</u>	<u>Weight of Precipitate</u>	<u>Nickel Found.</u>
	.5417	.1026		.0616	.01091
.1024	.5415	.1025	.01093	.0617	.01095
	.5416	.1026		.0619	.01098
.01017	.0539	.01021	.1045	.5675	.1042
	.0534	.01012		.5683	.1043

For accuracy and convenience the solutions should contain

about/.....

about 30-50 ng. copper or nickel. For values less than this the results tend to be inaccurate owing to the small weight of the precipitate; for values greater than this undue time is consumed in filtration, besides involving an unnecessary wastage of salicylaldehyde.

Interfering Elements.

The least satisfactory part of the literature dealing with salicylaldehyde is that concerning interfering elements. As seen above (25) such comments as there are deal mainly with non-interfering elements, and where there is any mention of interfering ions, no attempt is made to develop procedures whereby such interference may be eliminated. The remainder of this section is devoted to a study of the effects of certain ions, and the development of methods which may be used in their presence if they interfere.

Zinc.

Nickel cannot be estimated in the presence of zinc with salicylaldehyde following the normal procedure, because zinc precipitates as hydroxide with ammonia. Estimations were carried out to test Pearson's statement (116) that in the presence of zinc, the nickel should be precipitated at a pH of exactly 6.5. A number of nickel-zinc solutions of pH's between 6.3 and 6.7 were taken and the nickel determined with salicylaldehyde. The results, however, were found to be highly variable, and were always lower than the theoretical value. A different method was therefore sought to eliminate the interference of zinc. The most satisfactory

procedure/....

procedure was found to be the addition of citric acid. This held the zinc in solution, and the nickel could then be estimated from an ammoniacal solution in the usual way.

The procedure is to add 3 g. citric acid to the solution, then sufficient ammonia to make the solution ammoniacal, and precipitate the nickel by the dropwise addition of the salicylaldoxime reagent.

The comment of Biefeld and Howe (38) on Pearson's statement, 'perhaps the presence of other salts affect the solubility of the nickel complex as in the case of zinc' has, in the case of zinc at any rate, no foundation. Pearson's proposal was simply an attempt to estimate nickel at a pH just below that at which zinc precipitated.

Table 3 below, shows the results of the analysis of two zinc-nickel mixtures with salicylaldoxime and citric acid.

Table 3.

Zinc Present	Nickel Present	Weight of Precipitate	Nickel Found
.04 g.	.05345 g.	.3012 g.	.05344 g.
		.3016	.05352
.06	.04543	.2561	.04543
		.2566	.04552

Cobalt.

Cobalt interferes in the estimation of nickel with salicylaldoxime but not in that of copper. In ammoniacal solutions cobalt, with/...

with salicylaldehyde, gives a mud-brown precipitate. Due to the similarity of the properties of nickel and cobalt it was found very difficult to evolve a method which would prevent the interference of the one without similarly affecting the other, and it was finally decided to use a modification of the recently proposed cyanide method (see pp. 56-57).

Procedure.

To the cobalt-nickel solution was added dropwise a 1% aqueous solution of sodium cyanide with thorough stirring, until the precipitate which at first formed, redissolved. After diluting the solution to 150 ml., sufficient hydrogen peroxide (15%) was added to turn the solution a honey-yellow colour - 5 ml. was usually sufficient. The solution was then boiled down until excess peroxide had been eliminated, and the evaporation continued until the volume was about 75 ml. During the course of the heating it was generally found that the colour changed and a precipitate formed. If this occurs more sodium cyanide should be added to clear the solution. As it is desirable to avoid a large excess of cyanide, the addition should be dropwise. When the solution had evaporated down to 75 ml., 10 ml. formaldehyde (40%) were added. (The solution should then have a distinct odour of formaldehyde; if not a further 5 ml. are added). The solution was warmed for five minutes and then cooled. The salicylaldehyde reagent was then added in the usual way, and the precipitate filtered off from the cold solution.

Discussion/...

Discussion And Results.

The results of several cobalt-nickel separations are shown in Table 4 below. In view of the difficulty of estimating nickel in the presence of cobalt, this method is seen to offer a valuable and comparatively simple method for their separation. In general, the cyanide method offers a powerful means for separating nickel from a large number of ions (see pp. 56-57), and its application is strongly recommended, particularly in preference to more antiquated procedures (such as the use of hydrogen sulphide or sodium hydroxide) when it is required to separate nickel from a number of other ions.

Table 4.

<u>Nickel Present.</u>	<u>Weight of Precipitate.</u>	<u>Nickel Found.</u>	<u>Cobalt Present.</u>
.03570 g.	.2010 g.	.03567 g.	.0112 g.
	.2016	.03577	
.02968	.1671	.02965	.0221
	.1675	.02968	
.03022	.2155	.03020	.0421
	.2155	.03023	

Lead.

Lead interferes in the estimation of nickel with salicylaldehyde but not in that of copper. No method could be found or devised to keep the lead in solution while the nickel complex was precipitated; the/....

the insolubility of most lead compounds rules out most possibilities. It is therefore necessary to remove the lead preparatory to performing the nickel estimation, e.g. as lead sulphate.

Iron.

In sodium acetate-acetic acid solutions, iron forms a dark brown complex with salicylaldoxime, which, though soluble, contaminates the copper-salicylaldoxime precipitate, as shown by Biefeld and Howe (38). To counteract this, a method was developed in which a soluble fluoride was added to the solution; this forms a complex with the iron of sufficiently low instability constant to remain in solution when the salicylaldoxime is added. It was first shown qualitatively that a solution of iron and potassium fluoride gave no colour when salicylaldoxime was added. Next it was tested quantitatively on a copper-iron mixture, following the procedure described below.

Procedure.

The copper-iron solution was buffered with acetic acid and sodium acetate in the usual way for the estimation of copper. To the cold solution was added 50 ml. of a 4% solution of potassium fluoride. The salicylaldoxime reagent was then added in the usual way, with thorough stirring to coagulate the precipitate. After the precipitate had coagulated, it was filtered through a sintered glass crucible and washed 10 times with cold water. It was dried at 100°C. and weighed.

Discussion And Results.

If the fluoride is dissolved in the solution by adding in the
solid/....

solid form and warming, the solution goes slightly cloudy, and the results obtained are high. It was found, however, that if the fluoride was first dissolved and then added in the cold no interfering precipitate was produced, and the results were satisfactory. The method was tested on four samples containing the same amount of copper, but different amounts of iron. Since, apart from very small concentrations, the amount of iron occluded by the copper is directly proportional to the amount of iron present, the justification of the method will lie in the concordancy of the results.

Table 5 below, shows the results obtained, and illustrates the accuracy of the method.

Table 5.

<u>Copper Present</u>	<u>Weight of Precipitate</u>	<u>Copper Found</u>	<u>Iron Present</u>
	.4115 g.	.07789 g.	.022 g.
.07776 g.	.4106	.07776	.029
	.4108	.07780	.051
	.4113	.07789	.062

In ammoniacal solutions iron precipitates as ferric hydroxide, and thus iron interferes in the estimation of nickel with salicylaldoxime. Attempts to hold the iron in solution with potassium fluoride were at first unsuccessful, as the characteristic reddish-brown complex formed on addition of the salicylaldoxime. More

careful/....

careful investigation, however, showed that at pH's below 7.5, the salicylaldoxime could be added without the formation of this complex. As soon as the pH exceeded 7.5 the solution went red-brown. The estimation of nickel in the presence of iron was carried out as follows:-

Procedure.

To the nickel solution containing iron was added in the cold 50 ml. of a 4% solution of potassium fluoride. The salicylaldoxime reagent was added, and then dilute ammonia dropwise, very slowly and with thorough stirring. After each drop the colour of the solution would flash reddish-brown, but on stirring the colour would disappear. After some time, as more ammonia was added, the colour would tend to become more permanent and require more stirring to cause its disappearance. The addition of ammonia was stopped just before the colour of the solution became a permanent red-brown. The solution was then allowed to stand for fifteen minutes. At the end of that time one drop of ammonia was added to test for the formation of any further precipitate (This requires careful observation owing to the simultaneous formation of the red-brown colour). If no precipitate formed, the mixture was filtered, and the precipitate washed, dried and weighed as usual.

Discussion And Results.

This method was found to be quite satisfactory for holding the iron in solution. The addition of ammonia to the right stage becomes quite easy after a little experience in detecting the colour

change/....

changes, which are very characteristic. If any difficulty is experienced, the ammonia can be added dropwise until a slight excess is present (as judged from the colour), and then dilute hydrochloric acid drop by drop, until the solution clears.

Table 6, below, contains the results of two analyses for nickel in solutions containing iron.

Table 6.

<u>Nickel Present</u>	<u>Weight of Precipitate</u>	<u>Nickel Found</u>	<u>Iron Present.</u>
.04018 g.	.2264 g.	.04017 g.	.055 g.
	.2271	.04029	
.05519	.1872	.05521	.040
	.1874	.05524	

Conclusion.

Salicylaldehyde is an excellent reagent for the separation of copper from nickel, and for the estimation of both. For nickel the accuracy and reproducibility of the results are almost identical with those obtained using dimethylglyoxime, though salicylaldehyde is a considerably more convenient reagent to work with. The precipitate coagulates almost immediately, as compared with the hour period of digestion which is necessary for the nickel-dimethylglyoxime precipitate. It is quite unnecessary to allow the solution to stand overnight as Biesfeld and Bowe (36) state. There is not the danger of precipitation of excess reagent, and the precipitate is less soluble in alcohol. Further,

very/....

very little washing is required, whereas the dimethylglyoxime precipitate must be washed a number of times with hot water. Its big disadvantage is the interference of cobalt, which does not interfere when dimethylglyoxime is used. Of the other ions which interfere, lead is the only one which causes much trouble, the effects of the others being eliminated by fairly simple procedures.

The results obtained for copper by the use of this reagent compare very favourably with those of the better known analytical procedures. The results are not quite as accurate nor as precise as those obtained using potassium thiocyanate, but its use offers several advantages. The precipitate coagulates in 15 minutes instead of the minimum period of four hours necessary with potassium thiocyanate. Also the precipitate is not nearly so fine, so that filtration is much quicker. The thiocyanate precipitate requires extensive washing while the copper-salicylaldehyde precipitate is readily washed free from soluble impurities. The only common interfering element is iron. The copper precipitate is not quite as convenient to handle as the nickel precipitate; it has a tendency to creep and stick to the glass, and requires fairly extensive washing to be dislodged.

Salicylaldehyde is recommended as a reagent for determining nickel, when cobalt is absent, and also for copper where the highest accuracy is not required; for very accurate work the iodide method is the one which should be used.

The/....

The results of a number of estimations are shown in Table 2
overleaf, and the statistical calculations for these results on the
pages immediately thereafter.

Table 2/...

Table 2.

