THE PRECISE DETERMINATION OF COBALT IN THE SULFIDE

by

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Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

1927.
ACKNOWLEDGEMENT

The writer wishes to express his sincere appreciation and deep indebtedness to Doctor Malcolm W. Haring for the suggestion of the problem discussed on the following pages as well as for constant advice and counsel in the carrying out of the research.
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Introductory Statement

An examination of the standard analytical text-books discloses the fact that the methods by which cobalt can be determined quantitatively are not numerous and that those already developed are in many cases open to objections either because of the manipulative detail involved or because of susceptibility to error. Also from a qualitative standpoint it is evident that the separation of cobalt from the other members of the third group as the sulfide has not been fully studied.

The present work was, therefore, undertaken with a twofold objective in view. It was first desired to develop a satisfactory method for the quantitative determination of cobalt. The method once developed was to be used to study the completeness of precipitation of cobalt as the sulfide in solutions of varying pH values. The solutions were to be buffered in order to keep them at the desired pH value.
Review of literature

A perusal of the literature on the subject reveals the fact that the precipitation of cobalt as the sulfide has been used very little as a direct method for the quantitative determination of the metal and furthermore that no study has been made of the effect of pH value upon either the completeness of precipitation or the character of the precipitate. Fresenius (1) discusses the precipitation of cobalt by ammonium sulfide. His directions for the precipitation are: "Put the solution into a flask, add ammonium chloride then ammonia just in excess, then ammonium sulfide as long as a precipitate is produced, fill up to the neck with water, cork and allow to stand for twelve to twenty-four hours in a warm place. In the moist state exposed to the air the sulfide oxidises to the sulfate. In washing the precipitate after filtering, therefore, water containing ammonium sulfide is employed and the filter is kept full. It is advisable also to mix a little ammonium chloride with the wash water but its quantity should be gradually decreased, and the last water must contain none." The sulfide is then redissolved in aqua regia containing an excess of hydrochloric acid and the cobalt is weighed as the metal after precipitation and reduction of the hydroxide. Fresenius adds that there are no sources of error in the precipitation with ammonium sulfide. This statement will receive further comment in the course of this paper.
The present and expected characteristics of the markets and economic activities are undergoing a significant transformation due to the rapid advancement of technology and the increasing complexity of global trade. The interdependence of economies is more pronounced than ever before, leading to interconnectedness in various sectors. This global interconnectedness is not limited to trade and commerce but extends to knowledge, information, and culture. The integration of economies is facilitated by the rapid development of communication technologies, allowing for real-time exchange of ideas and resources. In recent years, the global economy has experienced unprecedented growth, driven by innovation and technological progress. However, this growth has been unevenly distributed, with some regions and industries benefiting more than others. The need for balanced and sustainable economic development has become increasingly evident. The role of governments in fostering economic growth has evolved, with a greater emphasis on creating enabling environments that support innovation and entrepreneurship. The international community has recognized the importance of addressing global challenges such as climate change, poverty, and inequality, necessitating collaborative efforts among nations to find solutions. Overall, the future of the global economy is shaped by the interplay of various factors, including technology, resource availability, and geopolitical stability.
are precipitated as sulfides. Filter and wash with hot water. The filtrate may still contain small amounts of nickel and cobalt. Concentrate it and add colorless ammonium sulfide. Make slightly acid with acetic acid, warm and filter. If a precipitate is obtained, collect it on a separate filter. Repeat this testing of the filtrate until no further precipitation is produced.

Wash the precipitated sulfides from the filters, as completely as possible, into a small porcelain dish or casserole. Dry and burn the filters and add the ash also. Dissolve the whole in hydrochloric acid and a little nitric acid. The solution now contains nickel, cobalt and possibly zinc. To remove the latter, evaporate to small volume, add two or three grams of ammonium chloride, Fresenius (4), evaporate to dryness on a water bath and then heat carefully until all the ammonium chloride is expelled. The zinc is driven off at the same time. Then cool dissolve the residue in nitrohydrochloric acid and expel the excess of acid by evaporating nearly to dryness.

The cobalt is then precipitated as hydroxide with potassium hydroxide and some bromine water. After ignition of the hydroxides the results are reported as combined nickel and cobalt unless nickel is to be determined separately, in which case it is precipitated as the hydroxide by red mercuric oxide while cobalt is retained in solution in the form of potassium cobalticyanide.