Theoretical Copper. g.	Weight of Precipitate g.	Copper Found. g.	Theoretical Nickel g.	Weight of Precipitate g.	Nickel. Found. g.
	.2927	.05544		.2882	.05115
.05545	.2928	.05546	.05106	.2878	.05106
	.2926	.05545		.2877	.05105
	.5812	.1101		.5595	.09922
.1100	.5813	.1101	.09951	.5595	.09926
	.5809	.1100		-	-
	.2315	.04384	.02556	.1441	.02557
.04375	.2316	.04385		.1443	.02561
	.2310	.04375		.1442	.02559
	.1727	.03271		.1440	.02555
.03264	.1728	.03273	.02556	.1441	.02557
	.1725	.03267		.1442	.02559
.05580	.2984	.05584	.04532	.2550	.04524
	.2945	.05575		.2552	.04527
	.3657	.06925		.2055	.03645
.06925	.3645	.06908	.03642	.2056	.03648
	.3657	.06925		.2052	.03641
	.1723	.03263		.2071	.03675
.03264	.1725	.03268	.03670	.2069	.03671
	.1724	.03265		.2067	.03667
	.2188	.04145		.3336	.05919
	.2185	.04135		.3336	.05919
	.2186	.04141		.3340	.05926
.04141	.2182	.04133	.05936	.3339	.05924
	-	-		.3345	.05933
	.3671	.06955		-	-
	.3676	.06963		-	-
	.3669	.06950	-	-	-
.06958	.3665	.06942		-	-
	.3670	.06952		-	-
	.3638	.06892		.3140	.05565
.06900	.3637	.06889	.05572	.3137	.05565
	.3640	.06895		.3134	.05560
	.3449	.06911		.3134	.05560
	.3647	.06907		.3138	.05566
	.3052	.05781		.4469	.07929
	.3061	.05797		.4469	.07929
.05792	.3059	.05794	.07934	.4467	.07925
	.3052	.05781		.4464	.07920

The Statistical Terms.

Copper

Standard Deviation ($\times 10^4$)	Accuracy ($\times 10^4$)	Probable Error ($\times 10^4$)	Standard Error ($\times 10^4$)
1.526	1.752	1.414	1.226
7.071	10.00	4.714	4.085
5.477	11.60	3.651	3.389
3.082	8.357	2.057	1.760
7.610	9.220	5.207	5.525
9.274	12.020	6.183	4.988
2.550	5.000	1.700	1.472
2.538	6.216	3.692	2.769
7.694	9.874	5.129	5.441
9.527	9.747	6.357	4.260
8.660	9.507	5.773	4.550

Nickel

4.359	5.000	2.906	2.517
2.828	27.18	1.885	2.000
2.000	4.183	1.333	1.154
2.000	2.345	1.333	1.154
2.236	9.434	1.497	1.581
3.606	4.359	2.404	2.082
4.000	4.183	2.667	2.510
5.809	14.46	3.873	2.087
5.809	9.661	3.873	2.087
4.281	11.56	2.854	2.141

The Statistical Terms Expressed As Percentages.

Copper.

<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error</u>
.02752	.03123	.02550	.02215
.06428	.09090	.03404	.02948
.01252	.02653	.08349	.07750
.09445	.2555	.06304	.06458
.1400	.1690	.09333	.09906
.1340	.1736	.08990	.07202
.07830	.09189	.05208	.04510
.1338	.1501	.06915	.06696
.1106	.1419	.07372	.04832
.1380	.1413	.09215	.06034
.1495	.1641	.09965	.07474

Nickel

.08537	.09792	.05692	.04929
.02842	.02732	.01694	.02010
.07825	.1637	.05217	.04515
.07825	.09170	.05217	.04515
.04934	.2082	.03288	.03489
.09906	.1197	.06601	.05713
.1090	.1140	.07236	.06294
.09764	.1628	.06524	.03517
.1042	.1377	.06790	.03745
.05395	.1452	.03596	.02699

	<u>Copper</u>	<u>Nickel</u>
Mean Standard Deviation	.1097%	.07837%
Mean Accuracy	.1523%	.1512%
Mean Probable Error	.07237%	.05208%
Mean Standard Error	.06066%	.04243%

The/....

2. The Iodometric Estimation Of Copper.

Just as dimethylglyoxime is the standard reagent for the determination of nickel, so the iodometric procedure is standard for copper estimations. It has already been described at length in the theoretical section, and the extension of that description here is to the following points:-

- (i) To perform a number of estimations on solutions of varying copper-nickel concentration ratio to determine whether the presence of nickel has any effect on the final result.
- (ii) To develop a convenient and accurate procedure.
- (iii) To establish the precision and accuracy of the results to furnish a standard with which other methods may be compared.

Procedure.

To 50 ml. aliquots of the solution containing copper and nickel was added 2 ml. 6 N hydrochloric acid and 5 ml. of a 50% solution of potassium iodide. The solution was stirred for a minute and then at once titrated with standard approximately .1 N sodium thiosulphate solution until the iodine colour had almost disappeared. 2 ml. of a 1% starch solution were added and the titration continued dropwise until the starch colour just disappeared. 10 ml. of a 20% solution of potassium thiocyanate were then added and the flask swirled vigorously. This produced a reappearance of the blue colour. The titration was continued dropwise until the blue colour had finally disappeared.

The/....

The Effect of pH.

The question of the influence of pH becomes important when copper is to be determined in alloys or ores, which are first dissolved in excess acid. To determine what effect the presence of free acid had, a number of determinations were made on copper solutions containing various concentrations of acids. In each case, a known volume of acid was run into the copper solution to be used for the determination, and the pH of the solution determined by means of a Beckmann pH meter using an identical solution to which the same volume of acid had been added. The results are shown in Table 9, over.

Table 9/....

Table 9.

<u>pH Of Solution</u>	<u>Copper Taken</u>	<u>Copper Found</u>	<u>Acid Added.</u>
2.0	.1572	.1571	
1.2	.1572	.1572	
0.80	.1572	.1571	
0.65	.1572	.1570	Hydrochloric
0.52	.1572	.1575	
0.40	.1572	.1573	
0.31	.1572	.1575	
0.20	.1572	.1578	
0.17	.1572	.1582	
1.7	.1569	.1567	
1.1	.1569	.1568	
0.75	.1569	.1570	
0.62	.1569	.1570	Sulphuric
0.49	.1569	.1570	
0.41	.1569	.1573	
0.36	.1569	.1576	
0.31	.1569	.1577	
0.24	.1569	.1582	
1.4	.1282	.1286	
1.2	.1282	.1285	
0.95	.1282	.1284	
0.75	.1282	.1285	Nitric
0.50	.1282	.1284	
0.45	.1282	.1267	
0.39	.1282	.1292	
0.38	.1282	.1304	

Discussion/....

Discussion.

The standard procedure for copper as outlined in the textbooks is to add the potassium iodide and potassium thiocyanate in the solid form. It was found preferable, however, to add them as solutions. This was found to increase the reproducibility of the results (owing to the greater standardisation of conditions), besides being more convenient if numerous titrations are being performed. The volumes were measured with 5 and 10 ml. measuring cylinders to an accuracy of within 5%.

The thiosulphate solutions were standardised against standard copper sulphate solutions using a procedure identical to that outlined above.

The addition of varying amounts of nickel to the solutions was found to be completely without effect on the final results.

Small amounts of hydrochloric and sulphuric acids do not affect the results, but nitric acid tends to make the results high. This, the writer suggests, is due to the presence of oxides of nitrogen. It is recommended that any nitric acid used to dissolve the sample be completely eliminated by evaporation to fuming with sulphuric acid, and the pH of the solution subsequently adjusted by the addition of acetic acid. For ordinary estimations (i.e. where no acid is initially present) the use of hydrochloric acid is recommended.

Conclusion.

The iodometric method is, from all aspects, the best procedure, either volumetric or gravimetric, for the determination of copper. Not only is it the quickest and most convenient method, but it is

also/....

also the most accurate. Very few ions interfere with the reaction. The procedure outlined above gives results of the highest order of accuracy.

For the determination of copper in copper-nickel mixtures this procedure is unhesitatingly recommended.

The results of a series of estimations of copper in copper-nickel mixtures is given in Table 10 over.

Table 10/...

TABLE 10

Theoretical Copper g.	Volume Of $\text{Na}_2\text{S}_2\text{O}_5$ ml.	Copper Found. g.	Theoretical Copper g.	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ ml.	Copper Found. g.
.1434	27.88	.1434	.2395	46.62	.2399
	27.86	.1432		46.61	.2398
	27.90	.1435		46.62	.2399
	27.87	.1433		46.62	.2399
	27.86	.1432		46.60	.2397
	27.86	.1432		46.61	.2398
	27.88	.1434		46.62	.2399
	27.87	.1435		46.60	.2397
.1849	35.96	.1849	.2109	41.00	.2109
	35.95	.1849		41.01	.2109
	35.96	.1849		41.05	.2110
	35.95	.1849		41.02	.2110
	35.96	.1849		41.00	.2109
	35.95	.1849		41.00	.2109
	35.95	.1849		41.00	.2109
	35.95	.1849		41.05	.2110
.2111	41.06	.2112			
	41.05	.2111			
	41.08	.2113			
	41.06	.2112			
	41.05	.2111			
	41.06	.2112			
	41.02	.2110			
	41.08	.2113			

Table 11/...

TABLE 11.

The Statistical Terms.

<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error.</u> <u>(x 10⁴)</u>
1.134	1.464	0.7560	0.4012
0.000	0.000	0.0000	0.0000
1.069	1.310	0.7126	0.3780
0.9258	4.056	0.6172	0.3274
0.6547	0.6547	0.4264	0.2316

TABLE 12.

The Statistical Terms Expressed As Percentages.

0.07911	0.09757	0.0572	0.02798
0.000	0.000	0.000	0.000
0.05066	0.06205	0.03376	0.01791
0.03866	0.01686	0.02637	0.01367
0.03106	0.03106	0.02022	0.01098

Mean Standard Deviation	0.05989%
Mean Accuracy	0.02186%
Mean Probable Error	0.02661%
Mean Standard Error	0.01411%

5. The Separation And Determination Of Copper With Sodium

Thiosulphate And The Determination Of Nickel With Dimethylglyoxime

One of the standard methods for separating copper from other ions is ^{by}precipitation by hydrogen sulphide. This procedure, however, is little used today, and, in particular, has been shown (50) to be highly unsatisfactory when nickel is present. It was decided to investigate the more recent variation which involves the precipitation of copper as cupric sulphide by means of sodium thiosulphate. This procedure depends on the fact that copper, in an acid solution, is precipitated as cupric sulphide when boiled with sodium thiosulphate. The copper sulphide is filtered off, dissolved in nitric acid, and the copper determined iodometrically.

Procedure.

To a 50 ml. aliquot of the copper-nickel solution 20 ml. 6 N sulphuric acid was added, and then 50 ml. of a 20% solution of sodium thiosulphate for every 0.1 g. copper present. The solution was warmed to near boiling point and then left to digest on a steam bath until all the cupric sulphide, together with the free sulphur, which is also formed during the course of the reaction, had precipitated. When the supernatant liquid was quite clear, the solution was filtered hot, the filtrate being collected in a 400 ml. beaker. The precipitate was washed five times with warm water, the washings being added to the rest of the filtrate.

The precipitate and filter paper were transferred to a 300 ml. conical flask, and 10 ml. 6 N Nitric acid were added. The flask was heated gently for 15 minutes or until all the precipitate had

dissolved/...

dissolved. The sides of the flask were then washed down with distilled water; 5 ml. 6 N sulphuric acid added, and the heating continued until white fumes were evolved.

The solution, when cold, was diluted with 20 ml. of water. Ammonia was added dropwise from a burette until a permanent blue colour remained. The excess of ammonia was boiled off. After the solution had cooled, glacial acetic acid was added dropwise until the blue colour just disappeared, and then a further 2 ml.

The copper in this solution was then estimated iodometrically exactly as described in the previous section (p. 99)

Discussion And Results.

As the filtrate was required for the estimation of nickel, it was found necessary to digest the solution for a longer period than that specified in the original paper (51), otherwise the excess sodium thiosulphate would precipitate sulphur when the solution was warmed during the nickel estimation. It was found that, as long as the supernatant liquid in the beaker was completely clear before the solution was removed from the steam bath, no trouble was experienced in this connection.

To test for any occlusion of nickel by the cupric sulphide precipitate the following test was performed:- The cupric sulphide precipitate was re-dissolved in nitric acid, and the copper in this solution re-precipitated as cupric sulphide with sodium thiosulphate following the procedure outlined above. The solution was filtered and nickel tested for in the filtrate with dimethylglyoxime

and/...

and ammonia. After standing for a week the solution showed no coloration.

The standard procedure (52) recommends burning off the filter paper and then dissolving the cupric sulphide in nitric acid. It was found, however, that the filter paper did not in any way interfere with the titration. To increase the convenience of the method, the filter paper and precipitate were therefore transferred directly to the flask, where the precipitate was dissolved in nitric acid.

An alternative procedure (51) recommends that the sulphide be ignited to the oxide, which is fused with potassium disulphate. The melt is dissolved in water and the copper determined iodometrically. This variation, besides being considerably longer, was found to suffer from three other disadvantages, viz. that it is difficult to get the fusion to go to completion, that any other than very gentle heating causes the mixture to sputter uncontrollably, and that complete solution of the final melt is often difficult.

The use of acetic instead of hydrochloric acid originated from Whitehead and Miller 's statement (15), which was found also, to apply to the Foote and Vance method, that variations in the amount of acetic acid have less effect on the final results than variations in the volumes of other acids.

Conclusion.

The results show this procedure to be a very excellent one for estimating copper. The results are superior to those obtained using salicylaldoxime, and only slightly inferior to those of the potassium thiocyanate estimation. This procedure is not particularly suitable for/...

for the occasional determination of copper, but it is especially applicable to large scale routine analyses, particularly where the copper is originally in the form of an ore or alloy. The technique conforms very well to routine procedure. First, it is obvious that a very large number of separations can be performed simultaneously, and secondly, a second set of copper solutions may be put on the water bath to digest while the first set are being titrated. After a little experience the procedure may be made almost continuous.

The Determination Of Nickel In the Filtrate With Dimethylglyoxime.

Dimethylglyoxime is, of course, the standard reagent used for the determination of nickel. The purposes of its inclusion in this thesis are firstly to furnish a standard with which other analytical procedures for nickel may be compared, and secondly to clear up certain points about which some ambiguity exists in the literature. The procedure for the estimation of nickel using dimethylglyoxime is first described, and this is followed by discussions on the influence of the presence of copper and cobalt on the estimation.

Procedure.

The filtrate from the thiosulphate separation of copper was transferred to a beaker and warmed to 70°C. A 1% solution of dimethylglyoxime in alcohol was added in 25% excess, followed by the dropwise addition of dilute ammonia from a burette, with thorough stirring, until precipitation was complete. The solution was digested on a water bath for about an hour, or until the red precipitate had completely coagulated. A few drops of dilute ammonia

were/...

were added to the supernatant liquid to test for complete precipitation, and if no further precipitate formed, the mixture was filtered through a sintered glass crucible. The precipitate was washed thoroughly with hot water until free from chloride and dried and weighed as $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$.

Nickel And Copper.

Copper gives a very sensitive colour reaction with dimethylglyoxime, which will show the presence of 1 part in 10,000,000. It is generally stated that small amounts of copper may be present without interfering in the gravimetric estimation of nickel with dimethylglyoxime, e.g. 'moderate amounts of copper, etc., do not interfere' (102).

To test at what stage the copper starts to interfere in the estimation the following tests were carried out:- To a number of beakers containing the same amount of a standard nickel solution were added varying amounts of a standard copper solution and the nickel estimated as described above. The results are shown in Table 15, over.

Table 15/...

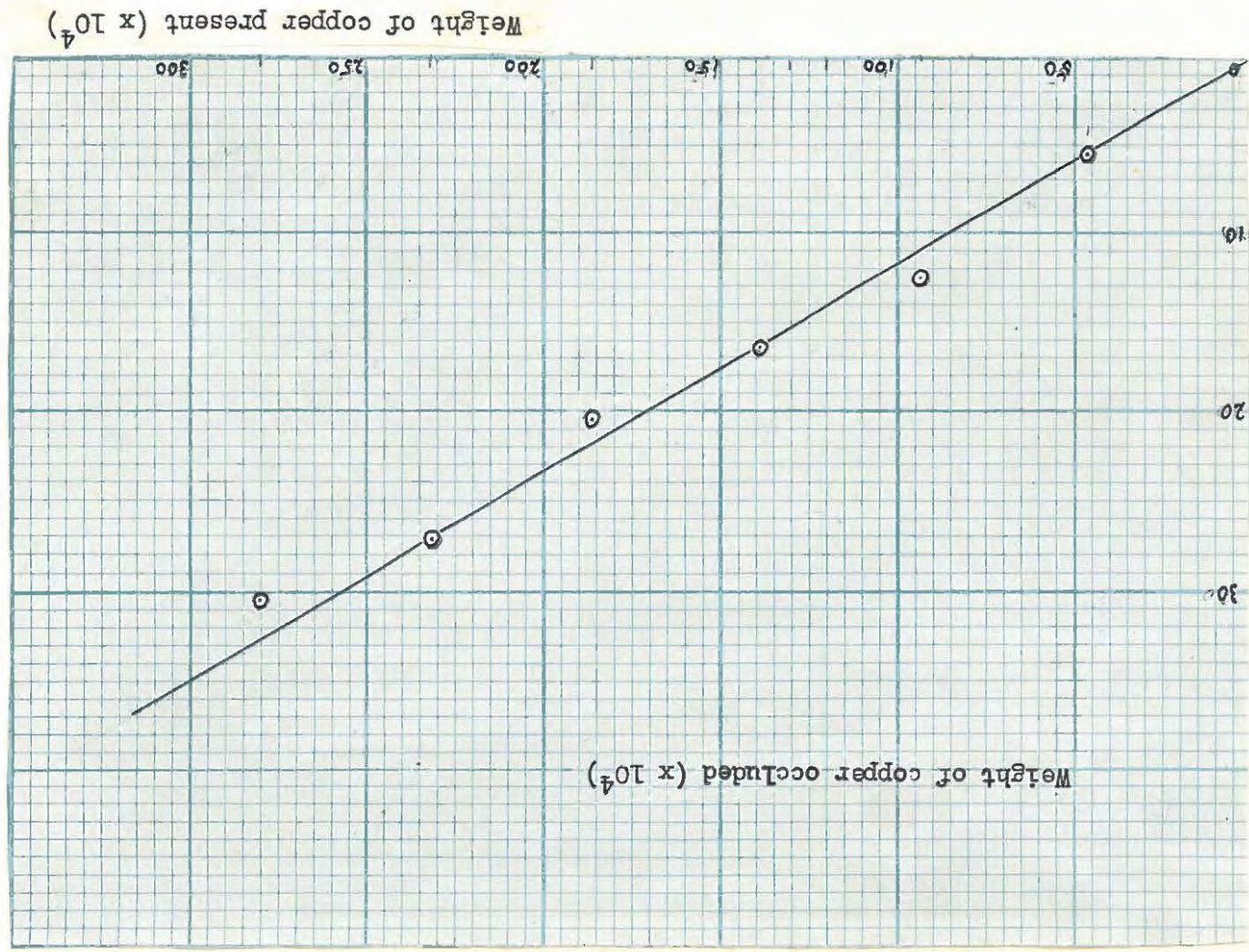


TABLE 13.

<u>Weight of Precipitate g.</u>	<u>Weight of Copper Present g.</u>	<u>Weight of Entrained Precipitate g.</u>	<u>Weight of Copper Occluded. g.</u>
.1564	0.	0.	0.
.1590	.004657	.0026	.0005606
.1625	.009314	.0059	.001272
.1640	.01397	.0076	.001639
.1661	.01863	.0095	.002047
.1692	.02329	.0128	.002731
.1705	.02794	.0141	.003040

The results are illustrated graphically in the accompanying graph, in which the actual weight of copper occluded is plotted against the weight of copper present. The graph shows that the weight of copper occluded is proportional to the weight of copper present. The figures show that the occlusion is of the order of 10% of the copper present. It is evident then, that except for very small quantities of copper (below 2-4 mg., depending on the amount of nickel present), the precipitate is contaminated by the presence of copper to an extent which makes the direct estimation of nickel impossible. For all practical purposes, copper must be regarded as an interfering ion; the question of the procedure to be adopted in its presence will be discussed in subsequent pages, (see p. 136)

Nickel/....

Nickel And Cobalt.

One of the particular values of the dimethylglyoxime reagent is that it can be used to estimate nickel in the presence of cobalt. To show its applicability to cobalt-nickel mixtures a set of readings similar to those made on copper-nickel mixtures were made on cobalt-nickel mixtures. The results are shown in Table 14 below.

TABLE 14.

<u>Weight Of Cobalt Present</u> <u>(g.)</u>	<u>Weight of Dimethylglyoxime</u> <u>Precipitate (g.)</u>
.004028	.1698
.008056	.1699
.01070	.1698
.01913	.1701
.02014	.1698
.02215	.1697
.02417	.1698
.03357	.1703
.06713	.1697

These results show that cobalt does not interfere in the nickel estimation even when the weight of cobalt present is twice that of nickel.

Conclusion.

As would be expected, the results show that dimethylglyoxime is the best reagent for nickel tested in the course of this work.

Its/....

Its two great advantages are that it is inexpensive, and that cobalt does not interfere. The two disadvantages that are generally attributed to it, viz. the solubility of the precipitate in excess alcohol, and the tendency of the reagent to precipitate in aqueous solutions, were never found to manifest themselves. Under ordinary conditions they have negligible effect and can be discounted. Dimethylglyoxime is not as convenient to work with as salicylaldehyde, but as long as the price difference exists between the two, it will certainly remain the standard reagent for nickel.

The results of a series of separations are shown in Table 15, over.

TABLE 15.

Theoretical Copper g.	Volume Of Na ₂ S ₂ O ₃ ml.	Copper Found g.	Theoretical Nickel g.	Weight Of Precipitate g.	Copper Found g.
.1728	34.37	.1728	.04550	.2242	.04553
	34.45	.1732		.2231	.04551
	34.50	.1724		.2243	.04553
	34.55	.1726		.2250	.04529
	34.40	.1729		.2227	.04524
	34.39	.1728		.2239	.04546
	34.34	.1726		.2237	.04543
	34.39	.1726		.2237	.04543
.2192	42.62	.2192	.05867	.2906	.05886
	42.55	.2189		.2906	.05802
	42.60	.2191		.2905	.05899
	42.47	.2185		.2901	.05891
	42.65	.2194		.2900	.05889
	42.62	.2192		.2906	.05902
	42.59	.2191		.2900	.05899
	42.64	.2193		.2904	.05896
.1831	35.90	.1831	.05530	.2722	.05529
	35.67	.1834		.2724	.05533
	35.60	.1831		.2725	.05535
	35.54	.1828		.2722	.05529
	35.60	.1826		.2721	.05527
	35.60	.1831		.2715	.05514
	35.53	.1827		.2721	.05527
	35.59	.1830		.2725	.05535
.1497	29.10	.1496	.05834	.1890	.05839
	29.14	.1498		.1867	.05833
	29.12	.1497		.1866	.05831
	29.07	.1495		.1891	.05841
	29.15	.1498		.1889	.05837
	29.05	.1494		.1868	.05835
	29.06	.1495		.1881	.05830
	29.09	.1496		.1892	.05844
.2355	45.80	.2356	.05554	.2731	.05547
	45.68	.2350		.2735	.05555
	45.77	.2354		.2736	.05556
	45.74	.2353		.2734	.05552
	45.82	.2357		.2737	.05559
	45.75	.2353		.2731	.05547
	45.75	.2353		.2729	.05543
	45.70	.2355		.2728	.05542

Table 15/...