There are numerous cases where cobalt has been determined by weighing up as the metal in the final step. For example, Fresenius
An investigation which partially parallels the one under discussion was carried out with zinc by Halee and Ware (9). Zinc was precipitated as the sulfide from carefully controlled buffer mixtures composed of ammonium formate and formic acid. The completeness of precipitation as a function of hydrogen-ion concentration was fully studied in the same manner as in the present investigation. The sample was finally weighed as the sulfate and not as the metal.

The literature reveals no further work differing greatly in principle from that already cited.
Discussion of Principles

Imasmuch as this investigation has to do with the development of a method for the quantitative precipitation of cobalt as the sulfide and with the completeness of precipitation in buffered solutions of varying hydrogen-ion concentration, it will be advisable to discuss some of the principles involved.

The method is based on the relative insolubility of cobalt sulfide in solutions of low acidity. The small amount remaining in solution may be considered to be fully dissociated into cobalt and sulfide ions. Likewise the dissolved sulfide is in equilibrium with the solid sulfide so we may write: \( \text{CoS} \overset{\text{Solid}}{\longrightarrow} \text{CoS} \overset{\text{Dissolved}}{\rightarrow} \text{Co}^{+} + \text{S}^{2-} \).

The concentration of the dissolved sulfide is constant under these conditions and hence \( \frac{\text{CoS}}{\text{CoS}^{\text{Dissolved}}} = K_{b} \), where \( K_{b} \) is the solubility constant. Also \( \frac{[\text{Co}^{+}][\text{S}^{2-}]}{[\text{CoS}^{\text{Solid}}]} = K_{f} \), where \( K_{f} \) is the dissociation constant. Since \( \text{CoS}^{\text{Diss}} \) is a constant the last equation may be written \( [\text{Co}^{+}][\text{S}^{2-}] = K_{b} \cdot K_{f} \cdot [\text{CoS}] \), where \( K_{b} \cdot K_{f} \cdot [\text{CoS}] \) is the familiar solubility product constant.

The quantities \( [\text{Co}^{+}] \) and \( [\text{S}^{2-}] \) are the effective ion concentrations or activities. A distinction must be drawn between concentration of dissolved sulfide and activity. The ratio of the activity to the total concentration of the electrolyte is the activity coefficient or the thermodynamic degree of dissociation. Creighton and Fink (10). Whenever concentrations are mentioned activities are to be understood unless otherwise stated.

Hence the solubility product constant is the product of the activities of cobalt and sulfide ions which determines the amount of cobalt sulfide
which remains in solution. This activity product is fixed and
definite. If one of the quantities involved in the product is in-
creased the other must decrease as required by the solubility product
constant.

The solubility product of cobalt sulfide quoted in Landolt-
Bernstein (11) is the value calculated by Bruner and Pawlowski (12)
by use of the modified equation of Bodlander, namely
\[ Q = e^{23100} = E_A + E_K - 0.029 \log L. \]
In this equation \( Q \) is the heat of formation of
the sulfide, \( E_A \) is the discharge potential of the anion, \( E_K \)
that of
the cation and \( L \) is the solubility product. The value given for
cobalt sulfide is \( 3 \times 10^{-26} \). The value given for beta zinc sulfide
is \( 1.2 \times 10^{-25} \) and for nickel sulfide \( 1.4 \times 10^{-24} \). On the other
hand, the value quoted by Seldell (13) from work done by Weigel (14)
in 1906 by use of the electrolytic conductivity method, assuming
complete dissociation and hydrolysis, for the solubility of cobalt
sulfide in water at 18 degrees, gives a solubility product of \( 1.7 \times
10^{-9} \). This value is extremely different from the one in Landolt-
Bernstein. The results obtained in the present investigation
are more nearly in accordance with the value quoted by Seldell
so that the discussion will be conducted in the light of the latter
value.