TABLE 16.

The Statistical Terms.

Nickel

<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error</u> <u>(x 10⁴)</u>
15.17	11.40	7.800	4.032
6.969	6.557	4.573	2.319
6.918	6.866	4.444	2.358
7.463	5.099	3.398	1.805
7.551	5.816	3.878	2.057

Copper

2.420	2.420	1.613	0.8559
3.047	2.778	1.852	0.9626
2.927	2.618	1.745	0.9258
1.732	1.464	0.972	0.5299
2.479	2.171	1.447	0.7678

Table/17

TABLE 17

The Statistical Terms Expressed As Percentages.

Nickel.

<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error</u>
.2504	.5354	.1870	.0861
.1114	.1184	.07423	.03943
.1206	.1251	.08037	.04265
.1329	.1946	.08861	.04702
.1047	.1356	.07980	.03704

Copper

.1401	.1401	.09452	.04855
.1268	.1390	.08441	.04483
.1430	.1599	.09532	.05792
.09786	.1157	.06524	.03540
.09219	.1053	.06146	.03280

	<u>Copper</u>	<u>Nickel</u>
Mean Standard Deviation	.1200%	.1174%
Mean Accuracy	.1320%	.1434%
Mean Probable Error	.0800%	.07826%
Mean Standard Error	.04406%	.04152%

* Excluded

4. The/....

4. The Separation And Determination Of Copper With Potassium Thiocyanate And The Cyanometric Estimation Of Nickel.

The use of potassium thiocyanate is generally recognised as the best gravimetric procedure for the determination of copper, and since nickel does not interfere, it may be applied to the separation of copper from nickel, as well as to the estimation. The nickel in the filtrate may be determined by any method that is chosen.

Procedure.

A few drops of 6 N hydrochloric acid were added to the copper-nickel solution and then 10 ml. of a 20% solution of sodium metabisulphite. A slight excess of a freshly prepared solution of potassium thiocyanate (10%) was added dropwise from a burette with thorough stirring. The solution was allowed to stand overnight. Before the solution is filtered, the precipitate must be pure white and the solution must smell of sulphur dioxide; if either of these conditions is absent 5 ml. more of the sodium metabisulphite solution should be added. Finally the mixture was filtered through a fine sintered glass crucible. The precipitate was washed at least ten times with a solution prepared by adding 1 g. potassium thiocyanate and 0.5 g. sodium metabisulphite to 1000 ml. water. Finally it was washed three or four times with 20% alcohol. This removes excess potassium thiocyanate. The precipitate was dried to constant weight at 115°C . and weighed as $\text{Cu}(\text{CN})_2$.

Discussion/...

Discussion And Results.

There was found to be negligible difference between results obtained from precipitation performed in the hot and in the cold. It was found preferable to allow the solution to stand overnight, and not for the shorter period of 2 hours recommended by some texts. The precipitate coagulates incompletely in the shorter time, and the sintered glass crucible (which has to be fine because of the fineness of the precipitate) is liable to become clogged. The washings tend to become rather laborious at best, and it is false economy to try to save time by decreasing the time the solution stands. It is also advisable to leave the solution to stand overnight in a dark place, as the precipitate is slightly decomposed by light.

The key to the success of the final result lies in sufficient washing and it is essential that the washings be repeated until constant weight is obtained.

Conclusion.

The results show that a high degree of accuracy and precision can be obtained by the use of this reagent. It gives better results than any other procedure investigated by the writer except the iodometric method, and the accuracy and reproducibility are of the same order as those obtained in the determination of nickel with diethylglyoxime.

In spite of the excellence of the results the author recommends that, except in special cases, another method be chosen. Salicyl-doxime gives results only slightly less accurate and an estimation
with/....

with it occupies only a fraction of the time needed for a thiocyanate determination. If greater accuracy is required an iodometric estimation is to be preferred. For routine purposes, either separation with sodium thiosulphate and subsequent iodometric titration, or iodometric titration alone are preferable, the choice being dependent on the presence of other ions.

The Cyanometric Estimation Of Nickel.

The cyanide method is the volumetric method most widely used for the estimation of nickel. It is applied here to the estimation of the nickel in the filtrate from the thiocyanate separation of copper, and affords an example of the necessity to remove one of the substances used in a previous estimation.

Just as potassium cyanide reacts with silver iodide to form $KAg(CN)_2$, so potassium thiocyanate forms $KAg(CNS)_2$, thus interfering in the estimation. The first procedure the writer used in an attempt to eliminate this interference was oxidation with bromine water to sulphate, which could then be precipitated with barium nitrate (chloride could not be used, as it would react with the silver nitrate). The other products from the oxidation, however, were found to interfere in the cyanometric titration. The separation was finally effected with mercurous nitrate, which formed the insoluble mercurous thiocyanate which was filtered off.

Procedure.

1. The potassium cyanide solution was first standardised against standard silver nitrate solution as follows:- 50 ml. of the potassium cyanide solution in a conical flask were diluted to about 150 ml. and 2 ml. of the potassium iodide reagent added. This solution was titrated with a standard silver nitrate solution until a faint permanent opalescence was obtained.
2. A 5% solution of mercurous nitrate (the amount of excess thiocyanate present could be calculated from the amount of copper found and of thiocyanate added) was added in 25% excess to the filtrate/...

filtrate from the thiocyanate separation. The solution was allowed to stand for two hours, after which time the insoluble mercurous thiocyanate was filtered off through a fine filter, the filtrate being collected in a beaker. The precipitate was washed five times with water, the washings being allowed to drain into the beaker.

The filtrate was boiled down to about 150 ml. and transferred to a flask. The solution was made slightly ammoniacal by the addition of ammonia until a slight excess was present (from smell) and then a further 5 ml. added. 5 ml. of the silver nitrate solution were measured in from a burette, and about 2 ml. of the potassium iodide solution were added. The solution was then titrated with the standard potassium cyanide solution, slowly and with constant stirring until the turbidity just disappeared. Near the end-point the addition should be very cautious and the solution thoroughly shaken. If the end point is passed, 5 ml. more silver nitrate solution are added and the titration continued as before.

Solutions.

The solutions used were prepared as follows:-

N/10 Silver Nitrate. 16.99 g. silver nitrate were dissolved in 1000 ml. water.

Potassium Iodide Solution. 200 g. potassium iodide were dissolved in 1000 ml. water.

N/10 Potassium/....

N/10 Potassium Cyanide. 13.5 g. potassium cyanide and 7 g. potassium hydroxide were dissolved in 1000 ml. water. The potassium hydroxide increases the stability of the solution. If the solution is to be used over any length of time it is advisable to store it in a bottle connected to a burette, and to protect it from the carbon dioxide of the atmosphere by means of a soda-line tube. Over a period of a few weeks, however, the alteration was found to be negligible.

Discussion And Results.

As already stated (p.69) almost all the descriptions of this procedure differ in the normality and volume of silver nitrate that they recommend. A series of estimations were carried out to test their relative values. Actually little appreciable difference was found between them. The author's preference is for 5 ml. of a .1 N solution which volume and normality he found to make the end-point rather easier to detect.

Two precautions which must be observed in the cyanide method are:-

- (i) A large excess of ammonia is to be avoided, as the silver iodide is soluble in large excess.
- (ii) The silver nitrate should not be stronger than that indicated, as the silver iodide may settle out as a curdy precipitate in stronger solutions.

Conclusion.

The cyanide method is valuable for routine analyses in which
a high/....

high degree of accuracy is not desired. Its use for the occasional estimation of nickel is not recommended, as one of the main factors influencing the results is the experimenter's experience in detecting the end-point. Once he has standardised his own procedure, results of reasonable accuracy may be obtained.

A further disadvantage is the interference of cobalt.

The results obtained in a series of determinations are shown in Table 12. It should be noted that an additional source ^{/of error} is introduced here, as the determination is performed on a solution from which two separations by means of precipitation and subsequent filtration have been carried out.

TABLE 18

Theoretical Copper g.	Weight of Precipitate g.	Copper Found. g.	Theoretical Nickel g.	Volume AgNO ₃ ml.	Volume KCN ml.	Nickel Found g.
.07959	.1529	.07989	.06822	5.00	51.50	.06819
	.1522	.07952		4.98	51.28	.06814
	.1527	.07979		4.98	51.58	.06825
	.1527	.07979		5.28	51.70	.06829
	.1526	.07975		5.02	51.40	.06822
	.1525	.07968		5.00	51.59	.06838
	.1525	.07958		5.00	51.29	.06815
	.1525	.07958		4.98	51.40	.05825
.1860	.3561	.1861	.1036	4.98	44.86	.1039
	.3566	.1863		5.01	44.70	.1034
	.3563	.1862		5.03	44.67	.1032
	.3563	.1862		4.96	44.63	.1032
	.3568	.1864		5.07	44.82	.1035
	.3565	.1862		5.07	44.80	.1035
	.3563	.1862		5.53	45.48	.1040
	.3564	.1862		5.01	44.74	.1035
.1192	.2280	.1191	.08221	5.02	56.60	.08202
	.2283	.1193		4.99	56.49	.08187
	.2281	.1192		4.98	56.42	.08172
	.2283	.1193		5.17	56.85	.08230
	.2279	.1191		5.30	56.99	.08231
	.2282	.1192		5.00	56.63	.08221
	.2281	.1192		5.02	56.71	.08235
	.2283	.1193		-	-	-
.1418	.2717	.1420	.07875	5.00	35.17	.07856
	.2715	.1419		4.98	35.41	.07888
	.2716	.1419		4.95	35.55	.07877
	.2712	.1417		5.46	36.65	.07832
	.2716	.1419		5.00	35.58	.07872
	.2716	.1419		5.00	35.40	.07877
	.2710	.1416		4.98	35.42	.07888
	.2713	.1418		5.00	35.52	.07929
.1702	.3257	.1702	.08405	4.96	37.27	.08428
	.3259	.1703		5.00	37.29	.08395
	.3265	.1706		5.00	37.32	.08404
	.3259	.1703		4.97	37.57	.08450
	.3258	.1703		4.99	37.35	.08408
	.3257	.1702		5.01	37.53	.08403
	.3260	.1703		5.00	37.36	.08412
	.3256	.1701		-	-	-

TABLE 19

The Statistical Terms.

Copper

<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error.</u> <u>(x 10⁴)</u>
12.91	17.19	6.61	4.565
0.9258	2.565	0.6172	0.3274
0.8452	0.8542	0.5634	0.2989
1.365	1.559	0.9080	0.4820
1.464	1.732	0.9680	0.5178

Nickel

7.846	8.124	5.230	2.774
2.927	3.028	1.952	1.035
24.55	26.75	16.37	8.684
25.26	28.77	16.84	8.953
18.61	22.38	12.54	6.653

Table 20/....

TABLE 20

The Statistical Terms Expressed As Percentages.

Copper

<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error</u> <u>(x 10⁴)</u>
.1622	.2155	.1081	.05736
.08093	.1378	.03396	.01760
.07092	.07167	.04728	.02508
.09612	.1099	.06405	.03321
.08604	.1017	.05736	.03851

Nickel

.1160	.1163	.07667	.04113
.2625	.2320	.1084	.0988
.2986	.3253	.1991	.1056
.3207	.3654	.2141	.1134
.2259	.2663	.1492	.07916

	<u>Copper</u>	<u>Nickel</u>
Mean Standard Deviation	.09324%	.2482%
Mean Accuracy	.1273%	.2731%
Mean Probable Error	.06214%	.1655%
Mean Standard Error	.03431%	.06779%

5. The Estimation Of Copper By The Iodate Method And The
Determination Of Nickel With Oxine.

When copper is precipitated as cuprous thiocyanate there are a number of volumetric variations (see pp. 17 - 23) in which the precipitate is redissolved and the copper estimated. The best known of these is the iodate method, which is also generally considered the most accurate volumetric procedure, after the iodide method, for the determination of copper. It was studied here firstly to see how it compared with the direct gravimetric procedure, and secondly to assess its usefulness as a volumetric procedure.

Procedure.

The copper was precipitated with potassium thiocyanate exactly as described above (pp. 117 - 119). The precipitated cuprous thiocyanate was filtered through a Whatman No. 542 filter, and washed twelve times with a solution of 1 g. potassium thiocyanate and 0.5 g. sodium metabisulphite in 1000 ml. water, and then four times with 20% alcohol. The last washing was allowed to drain into a test-tube containing ferric chloride solution to test for complete removal of thiocyanate. (If the test shows thiocyanate present, the washing must be continued until the test is negative). After draining, the washed precipitate was transferred with the filter paper to a 250 ml. stoppered flask containing 30 ml. concentrated hydrochloric acid, 20 ml. water and 5 ml. chloroform (or carbon tetrachloride). The 0.1 N potassium iodate solution was then added fairly rapidly, the

contents/...

contents of the flask being constantly swirled. When the iodine colour had just disappeared from the solution, the flask was stoppered and the contents shaken very vigorously for at least a minute. The organic layer would now be coloured strongly purple. From that point the potassium iodate was added dropwise, the stoppered flask being shaken after each addition, until the iodine colour disappeared from the solvent layer.

Preparation Of 0.1 N Potassium Iodate.

Potassium iodate was dried for one hour at 120°C . and then allowed to cool in a desiccator. 5.351 g. were then weighed out into a 1000 ml. flask. The solution will keep indefinitely. A solution thus prepared was standardised against a standard copper solution and the normality was found to be theoretical.

Conclusion.

The iodate method suffers from a number of disadvantages which are not offset by its advantages. For one thing each estimation is extremely time-consuming; not only does the solution stand overnight, but the precipitate must be washed a large number of times. A very close filter is necessary owing to the fineness of the precipitate, and the washing is very laborious. The washings with alcohol are particularly slow, each addition taking about half an hour to drain. Further, it was found that the precipitate must not be left exposed to the air in the filter for any time, as it cakes, and the reaction with the iodate is very difficult to bring about, only very extensive shaking will make it go to completion.

The end/...

The end-point is very accurate and can be determined readily to within half a drop. On the whole, however, the method offers no advantages over the gravimetric procedure, and the author sees no grounds for recommending it.

The iodometric procedure is infinitely superior on all counts as a volumetric method. If it is wished to use thiocyanate, the gravimetric procedure is preferable.

The Estimation Of Nickel With Oxine.

Oxine is one of the best known of organic precipitants; its most notable characteristic is the large number of ions with which it forms insoluble precipitates. Its use in the estimation of magnesium and aluminium is fairly widely known, but not so its application to the determination of copper and nickel. It was studied here, firstly to establish the best experimental procedure of which no full description is available in English, secondly to determine whether its use offers any advantage over the normal analytical procedures, and thirdly to establish how the results obtained with its use compare with the results obtained by using other methods.

There are two normal procedures available. In both, the nickel is first precipitated in an acetic acid-sodium acetate buffer solution of pH 5. The precipitate may then either be weighed as $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2 \text{H}_2\text{O}$ after drying at 105°C ., or it may be dried at 140° and weighed as the anhydride.

Preparation of Oxine Solution.

The oxine solution may be prepared in either of the following

ways :-

ways:-

- (i) 2 g. oxine are dissolved in 100 ml. 2 N acetic acid, and dilute ammonia added dropwise with stirring until a slight precipitate forms. A few drops of acetic acid are added to dissolve the precipitate. The solution is stable more or less indefinitely.
- (ii) 2 g. oxine are dissolved in 100 ml. ethyl alcohol (95%), methyl alcohol or acetone. This solution, though much more convenient to prepare, has the disadvantage that it decomposes fairly rapidly, particularly if exposed to light, and is stable for only about a week.

A set of comparative estimations were performed on nickel solutions using oxine reagent prepared according to both of the above methods. No significant difference could be found in the results obtained. The second method of preparation is to be preferred if the reagent is to be used for a limited number of estimations, but it should be prepared in bulk by the first method if it is to be used over any considerable period of time.

Procedure.

To the filtrate from the thiocyanate separation of copper was added 4 g. sodium acetate and 10% of glacial acetic acid. The solution was warmed to about 60°C., and the oxine solution in 25% excess added dropwise with constant stirring. If the approximate amount of nickel present is not known, the presence of excess

oxine/....

oxine can be seen from the yellow colour the solution acquires when excess oxine is present. The solution was raised to boiling, being stirred all the time to avoid bumping, and kept at the boiling point for five minutes. The solution was allowed to stand overnight (6 hours) until quite cold, and was then filtered through a sintered glass crucible. The precipitate was washed thoroughly with cold water, dried for two hours at $100 - 105^{\circ}\text{C}.$, and weighed as $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2 \text{H}_2\text{O}$. After the precipitate had been washed and dried to constant weight, the temperature was raised to $140-145^{\circ}\text{C}.$, and the drying process continued for another two hours. The precipitate was then weighed as $\text{Ni}(\text{C}_9\text{H}_6\text{ON})_2$.

Discussion.

It was found that on adding the oxine solution to the nickel solution in the cold, a heavy flocculent greenish precipitate formed. Attempts to estimate the nickel by weighing this precipitate were unsuccessful, the results being very discordant. On boiling the mixture, however, this precipitate readily coagulated, but the nickel could not be estimated by filtering and weighing this precipitate owing to its solubility in hot water. It was therefore necessary to allow the solution to cool completely before filtering.

It was found necessary to keep the excess of oxine added below about 40%. Oxine is much less soluble in cold than in hot water, and may precipitate in amounts exceeding this value. This procedure, however, affords no difficulty as a 5% excess of oxine is at once shown by the colour of the solution.

It was/...

It was found necessary to dry for two hours in the first case because the temperature was just over 100°C . and the moisture evaporated only slowly, and in the second case because the conversion to the anhydride was incomplete in any shorter time.

Conclusion.

Oxine gives reasonably good results in nickel estimations, by weighing the complex either in the hydrated or the anhydrous forms. There is little to choose between these two; the accuracy is effectively the same. Weighing the hydrated form appears to give slightly more reproducible results.

Two disadvantages attending its use are firstly, the large number of interfering ions which also precipitate with oxine, and secondly, the necessity of allowing the precipitate to stand overnight.

The use of oxine then does not offer any particular advantages. It is a moderately good reagent for determining nickel from solutions containing nickel as the only metallic ion, but it is considered advisable to avoid it if other ions are present in the solution.

TABLE 21

<u>Theoretical Copper (g)</u>	<u>Volume KIO₃</u>	<u>Copper Found.</u>
.03375	36.10	.03370
	36.18	.03378
	35.93	.03355
	36.13	.03374
	35.82	.03344
	36.03	.03364
	36.07	.03367
	35.96	.03360
.03900	39.35	.03911
	39.42	.03916
	39.26	.03905
	39.55	.03931
	39.31	.03908
	39.31	.03908
	39.20	.03896
	39.25	.03901
.04328	43.77	.04357
	43.58	.04316
	43.69	.04320
	43.64	.04324
	43.60	.04320
	43.52	.04312
	43.71	.04351
	43.53	.04318
.03762	37.90	.03772
	38.00	.03785
	37.95	.03778
	38.02	.03784
	37.80	.03762
	37.93	.03770
	38.08	.03790
	37.98	.03780
.02803	28.10	.02797
	28.10	.02797
	28.05	.02795
	28.01	.02789
	28.20	.02806
	28.15	.02802
	28.16	.02803
	28.09	.02797

TABLE 22

Theoretical Nickel (g)	Weight of Precipitate (H)	Nickel Found	Weight of Precipitate (A)	Nickel Found
.03712	.2420	.03716	.2201	.03716
	.2419	.03701	.2185	.03690
	.2429	.03716	.2203	.03719
	.2413	.03692	.2181	.03685
	.2417	.03696	.2190	.03698
	.2423	.03705	.2199	.03713
	.2426	.03710	.2200	.03715
	.2422	.03704	.2198	.03711
	.2765	.04226	.2506	.04231
	.2759	.04220	.2502	.04225
.04228	.2766	.04232	.2503	.04227
	.2752	.04210	.2497	.04215
	.2759	.04221	.2503	.04227
	.2767	.04234	.2509	.04236
	.2755	.04215	.2498	.04218
	.2760	.04223	.2498	.04217
	.1852	.02835	.1681	.02839
	.1847	.02828	.1675	.02829
.02823	.1855	.02837	.1680	.02836
	.1849	.02829	.1678	.02830
	.1845	.02823	.1675	.02828
	.1848	.02824	.1674	.02827
	.1856	.02839	.1685	.02844
	.1851	.02832	.1676	.02830
	.2516	.03860	.2263	.03855
	.2524	.03862	.2290	.03866
.03867	.2519	.03854	.2262	.03854
	.2530	.03871	.2291	.03869
	.2519	.03856	.2265	.03859
	.2526	.03868	.2292	.03868
	.2522	.03869	.2267	.03860
	.2526	.03865	.2291	.03868
	.3142	.04807	.2849	.04810
	.3143	.04809	.2852	.04815
.04811	.3132	.04799	.2835	.04787
	.3146	.04814	.2850	.04812
	.3142	.04807	.2850	.04812
	.3145	.04812	.2852	.04815
	.3136	.04798	.2844	.04801
	.3137	.04800	.2841	.04796

H = Precipitate in hydrated form

A = Precipitate in dehydrated form.

TABLE 23

The Statistical Terms.

Copper

<u>Standard Deviation</u> (x 10 ⁴)	<u>Accuracy</u> (x 10 ⁴)	<u>Probable Error</u> (x 10 ⁴)	<u>Standard Error</u> (x 10 ⁴)
10.53	14.57	7.02	3.725
10.95	10.95	7.30	3.673
8.238	9.404	5.552	2.914
9.860	10.25	5.920	3.141
6.412	7.691	3.608	1.914

Nickel

(Precipitate weighed in hydrated form)

9.734	11.51	5.322	3.089
8.220	9.878	5.486	2.911
5.916	6.145	3.944	2.092
7.221	9.921	4.814	2.554
8.044	10.27	5.362	2.945

Nickel

(Precipitate weighed in anhydrous form)

15.48	15.05	8.986	4.767
7.601	8.229	5.301	2.758
6.106	6.176	4.070	2.159
5.976	7.838	3.986	2.115
10.25	11.56	6.034	3.624

Table 24.