In order that the solubility product be satisfied and a pre-
cipitate form, the product of the activities of sulfide ion and
cobalt ion must equal \( 1.7 \times 10^{-9} \). If the salt is somewhat soluble
the concentration of unionized salt must also be equalled. Chapin (14a).
The concentration of sulfide ion furnished by an aqueous solution of hydrogen sulfide is very small. However, it is sufficiently large to cause cobalt to be precipitated completely enough for determination as the sulfide. Now as hydrogen ions furnished by a stronger acid are introduced, the ionisation of hydrogen sulfide and hence the concentration of sulfide ion is rapidly reduced. Bruner and Sawadski, Chem. Zentr. (1910) (15). The relation between the concentration of the sulfide ion and that of the hydrogen ion, the relation which is of primary importance in considering the precipitation of metal sulfides in acid solutions is given by the following equation: \[ \frac{[\text{H}]^2}{[\text{S}^2-]} \cdot k \cdot K = 1.1 \times 10^{-23} \]

Stieglitz (16). The concentration of the sulfide ion is thus inversely proportional to a square of the concentration of the hydrogen ion. A thousandfold increase in the concentration of the latter, which is very nearly the effect produced by the presence of 0.1 molar hydrochloric acid ([H] = 0.091), reduces the concentration of sulfide ion in the saturated aqueous solution a millionfold. If we call \[ \frac{[\text{S}^2-]}{[\text{H}]^2} \text{Ag} \] the concentration of the sulfide ion in the acid solution, \[ \frac{[\text{S}^2-]}{[\text{H}]^2} \text{Ag} = 1.1 \times 10^{-23} / (0.091)^2 = 1.3 \times 10^{-21} \] whereas in the absence of acid \[ [\text{S}^2-] = 1.2 \times 10^{-15} \]. The latter value is derived from the value for the dissociation constant for the secondary ionization of hydrogen sulfide.

A point is thus finally reached at which the concentration of sulfide ion has become so very small that the product of the cobalt and sulfide ion activities is no longer equal to \( 1.7 \times 10^{-9} \).
Consequently cobalt sulfide will either dissolve or fail to precipitate, as the case may be. The object of this investigation was to find the point at which incomplete precipitation begins. This was to be done by systematically lowering the pH value by small increments. It is, of course, obvious that the precipitation of cobalt sulfide itself will lower the pH value as a result of liberation of mineral acid until precipitation ceases unless steps are taken to suppress this lowering. A means of bringing about this suppression lies in the use of alkaline solutions or suitable buffer solutions.

The action of so-called buffer solutions may be most clearly explained by means of the theory of mixed electrolytes. Craighton and Fink (17). Whenever two binary electrolytes are present in solution, their four ions may react to form the four undissociated substances, the amount formed of each being governed by the equilibrium equations applicable to the respective substances. When all the four possible products are strong electrolytes, the ions react to but a negligible extent. The case is quite different, however, when one of the possible products is a weak electrolyte. For example, if ammonium and acetate ions (ammonium acetate) are introduced into a solution containing hydrogen and chlorine ions (hydrochloric acid), there is a great tendency for the acetate and hydrogen ions to combine to form undissociated acetic acid for $K_{\text{HAc}} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = 1.8 \times 10^{-5}$.

Since this ratio must always be satisfied, it is evident, therefore, that hydrogen and acetate ions must unite with one another to form undissociated molecules of acetic acid. Furthermore, this
union must proceed until the activities of these ions are reduced and
the activity of undissociated molecules is increased to such an extent
that the product of the activities of the ions divided by the activity
of the undissociated molecules is equal to 1.0 x 10^{-5}. This results
in the conversion of practically all of the ammonium acetate into
acetic acid. The reaction which takes place in this case may be
written: \[ \text{NH}_4^+ + \text{Ac}^- + \text{H}^+ + \text{Cl}^- = \text{NH}_4^+ + \text{Cl}^- + \text{HAc} \].

Or, omitting those substances which occur on both sides of the equation,
simply: \[ \text{H}^+ + \text{Ac}^- = \text{HAc} \]. Similarly when a solution of a strong base is
added to a solution of a salt of a weak base, the weak base is
"liberated".

If to a liter of pure water one cubic centimeter of 0.01 normal
hydrochloric acid were added the pH value would drop from 7 to 5,
while the addition of the same quantity of 0.01 normal sodium hydrosul.
would bring about a similar rise in the pH value. On the other hand,
if the solution of acid or alkali were added to a liter of a solution
of a weak acid, HA, and its salt, NaA, the resulting change in pH would
be scarcely appreciable. In the latter case change in pH on the
addition of acid or alkali is opposed by the reaction: \[ \text{A}^- + \text{H}^+ = \text{HA} \]
or \[ \text{H}_3^+ + \text{OH}^- = \text{H}_2\text{O} + \text{H}^- \].