The Statistical Terms Expressed as Percentages.

Copper

<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error.</u>
.2421	.4319	.7614	.1104
.2901	.2801	.1867	.09888
.1903	.2187	.1283	.06733
.2348	.2705	.1565	.08498
.1931	.2744	.1287	.06825

Nickel

(Precipitate weighed as hydrated form)

.2353	.3101	.1569	.08328
.1946	.2336	.1297	.06885
.2088	.2169	.1593	.07386
.1909	.2623	.1273	.06753
.1672	.2135	.1115	.05914

Nickel

(Precipitate weighed in anhydrous form)

.3632	.4050	.2421	.1284
.1803	.1946	.1390	.06524
.2156	.2181	.1436	.06524
.1545	.2037	.1030	.05464
.2130	.2403	.1421	.07534

	<u>Copper</u>	<u>Nickel (Anhydrous)</u>	<u>Nickel (Hydrated)</u>
Mean Standard Deviation	.2421%	.2253%	.1994%
Mean Accuracy	.2951%	.2523%	.2475%
Mean Probable Error	.1617%	.1593%	.1329%
Mean Standard Error	.08597%	.07997%	.07053%

G. The/...

8. The Estimation Of Nickel In The Presence Of Copper With Dimethylglyoxime And The Estimation Of Copper With Oxine.

Almost all the precipitants for nickel precipitate copper as well, though there are several substances which will precipitate copper without interference from nickel. Also, in separative procedures depending on variations in pH, it is almost always the copper which has the wider pH range for quantitative reaction so that the copper is generally the first removed. In the best method for copper estimation, viz. the iodometric method, nickel does not interfere; there is, however, no parallel method for nickel. In fact, in analyses of copper-nickel mixtures it is a fairly general rule to separate and estimate the copper first, and to determine the nickel subsequently in the filtrate. Of the seven methods treated in this thesis six are of this type. In this section it is proposed to deal with a procedure by which nickel, in the presence of copper, can be estimated by the use of dimethylglyoxime.

It has already been shown (p. 110) that copper, except in minute quantities, interferes in the estimation of nickel with dimethylglyoxime. In a recent paper ⁽¹⁰⁹⁾ Ranedo states that the addition of a solution of sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) to the copper-nickel solution prior to adding the dimethylglyoxime will eliminate this interference. This modification is apparently little known as no reference to it could be found in any English journals. It was therefore decided to incorporate it here, and include a more detailed description of certain points about which the author of the original paper is vague.

Procedure/....

Procedure.

To 50 ml. aliquots of the copper-nickel mixture was added 25 ml. of a 10% solution of sodium hyposulphite for every .1 g. copper present. A 1% alcoholic solution of dimethylglyoxime was added as usual, and then 5 ml. ammonia. The solution was allowed to stand for five minutes with constant stirring, after which it was filtered through a fine sintered glass crucible. The precipitate was washed with cold water and weighed as $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$.

Preparation Of 10% Sodium Hyposulphite Solution.

10 g. sodium hyposulphite were added to 100 ml. water, and the whole raised to boiling. When solution was complete, the solution was filtered to give a clear solution.

Discussion.

The original paper does not give any details apart from describing the procedure adopted in analysing a selected alloy. The first point investigated here was the effect of variations in the sodium hyposulphite concentration on the results. It was found that it was necessary to add 25 ml. of the 10% solution for every .1 g. copper present. Smaller volumes than this made the results high; larger volumes up to 75 ml. did not affect the final result (provided the solution was not allowed to stand for longer than 5 minutes before filtration).

Tests confirmed the original observation reported by Ransdo that heating caused the results to be high. It was also found that if the solution was allowed to stand for a time exceeding fifteen

to/....

to twenty minutes high results were obtained. Very intensive washing (at least twenty times) of the precipitate with water, however, reduced the results to the correct value.

It should also be noted that it is necessary to use a fine sintered glass crucible, as the nickel precipitate is not coagulated as it is in the normal procedure.

The important thing in this procedure is to allow the nickel solution to stand for just five minutes after the dimethylglyoxime and ammonia have been added. A longer time gives high results and a shorter time (less than a minute) gives low results.

Conclusions.

The use of sodium hyposulphite is completely successful in eliminating the interference of the copper. A comparison of the accuracy and precision obtained using this method with those obtained using the normal method when copper is absent (p.116) show the statistical terms to agree mutually to within less than 1%. The fact that the results obtained using this procedure are slightly superior to those the writer obtained using the normal method is probably the result of performing the estimation on the original aliquot, instead of on a filtrate from the original sample. The agreement, however, is so striking that it is hardly necessary even to propose this explanation.

The development of this procedure is an exceedingly valuable extension to the normal methods for determining nickel in the presence of copper. It obviates the necessity for removing the copper by a preparatory precipitation, and enables dimethylglyoxime

to/....

to be used without having to go through the longer cyanide separation (see p.56 and p. 88). It elevates dimethylglyoxime to the status of the prohibitively costly α -furildioxime, the only important reagent which can be used to determine nickel directly when copper is also present.

The procedure is, actually, at least as short as the ordinary dimethylglyoxime procedure, since the solution is filtered immediately, though this is to a certain extent offset by the slower filtering resulting from the presence of the uncoagulated precipitate.

This procedure is unhesitatingly recommended for the analysis of nickel in nickel-copper mixtures when the copper content is not also required.

The Estimation Of Copper With Oxime.

The reasons for the choice of oxime as a reagent for the determination of copper are the same as those listed on p. 129 where it was used to estimate nickel. Copper precipitates with oxime at all pH's above 2.2, so that the precipitation may be performed either in sodium acetate-acetic acid solutions or in alkaline solutions. The precipitate can either be dried at 105°C. and weighed, or dissolved in dilute hydrochloric acid and titrated iodometrically. Excess oxime does not interfere with the titration. The liberated iodine combines with the oxime giving $(C_5H_7NO.I_2)$, but the reaction with thio sulphate proceeds normally.

An interesting/.....

An interesting point which emerged during the course of the work was that in precipitating copper from the filtrate from the previous separation, the copper could only be precipitated completely in alkaline solutions. At a pH of 2 only very slight precipitation occurred, but it increased with increasing pH, becoming quantitative at a pH of 7. When dimethylglyoxime was used, however, the copper was completely held in solution in an alkaline medium. Further work on this was unfortunately prevented by lack of supplies of oxime.

Procedure.

The filtrate from the nickel separation was dark red, but turned a light yellow on stirring. To this solution was added 4 g. tartaric acid. A 20% solution of sodium hydroxide was added slowly with stirring until the solution was neutral. 15 ml. 2 N sodium hydroxide were then added. The solution was heated to 60°C. and the oxime solution (prepared as described on p.129) added dropwise with continual stirring, until a 25% excess was present (an excess is indicated by the colour of the solution going a lighter shade). The solution was raised to boiling and stirred until the precipitate had coagulated. The solution was then allowed to stand for 6 hours until quite cold, when it was filtered through a sintered glass crucible. The precipitate was washed first with a solution containing 1% sodium tartrate and 1% sodium hydroxide, and then with distilled water (five times with each). It was dried at 105°C. and weighed as $(C_9H_9ON)_2Cu$.

When/....

When the precipitate had been washed to constant weight, the sintered glass crucible and precipitate transferred to a beaker containing dilute hydrochloric acid, and the whole boiled until the precipitate had dissolved completely. Ammonia was then added dropwise until a permanent blue colour remained. The excess ammonia was boiled off and after cooling, 2 ml. 6 N hydrochloric acid added. The copper was then titrated iodometrically using .025 N sodium thiosulphate in the usual way (p. 99)

Discussion.

Berg (70) states that additions of more than 50 ml. 2 N sodium hydroxide give low results. The author found that volumes up to 50 ml. did not affect the results; the difference was probably due to the fact that Berg worked on volumes of 100 ml. while the volumes used here were about 300 ml. When more than 50 ml. were added, the results were low.

Conclusion.

The results obtained in the determinations of copper with oxine are of much the same order of accuracy as those obtained for nickel, and the remarks made on p.132 apply equally here. The results obtained are satisfactory but the procedure is time-consuming and a very large number of ions interfere. With the iodide and thiocyanate methods available, there is little reason for using it in preference to them.

The results obtained in a series of separations are shown in Table 25.

Table 25.

<u>Theoretical Nickel (g)</u>	<u>Weight of Precipitate.</u>	<u>Nickel Found.</u>
.02019	.0994	.02018
	.0995	.02017
	.0990	.02010
	.0996	.02023
	.0992	.02015
	.0994	.02018
	.0994	.02018
	.0994	.02018
.03410	.1661	.03414
	.1678	.03408
	.1677	.03406
	.1680	.03412
	.1680	.03412
	.1686	.03425
	.1681	.03414
	.1678	.03408
.04023	.1982	.04025
	.1980	.04022
	.1978	.04017
	.1983	.04027
	.1981	.04024
	.1980	.04022
	.1977	.04015
	.1982	.04025
.03595	.1771	.03597
	.1771	.03597
	.1771	.03597
	.1768	.03591
	.1771	.03597
	.1771	.03597
	.1766	.03587
	.1772	.03600
.04695	.2310	.04601
	.2314	.04699
	.2312	.04696
	.2311	.04694
	.2316	.04704
	.2314	.04699
	.2312	.04696
	.2314	.04699

Table 26

Theoretical Copper (g).	Weight of Precipitate	Copper Found	Volume Na ₂ S ₂ O ₃	Copper Found.
.04093	.2259	.04081	25.64	.04085
	.2264	.04090	25.65	.04087
	.2273	.04103	25.76	.04106
	.2263	.04088	25.66	.04089
	.2277	.04111	25.61	.04080
	.2268	.04095	25.67	.04090
	.2263	.04088	25.61	.04080
	.2260	.04083	25.65	.04086
.05194	.2872	.05186	32.54	.05186
	.2877	.05198	32.63	.05199
	.2875	.05194	32.58	.05192
	.2870	.05184	32.50	.05180
	.2879	.05201	32.61	.05196
	.2864	.05174	32.46	.05172
	.2881	.05205	32.60	.05195
	.2870	.05184	32.49	.05177
.03023	.1672	.03020	18.95	.03020
	.1675	.03022	18.92	.03015
	.1669	.03014	18.93	.03016
	.1670	.03016	18.95	.03020
	.1660	.02997	18.78	.02992
	.1675	.03026	18.98	.03024
	.1675	.03026	18.98	.03024
	.1667	.03010	18.93	.03016
.05459	.3016	.05449	34.07	.05442
	.3029	.05471	34.17	.05458
	.3018	.05451	34.12	.05450
	.3014	.05445	34.07	.05442
	.3022	.05459	34.12	.05450
	.3026	.05467	34.16	.05459
	.3020	.05455	34.14	.05453
	.3017	.05450	34.08	.05445
.02182	.1206	.02176	13.69	.02181
	.1209	.02184	13.62	.02171
	.1203	.02175	13.65	.02175
	.1207	.02180	13.65	.02175
	.1206	.02176	13.69	.02181
	.1207	.02185	13.71	.02184
	.1202	.02171	13.62	.02171
	.1208	.02182	13.68	.02179

Table 27.

The Statistical Terms.

Nickel

<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error.</u> <u>(x 10⁴)</u>
3.700	4.158	2.5067	1.329
5.916	6.535	3.944	2.092
4.158	4.259	2.772	1.470
4.070	4.071	2.714	1.440
3.926	4.597	2.618	1.389

Couper (Gravimetric.)

10.20	10.22	6.800	3.608
10.40	10.69	6.932	3.678
10.05	11.36	6.700	3.554
9.157	10.32	6.104	3.238
4.971	5.988	3.314	2.904

Couper (Volumetric).

8.123	9.864	5.416	2.874
10.10	12.35	6.740	3.572
10.26	12.79	6.840	3.629
6.698	12.15	4.465	2.369
4.857	7.121	3.236	1.718

Table 28

The Statistical Terms Expressed As Percentages.

Nickel

<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error</u>
.1862	.2059	.1242	.06583
.1735	.1916	.1156	.06134
.1034	.1059	.06907	.03655
.1132	.1132	.07550	.04006
.06642	.09566	.04428	.02349

Copper (Gravimetric)

.2492	.2496	.1662	.08814
.2002	.2058	.1335	.07082
.3324	.3759	.2216	.1176
.1677	.1891	.1119	.07298
.2276	.2745	.1518	.08054

Copper (Volumetric)

.1986	.2411	.1323	.07523
.1943	.2376	.1298	.06720
.3394	.4232	.2263	.1200
.1227	.2226	.0618	.04340
.2225	.3263	.1494	.07872

	<u>Nickel</u>	<u>Copper (G)</u>	<u>Copper (V)</u>
Mean Standard Deviation	.1285%	.2356%	.2155%
Mean Accuracy	.1423%	.2530%	.2902%
Mean Probable Error	.06574%	.1570%	.1437%
Mean Standard Error	.04526%	.08600%	.07691%

Alternative Method For Estimating Copper.

It was found that by adding sulphuric acid to the filtrate and boiling, cupric sulphide was precipitated just as it is with sodium thiosulphate. The cupric sulphide can then be redissolved in nitric acid and the copper estimated iodometrically. The procedure is exactly the same as that described on p. 106. The results, however, were not as good as those obtained when sodium thiosulphate was used. Table 29 below contains a set of results obtained using this procedure.

TABLE 29.

<u>Theoretical Copper</u>	<u>Volume of $\text{Na}_2\text{S}_2\text{O}_3$</u>	<u>Copper Found.</u>
<u>g.</u>	<u>ml.</u>	<u>g.</u>
	15.60	.02166
	15.67	.02177
	15.61	.02169
.02165	15.71	.02184
	15.64	.02174
	15.65	.02175
	15.69	.02181
	15.72	.02186

7. The Separation Of Copper By A More Electropositive Element And
The Estimation Of Nickel By Parr And Lindgren's Method.

The final method chosen for study in this thesis differs from all the others in that the copper is actually separated as metallic copper, which is then redissolved and estimated by one of the standard analytical procedures. The precipitation is accomplished by means of an element more electropositive than copper, such as zinc or aluminium, which will displace copper from its compounds in solution:

The precipitated copper is filtered off, redissolved in nitric acid and estimated either iodometrically or electrolytically. The iodometric method is to be preferred, since it was found that a certain amount of aluminium dissolves in the acid and is subsequently deposited on the cathode during electrolysis. In a control experiment carried out reproducing exactly the same conditions as are normally used, except that distilled water was used instead of a copper solution, the weight of the cathode was found to increase by 0.0031 g. If aluminium sheets of approximately the same surface area are used this figure is remarkably constant. If the electrolytic estimation is used, it is essential to run a blank and establish the 'blank value'.

The procedure adopted was that outlined in Scott's 'Standard Methods of Chemical Analysis' (53) with the addition of several improvements. Firstly, Scott directs 'heat the solution to boiling and keep at this temperature for about 10 minutes'. In fact,

this/.....

In fact, this time is completely inadequate for complete precipitation; it generally requires about an hour to effect complete precipitation. Actually it is better not to heat for any fixed time, but to continue heating until the copper begins to flake off the aluminium sheet. When the copper has flaked off the aluminium sheet leaving the latter bright and clean again, then all the copper has certainly been deposited.

Secondly, Scott advises the addition of 10% of sulphuric acid. It was found preferable not to exceed 5%. The great danger throughout this estimation is that the copper will at some stage be oxidised, and with the larger concentration of sulphuric acid, particularly if the solution is heated at all strongly, there was found to be a much greater probability of this occurring. Better results were obtained with the smaller volume of sulphuric acid and gentle heating throughout.

To prevent oxidation, the metallic copper is never allowed to become exposed to the air either in the filter or in the beaker. All washings are performed with hydrogen sulphide water, and the filter paper is never allowed to drain completely before the next addition of wash water.

Saturated hydrogen sulphide water is always added before the filtration to precipitate the last traces of copper, which are never completely removed by the aluminium. If the solution is heated until the aluminium sheet is clean, the amount of cupric sulphide deposited will be very small. This sulphide generally dissolves incompletely in the nitric acid, and the less there is of it,

the/....

the more accurate will be the final result.

When filtration is complete, Scott recommends that a hole be punched in the bottom of the filter and the copper washed through into a flask with a fine jet from a wash bottle. The disadvantage of this procedure is that it is impossible to remove completely all the copper, and particularly the cupric sulphide. This procedure must, of course, be used if the copper is finally to be estimated electrolytically, but if the iodometric method is to be used, it is preferable to transfer the filter paper, together with the metallic copper, directly into the flask. The presence of the paper in no way interferes with the titration.

Procedure.

To the beaker containing the copper-nickel solution was added a strip of aluminium sheet bent in the form of a triangle with the corners bent up at the ends. 5% of 6 N sulphuric acid were added and the beaker covered with a 'speedyvap'. The solution was warmed gently for ten minutes, and finally raised to boiling. The solution was allowed to continue boiling gently, the volume being kept constant by the addition of distilled water, until the precipitated copper began to flake off the aluminium sheet leaving it untarnished. When all the copper had finally flaked off, the heating was stopped and the cover and sides of the beaker washed down with distilled water. 25 ml. saturated hydrogen sulphide water were then added to precipitate the final traces of copper remaining in solution.

The /...

The solution was then decanted through a filter and the copper finally rinsed into the filter with a jet of hydrogen sulphide water. It is vital at this stage that the filter never be allowed to drain completely and that the copper in the beaker never becomes exposed to the air. The copper was washed six times in this way. While the final washing was draining, 5 ml. concentrated nitric acid were added to the beaker containing the aluminium foil and the whole heated to 60°C. (This is to dissolve any copper that may be remaining in the beaker or occluded by the aluminium). As soon as the filter had drained, it was removed from the funnel and placed in a 300 ml. conical flask. The nitric acid in the beaker containing the aluminium was at once poured into this flask and washed in well. The flask was warmed over a small flame until all the copper had dissolved. 5 ml. 6 N H_2SO_4 were added and the solution evaporated till white fumes were produced. Dilute ammonia was added dropwise until the solution was ammoniacal. After boiling off the excess ammonia, 6 N acetic acid was added dropwise from a burette until the solution was neutral, and then a further 2 ml. The solution was cooled and the copper estimated iodometrically with 0.05 N sodium thiosulphate.

The procedure followed for the electrolytic estimation was as follows:- After the copper had been filtered off, a hole was punched in the bottom of the paper and the copper washed through with a fine jet of water into a beaker below. The paper was washed

a number/....

a number of times with a fine jet of water, and finally the nitric acid from the beaker containing the aluminium sheet was poured through. The beaker containing the aluminium was washed out with water several times, the washings being poured over the filter paper. The copper in the beaker was dissolved by warming.

The nitric acid was neutralised with ammonia, and a mixture of 3 ml. concentrated sulphuric acid and 1 ml. concentrated nitric acid added. The copper was plated onto a platinum electrode for 45 minutes at 2 volts.

Conclusion.

The results obtained by this method are good, being of the same order as those obtained, for example, with the iodate method. It is strongly recommended that if it is used, iodometric titration be employed for the final determination of the copper. The use of an electrolytic procedure suffers from two disadvantages:-

- (i) It is necessary to run a blank.
- (ii) The cupric sulphide adheres very tenaciously to the filter paper and it is impossible to wash all of it through into the beaker.

The advantages of this procedure are similar to those of the separation of copper by means of sodium thiosulphate, viz. it is very useful when a large number of estimations are being performed. The results, however, are not as accurate as those obtained using the thiosulphate separation. It is, however, rather more convenient and it is recommended if a very high degree of accuracy is not required.

The Estimation Of Nickel By Parr And Lindgren's Method.

The method of Parr and Lindgren (120) is a modification of the usual diethylglyoxime method for estimating nickel, and is used mainly for small amounts of nickel. The nickel is precipitated with diethylglyoxime in the usual way, the precipitate filtered off and dissolved in sulphuric acid, and the excess sulphuric acid titrated back with standard potassium hydroxide.

Procedure.

The filtrate from the copper separation was warmed to 60°C and a 1% alcoholic solution of diethylglyoxime was added in 50% excess. Ammonia was added slowly until the acid (from the copper separation) was neutralised, and then a slight excess until precipitation was complete. The solution was digested on a water bath until the precipitate had coagulated, and was then filtered through a quantitative filter. The precipitate was washed eight times with cold water. The filter and precipitate were transferred to a beaker containing a measured excess of 0.05 N sulphuric acid, and the precipitate dissolved by warming. The whole was diluted to 200 ml., and, after thorough cooling, the excess sulphuric acid was titrated back with standard 0.1 N potassium hydroxide.

Conclusion.

This procedure is only suitable for very small quantities of nickel. For quantities greater than about 0.05 g. nickel the filtering is very slow and owing to the bulky nature of the precipitate it is impossible to transfer it to the flask without loss.

Even/.....

Even for small amounts the results are poor, and the writer finds no grounds for recommending this procedure. For small amounts of nickel, better results will be obtained by a gravimetric determination using α -furyldioxime or α -benzaldioxime, if available, or even salicyladoxime or diethylglyoxime.

The results are obtained in a series of determinations are shown in Table 30.

Table 20

Theoretical Copper g.	Volume Of $\text{Na}_2\text{S}_2\text{O}_3$ ml.	Copper Found. g.	Theoretical Nickel g.	Volume Of NaOH. ml.	Nickel Found. g.
.08045	25.65	.08017	.01407	21.10	.01418
	25.76	.08080		21.16	.01402
	25.86	.08026		21.18	.01587
	25.89	.08035		21.12	.01412
	25.72	.08046		21.10	.01418
	25.73	.08039		21.20	.01591
	25.75	.08054		21.16	.01402
	25.86	.08026		21.15	.01409
.05496	17.56	.05499	.02767	16.42	.02769
	17.57	.05496		16.40	.02771
	17.59	.05479		16.37	.02777
	17.52	.05486		16.45	.02755
	17.61	.05507		16.44	.02758
	17.58	.05499		16.41	.02768
	17.49	.05476		16.56	.02761
	17.61	.05483		16.46	.02754
.08803	26.16	.08808	.03257	14.71	.03256
	26.10	.08790		14.69	.03265
	26.02	.08786		14.69	.03265
	26.14	.08802		14.79	.03255
	26.08	.08784		14.73	.03260
	26.15	.08806		14.77	.03241
	26.11	.08792		14.70	.03260
	26.07	.08782		14.72	.03253
.07428	23.74	.07425	.01841	19.61	.01857
	23.71	.07416		19.66	.01827
	23.79	.07442		19.68	.01827
	23.70	.07415		19.71	.01818
	23.65	.07398		19.62	.01842
	23.66	.07406		19.67	.01826
	23.75	.07427		19.60	.01849
	23.72	.07418		19.74	.01811
.1287	41.07	.1284	.02567	17.72	.02591
	41.06	.1282		17.79	.02573
	40.92	.1280		17.76	.02573
	41.20	.1289		17.69	.02400
	41.09	.1285		17.72	.02591
	41.11	.1286		17.71	.02593
	41.11	.1286		17.81	.02593
	41.07	.1284		-	-

Table No. 31

The Statistical Terms.