This power of certain solutions to resist change in pH on the
addition of acids or alkalis has come to be known as buffer action
and the solutions which exhibit this action are termed buffer solutions.

Buffer solutions evidently possess a reserve acidity or alkalinity
Since in accordance with the law of mass action \( [H^+] [A^-] Z_a \)
it follows when \( [H^+] = Z_a \) or \( [A^-] = Z_a \) that the reserve acidity and
alkalinity of a buffer solution will be equal.

Thus if one wishes a solution of \( [H^+] = 1 \times 10^{-3} \), which shall
have equally effective buffer action towards added acid or added
base, an acid with a dissociation constant close to this value is
selected and mixed with the proper amount of its alkali salt.

Since in the present work it was necessary to obtain varying
pH values, the solution of acetic acid used was made up sufficiently
strong that it could be diluted to varying degrees to give any desired
pH when mixed with a fixed quantity of its ammonium salt. The stock
solution of acid prepared was 6.8 molar and a pure solution of this
acidity would give a pH of approximately two as calculated by the
equation \( [H^+] [A^-] = K_e [HA^-] \) and as experimentally confirmed.

An experimental study was made of the effect on pH of adding
cases in order that an indication might be obtained of the effectiveness
of the buffer action. This quantity of hydrochloric acid is
equivalent to that which would be set free during the precipitation by
hydrogen sulfide of 0.25 grams of cobalt metal in the form of the
chloride. The data obtained follow:
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Yield %</th>
<th>Temperature</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10.0</td>
<td>6.0</td>
<td>20.0</td>
</tr>
<tr>
<td>0.2</td>
<td>9.5</td>
<td>6.2</td>
<td>19.0</td>
</tr>
<tr>
<td>0.4</td>
<td>9.0</td>
<td>6.4</td>
<td>18.0</td>
</tr>
<tr>
<td>0.6</td>
<td>8.5</td>
<td>6.6</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table showing yield and effect of added material.  
Table showing yield of various material and effect of...
Graph I.

pH of various mixtures before and, as indirectly determined, after precipitation.
Graph II.
Curve showing increase in buffer action as concentration of acetic acid is increased.
the number of crystal nuclei formed so large that the cobalt sulfide precipitated has a gel-like structure because of its enormous surface. The factor of washing makes this form of the precipitate most undesirable but there is still a more important objection. This is the propensity to oxidation of the sulfide to the sulfate. The more surface possessed by the precipitate the greater this propensity. This is indicated by a simple form of the equation for the velocity of heterogeneous reactions, that is \[ \frac{dx}{dt} = kS(e-x) \], Getman (17a), where \( S \) represents the area exposed to the oxide, \( x \) denoting the amount of solid oxidized in the time \( t \), \( k \) being a constant. This equation must, of course, be integrated before it can be used. The tendency to oxidation forbids the precipitation of the sulfide in so weakly acid solutions and points to the highest possible limit of acidity. Furthermore, Graph II shows that buffering action is relatively small at these high pH values. However, this upper limit is unsuitable for the reason that the element of saturation is involved. If saturation of the solution with hydrogen sulfide is not complete the active mass of sulfide ion will not be at a maximum and precipitation will be incomplete. The resultant of these factors and the curve shown elsewhere in this paper point to a pH value of 2.95 as being optimum. Under these conditions the precipitate is in the form of relatively large crystals, is quick settling and easily washed without danger of oxidation if reasonable care be exercised.

In roasting the precipitate several considerations enter. In the first place, the precipitate becomes partially converted only to the sulfate instead of entirely to the oxide. The temperature of de-
composition of cobalt sulfide is placed at 700 to 770 degrees Centigrade. This factor, therefore, sets an absolute minimum temperature. There are still other elements to be considered. Time is of importance and a higher temperature shortens the time for roasting. The same temperature is used for reduction as for roasting and a higher temperature is required for the reduction for the reason that cobalt reduced at low temperatures is quite pyrophoric and could not be weighed with accuracy. If a temperature of 1000 degrees Centigrade is used for reduction the pyrophoric nature of the reduced cobalt entirely disappears. This might possibly be explained by sintering of the cobalt crystals at the higher temperature.
Description of Apparatus

The method as finally adopted involves no accurate volumetric measurements, all precise measurements being gravimetric. The balance used was carefully calibrated for sensitivity. The weights were accurately calibrated by the Richard's substitution method, (17b).

The hydrogen ion measurements were made with a Leeds Northrup Students' potentiometer. The hydrogen electrode used was a platinized platinum, Hildebrand type bubbling electrode. The normal calomel electrode was used as reference. The hydrogen was purified by passing successively through alkaline pyrogallate, alkaline permanganate and water, after being generated in a Hippi generator by the action of thirty percent sulfuric acid on zinc.

The hydrogen sulfide was generated in a Hippi apparatus and passed in succession through absorbent cotton and two bottles of distilled water.

The furnace used for roasting and reducing the sulfide was an ordinary electric combustion furnace capable of reaching a temperature of 1000 degrees centigrade.

The materials were all of "reagent" quality. Blanks were run on the acetic acid and ammonium acetate and a constant weight of 0.2 milligram subtracted from all determinations to take care of added non-volatile impurities. Stock solutions of acetic acid and ammonium acetate were made up in sufficient volume to permit the same solutions to be used throughout the work. The water used at all times was a
high grade of distilled water (specific conductivity $2 \times 10^{-6}$ mhos).

The prime requirement in the case of the substance to be studied, namely cobalt, was that it should be easily and quickly available in a form which possessed a definite composition, was stable under ordinary conditions, and could be weighed up with ease and dispatch.

First, of course, it was necessary to free the cobalt from the impurities present. The source of supply was "Baker's Analyzed" cobalt chloride hexahydrate which contained, according to the label, five hundredths percent of nickel and a smaller percent of iron. The method of purification was the usual one for cobalt and the one which was used by Baxter and Coffin (18) in their atomic weight determination of cobalt. It consists of the preparation of chloropentammines-cobaltichloride, Bilsz (19), which precipitates in a pure condition in the presence of nickel. Iron is removed previously when the cobalt solution is made ammoniacal. The cobalt complex is redissolved, after filtering and washing thoroughly with one to one hydrochloric acid, in dilute ammonia. It is then reprecipitated by making the solution strongly acid with hydrochloric acid, and finally filtered and washed with dilute acid as before. Two precipitations were considered sufficient since the cobalt obtained thereby failed to show any trace of nickel by use of dimethylglyoxime or the presence of iron on the addition of ammonia.

Once the cobalt was purified it had to be converted into a form possessing the characteristics mentioned above. Baxter and Coffin, loc. cit., used anhydrous cobalt chloride as their source of supply but the difficulties involved in preparing this and keeping it in a pure anhydrous form were prohibitive in this investigation. It was
then thought that the stable hemihydrate might be obtained but the
time required to secure the latter in a form entirely free from excess
moisture and other hydrates was unreasonably long. Even the hemihydrate
is not stable under all ordinary conditions.

An attempt was next made to prepare a standardized, concentrated
aqueous solution of cobalt chloride which could be weighed out in a
weight burette. On standing, however, the solution hydrolysed to an
appreciable extent. A small volume of tenth-normal hydrochloric acid
added to the solution would prevent this hydrolysis, but, even so, the
solution was not immune to changes in composition due to evaporation.

It was finally decided to reduce the cobalt to the metallic state
and use the pure metal as the starting point. The metal has all the
desired characteristics and is easily converted into any desired salt
by dissolving in the appropriate acid. The decision to use the metal
as the stock material came as a result of a change in analytical pro-
cedure. It was originally proposed to follow in part the procedure
of Fales and Taro, loc. cit., in their work with zinc. After pre-
cipitating zinc as the sulfide, these investigators converted the
sulfide to the sulfate and weighed it as such. It was found in the
case of cobalt sulfide impossible to bring about complete conversion
to the sulfate without too great danger of loss of some of the
material. This was because nothing short of aqua regia would dissolve
cobalt sulfide. As a consequence of this, the plan of procedure was
changed and the sulfide, after roasting, was reduced to cobalt metal.
It will readily be seen that if the end-product is cobalt metal, by using cobalt in the same condition as the starting material an excellent check is had on the accuracy of the analysis.