<u>Copper</u>			
<u>Standard Deviation</u> <u>(x 10⁴)</u>	<u>Accuracy</u> <u>(x 10⁴)</u>	<u>Probable Error</u> <u>(x 10⁴)</u>	<u>Standard Error.</u> <u>(x 10⁴)</u>
15.22	16.68	10.15	5.383
11.08	12.80	7.320	3.918
13.92	16.94	9.280	4.923
13.29	16.79	8.860	4.700
3.206	3.619	2.126	1.134
<u>Nickel</u>			
9.791	9.835	6.528	3.402
10.08	10.08	6.720	3.565
10.26	12.23	6.840	3.629
15.70	16.26	10.46	5.552
12.94	13.10	8.620	4.576

Table No. 32

The Statistical Terms Expressed As Percentages.

<u>Copper</u>			
.1691	.2075	.1200	.06689
.2018	.2329	.1345	.07129
.1581	.2152	.1054	.05594
.1788	.2260	.1192	.06025
.2492	.2967	.1651	.08612
<u>Nickel</u>			
.6958	.6930	.4638	.2461
.3642	.3642	.2429	.1298
.3151	.3764	.2100	.1114
.3529	.3919	.3683	.3016
.5409	.5486	.3696	.1917

	<u>Copper</u>	<u>Nickel</u>
Mean Standard Deviation	.1054%	.5538%
Mean Accuracy	.2356%	.5961%
Mean Probable Error	.1300%	.3691%
Mean Standard Error	.06650%	.1969%

Table 35

A Comparison Of the Procedures For the Determination of Copper and NickelNickel

<u>Method</u>	<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error</u>
1. Salicylaldoxime	.07837%	.1512%	.05203%	.04143%
2. Dimethylglyoxime	.1174	.1434	.07826	.04152
3. Cynanetric	.2402	.2731	.1355	.03779
4. Oxime. Hydrated	.1994	.2473	.1329	.07083
Anhydrous	.2253	.2523	.1525	.07307
5. Parr and Lindgren	.5538	.5961	.3691	.1259
6. Dimethylglyoxime (Benedo)	.1285	.1423	.08574	.04523

Note: Estimations 1 - 5 were performed on the filtrate from the original solution, while Estimation 6 was performed on the original solution.

Copper

<u>Method</u>	<u>Standard Deviation</u>	<u>Accuracy</u>	<u>Probable Error</u>	<u>Standard Error</u>
1. Salicylaldoxime	.1097%	.1523%	.07137%	.06066%
2. Idometric	.03089	.07186	.02961	.01421
3. Sodium Thiosulphate	.1200	.1320	.0600	.04406
4. Potassium Thiocyanate	.08324	.1273	.06214	.05451
5. Potassium Iodate	.2421	.2931	.1617	.06897
6. More Electropositive Element	.1954	.2356	.1500	.06250
7. Oxime. Gravimetric	.2356	.2690	.1579	.08000
Volumetric	.2155	.2902	.1437	.07891

Note: Estimations 1 - 6 were performed on the original solution, while Estimation 7 was performed on the filtrate from the original solution.

Table 54.

Copper

Reagent	Grade	Factor	Cost 25 g.
1. Salicylaldehyde	Eastman-Kodak	.1894	24/3d.
Sodium acetate	'Kahlbaum' pro analysi		1/-
Glacial acetic acid	C.P. (Du Pont).		
2. Sodium thiosulphate	'Kahlbaum' pro analysi		
Potassium iodide	'pro analysi' (Schering Kahlbaum)		10d.
Potassium thiocyanate	'Kahlbaum' pro analysi.		
3. Ditto	Ditto		9d.
4. Potassium thiocyanate	'Kahlbaum' pro analysi	.5526	1/-
Sodium metabisulphite	Ditto		
5. Potassium thiocyanate	'Kahlbaum' pro analysi		
Sodium metabisulphite	Ditto		
Potassium iodate	'Pro analysi' (S.R.)		1/3d.
6. Oxine	A.R.(B.D.H.)	.1906	4/3d.
7. Aluminium foil			
As 2.			

Table 35.

Nickel

Reagent	Grade	Factor	Cost 25 g.
1. Salicylaldehyde	Eastman-Kodak	.1774	24/6d.
2. Dimethylglyoxime	Schering-Kahlbaum	.2031	4/11d.
3. Potassium cyanide	'Kahlbaum pro analysis'		1/1d.
Silver nitrate	C.P. (Coleman and Bell).		5/10d.
Potassium iodide	'Pro analysis' (S.K.)		1/7d.
4. Oxine	A.R. (B.D.H.)		4/3d.
5. Dimethylglyoxime	Schering-Kahlbaum.		4/11d.
Sodium hyposulphite	A.R. (B.D.H.)		1/5d. (500 g.)
6. Dimethylglyoxime	As 2		

Note: The 'Grade' column describes the actual reagents used in the course of this work.

The 'Cost' column gives the prices of the reagents, according to the B.D.H. Catalogue, 1946.

DISCUSSION/....

DISCUSSION

From the statistical survey of the 700 results recorded in the previous pages it is evident that the analytical procedures here investigated fall clearly into three classes.

For the methods for the determination of copper, these are:-

1. The Iodometric method. This stands out very distinctly as ^{by} far the most accurate and precise method available for the determination of copper.
2. The accurate group. This group includes those methods which give excellent results in copper estimations without approaching those obtained by the iodide method. It includes the gravimetric estimations with potassium thiocyanate and salicylaldehyde, and the separation of copper with sodium thiosulphate and its subsequent iodometric estimation.
3. The less accurate group. The results in this group bear about the same relation to those in group 2 as the latter do to the iodometric procedure. It includes the gravimetric estimation with oxine, the volumetric iodate method, and the procedure using a more electropositive element.

Nickel estimations fall into the following three classes:-

1. The accurate group. This includes the gravimetric estimations with salicylaldehyde and dimethylglyoxime.

2. The less accurate group. This includes estimations with oxine and by the cyanide method.
3. The inaccurate group. The Farr and Lindgren method falls in this group.

This division is more or less what one would expect, as all the standard procedures fall into the more accurate categories. The only exception to this is the little used salicylaldehyde.

The choice of the procedure to be adopted in the analysis of a copper-nickel mixture is made fairly simple by the fact that the most accurate procedures are also those that are most convenient to carry out.

For an ordinary copper-nickel analysis the choice lies, quite definitely, in the author's opinion between the following:-

- (i) The determination of the copper in one aliquot by an iodometric titration, and the separation of the nickel in a separate aliquot with dimethylglyoxime, using sodium hydrosulphite to hold the copper in solution.
- (ii) The gravimetric determination of both with salicylaldehyde.

For a fairly large number of analyses, the author advises the selection of the first of these, since, once the solutions required for the iodometric titration have been prepared and standardised,

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a series of estimations can be performed in a matter of minutes. For a small number of analyses the author recommends the use of salicylaldehyde.

For routine determinations of copper, the separation with sodium thiosulphate is pre-eminent. The results obtained by this procedure are excellent, and provided sufficient apparatus and space are available, a very large number of separations can be effected simultaneously. In routine determinations of nickel, the newly developed cyanide process is extraordinarily useful, and affords complete separation of nickel from almost every ion that is likely to be present. The advantage of both these separations is that not only do they effect a clean separation from other ions, but they also enable the most accurate procedures (i.e. the iodide method, and the use of dimethylglyoxime or salicylaldehyde) to be used to complete the determination.

The author's particular partiality is towards salicylaldehyde, which he considers a reagent whose usefulness has been underestimated or ignored. The uncertainty concerning the ^{pH} conditions and interfering elements has been removed (see pp. 86-93), and he considers it, taking all factors into account, the most useful reagent discussed in these pages for both copper and nickel. For nickel, an estimation requires about half the time of a similar determination with dimethylglyoxime, and the results are statistically almost identical*. For copper, an estimation with salicylaldehyde is infinitely more convenient than one with thiocyanate, and the difference in accuracy and reproducibility is small.

* The only occasion when the use of dimethylglyoxime is preferable is when cobalt is also present.

Of the other methods, the iodate method should be avoided. It is extremely tedious and not particularly accurate, without offering any compensating advantages.

The cyanometric estimation of nickel should not be used except where it is required to analyse a large number of samples without any great accuracy.

Parr and Lindgren's method is an extremely poor method, and should on no account be used.

Oxine gives moderately good results for both copper and nickel, but it precipitates with so many ions, that its use is very restricted. It is always preferable to choose an alternative procedure rather than to remove the interfering ions. With other superior methods available there is no reason for using it even for determinations in pure solutions.

Lack of time has unfortunately prevented the study of many interesting reagents. For example, benzotriazole, anthranilic acid and quinaldinic acid, to judge from the accounts given of them in the literature, are extremely valuable and accurate reagents for determining copper. The section on nickel should desirably include an account of, at least α -furildioxime and α -benzildioxime. When it is realised that the work here included has necessitated the performance of about 2000 estimations (an average of about 4 a day), of which about 700 are included in the preceeding pages, the reason for their omission will perhaps be appreciated. A study of several points which have been only superficially dealt with in these pages,

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and work along similar lines on a number of lesser-known reagents would seem to offer a profitable field for future investigations.

SUMMARY/.....

SUMMARY.

(1) The use of salicylaldoxime as a reagent for the determination of copper and nickel has been investigated. This has been shown to be an excellent reagent for the determination of both. The pH conditions have been standardised. Methods have been developed to eliminate the interference of zinc, lead and iron.

(2) A method of separating nickel from cobalt, and a number of other ions, has been shown to give excellent results.

(3) A separation of copper with sodium thiosulphate has been studied and slightly modified so that the filtrate may be used to determine nickel.

(4) Nickel has been determined with dimethylglyoxime. It has been shown that cobalt does not interfere, but that, contrary to statements in the literature, copper effectively interferes at all concentrations. A procedure using sodium hydrosulphite has been used successfully to eliminate the interference of copper.

(5) The Iodometric procedure for the estimation of copper in the modified form used here has been shown to give results of great accuracy.

(6) Potassium thiocyanate has been shown to be the best precipitant for copper, but its use involves several disadvantages.

(7)/....

- (7) The procedure for separating copper by means of a more electro-positive element has been developed and found to give good results if the details specified are carefully adhered to.
- (8) The use of oxine in both copper and nickel determinations has been investigated and shown to give reasonable results for both.
- (9) Two volumetric procedures for copper and nickel, viz. the iodate method and the cyanide method, have been studied and shown to offer more disadvantages than advantages.
- (10) The method of Parr and Lindgren for nickel has been studied and found to be very poor from all points of view.
- (11) The results of these estimations have been analysed statistically.

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