A word might be said at this point in regard to a difficulty encountered in the roasting and reduction of the sulfide. The original plan was to burn off the oven-dried precipitate in a crucible and then transfer it to a weighed short length of Pyrex glass tubing one centimeter in diameter for roasting and reduction. The sulfide was heated until the Pyrex tube softened, which requires a temperature of over eight hundred degrees Centigrade. During the heating, the sulfide was exposed alternately to the oxygen of the air and to a stream of hydrogen. Even though treatment might be continued for hours, never in any case did the weight of the reduced metal decrease to the theoretical value. This fact may have been due to two reasons. First, not all of the sulfur trioxide may have been driven off. Secondly, cobalt reduced at low temperatures is quite pyrophoric (R. W. Landrum loc. cit.) and the material as it was weighed up may have been contaminated with oxide. At any rate, it was found necessary to abandon this plan of procedure and substitute the one which was used henceforth. This will be described in another place.
Discussion of Method and Results

Preliminary investigation indicated that two-tenths gram of metallic cobalt was the most suitable quantity for precipitation as the sulfide under the conditions selected. The metal was poured out upon a small watch glass, the total weight carefully determined by the method of swings, and approximately two-tenths gram accurately weighed out into each of two three hundred cubic centimeter Erlenmeyer flasks. About five cubic centimeters of concentrated hydrochloric acid were added to each and the tops of the flasks immediately covered with watch glasses, to protect against loss from effervescence. The flasks were placed on water baths and warmed until all the metal was in solution. The acid solutions were rinsed out into two hundred fifty cubic centimeter beakers and evaporated to dryness. Each beaker was then set on an asbestos-covered hot plate until the chloride had assumed the bright blue color of the anhydrous salt. This latter step was taken to insure complete removal of excess acid.

In the qualitative separation of the various groups of metals cobalt is precipitated as the sulfide from an alkaline solution, but it is well known that it will be completely precipitated from solutions the pH values of which are much less, provided steps are taken to neutralise the acid liberated during the precipitation. It was, therefore, next a question of finding a suitable buffer material. Preliminary investigation had disclosed the fact that
...the proper concentration and
enhance the optical output and
been freed of traces and described

...the wall was protected over the precipitation and its effect had to be kept

onto paper or filter paper a wafer paper

be removed and the filter paper sucked dry so the ether vapor

gathered poured into the filter paper which was thin concentrate in

trichloro (chloroform) on (of) me used. The bulk of the precipitation was

put into another concentration and taken which was the use of the ether

exceeded. By using this material all influence was eliminated. However,

voltage potential difference, namely assuming sources-constant acid,

sodium carbonate a voltage electrophoresis. In view of these conditions

the precipitation were weighed exactly into a glass tube until

precipitate at the outer shell more need of yet to less addition if

this mixing could express the precipitation to less by precipitation if

volatile matter would have to be washed out of the precipitation and

solution containing a new potential source were to be used the next

loss into the mixture by choice to opposite influences. If a further

result, then (2.2) It becomes therefore a matter of importance

the average hydrogen ion it makes certain a precipitation on

called on the water. Also possible measurements (2.3) It is also a known fact

more adequate mixture in comparison respectively to the mixture by the
the volume adjusted roughly to sixty-five cubic centimeters. The amount of buffer to be added was determined by calculating the amount of acid liberated during precipitation of the weight of metal taken, and then adding a considerable excess of buffer material as a safety margin. It was found that twenty-five cubic centimeters of approximately 0.4 normal ammonium acetate would answer this requirement very well, and this constant volume of solution was added to the sample. The volume of acetic acid to be added in each case was determined by the pH value desired. By making the total volume up to sixty-five cubic centimeters with water and determining the pH value of the solution in the same beaker in which the evaporation was carried out, the final volume was between ninety and one hundred cubic centimeters. The difference between these two volumes represented the amount of water required to rinse the electrodes and beaker. Only the initial pH value was determined because no equilibrium could be obtained in the hydrogen sulfide saturated filtrate. Hydrogen sulfide apparently acts as a poison to the platinized platinum electrode. The necessary information as to the effect of the acid liberated during the sulfide precipitation was obtained by adding hydrochloric acid in equivalent amount to the various buffer mixtures as explained earlier in this paper.

When the initial pH value had been determined, the solution was ready for precipitation. In preliminary work it was found that the sulfide had a striking tendency to be adsorbed on the walls of the flask. Apparently this tendency was less when the solution was
heated, and, furthermore, the precipitation was more rapid from hot solutions. Also the precipitate was more compact at the higher temperatures. In the light of these facts all precipitations were carried out in solutions which were heated just to the boiling point immediately before hydrogen sulfide was passed in. A further precaution which was found to be very helpful in preventing adsorption consisted of washing down the sides of the flask thoroughly with distilled water before heating. Hydrogen sulfide was not passed into the cobalt solution but simply into the space above the latter. All air was driven from the system by the incoming gas and during this time care was taken to have the cobalt solution free from all agitation, as it was found that if the solution was agitated and thereby splashed on the walls above the liquid surface adsorption was greatly increased. Ordinarily the flask should not be agitated before five minutes have elapsed and then a rotating movement is given to the contents. The hydrogen sulfide is then confined by pinching off the rubber exit tube and a slight positive pressure of the gas is built up. Precipitation continues as the solution cools and it more certain to be complete if a rapid rotating movement is given to the flask at intervals. As a result of this agitation the precipitate very soon settles out leaving a crystal-clear supernatant mother liquor.

The pH value of the solution exerts very interesting and important effects upon the character of the precipitate as well as upon the rate and completeness of precipitation. If the pH value at the start of the precipitation is near the neutral point the entrance of the hydrogen
sulfide into the space above the liquid is accompanied by black streamers of sulfide penetrating down through the liquid. Precipitation goes on rapidly even when the solution is perfectly free from agitation. Upon subsequent shaking the precipitate settles out in a very bulky flaky form leaving only a shallow depth of clear supernatant liquid. As the pH value decreases the rate of precipitation slows down and the bulkiness of the precipitate decreases steadily. Finally at the upper limit of hydrogen ion concentration the precipitate has become so compact that it forms only a thin layer on a small area on the bottom of the flask. It may also be said at this point that as the upper limit of acidity is approached it becomes very difficult to obtain complete precipitation. The reason for this is probably the same as that discussed by Weiss (23) with regard to the acid separation of zinc. With a given set of conditions the precipitation of zinc or of cobalt as the sulfide ceases when the pH value decreases to a certain value. The reaction between hydrogen sulfide and the cobalt or zinc salt is reversible and at a given acidity more sulfide can be precipitated if the active mass of the hydrogen sulfide in the solution be increased. Of course, in the presence of hydrogen ions from another source the active mass of the hydrogen sulfide, namely the concentration of sulfide ions, can be increased only to a certain definite limit. As the pH value of the solution decreases it becomes increasingly difficult to attain this limit because the factor of saturation of the solution with hydrogen sulfide becomes more important and a longer time must be allowed for the precipitation to insure that the saturation value for hydrogen
The preparation of the emulsion must be planned in a careful

**Letter paper**

as must the spitting of the paper to allow width up with the

filter paper which is carefully folded and placed in the box with the

sawdust and condensate are both printed down with a small piece of condenser.

The first paper thus attached is of the printing area of the water.

It is transferred to a watered papercraft which once on the white

correction is turned off. The result is of the same quality as well and surtouched

correctly is not due over on a clean frame and be sent to read much as the

excavator needed by a human being and the paper slightly burred off. The

watered paper” on which piece a condenser waist if cut off once

been corrected the paper is removed from the simmer and held over a

waxed a paper color due to correct surface. After the cutting has

then the protection is removed from the cover the where paper has

applied that the correction of the water is especially not necessary.

When the protection of the water is already been destroyed, the

Letter paper

 nervous to allow the preparation to set in contact with hydrogen sulphide

required to room temperature at the upper limit of moisture. It is in

case in the presence of the free disublimed before the solution has

emulsions at the Elson pressure and temperature have been reached.
The heating of the furnace is not started until the boat is in it because sudden heating of the small amount of filter paper in the boat produces gases inside the tube which often leads to more or less violent explosions inside the tube with resulting loss of material from the boat. By means of an ordinary water suction pump a slow current of air is drawn through the quartz tube to facilitate roasting. The roasting is continued for one-half hour from the time the interior of the tube has begun to glow at dull red heat. The furnace, of course, does not come up to full heat for some little time but this length of time appears to be sufficient. At the end of the time the tube which is held at each protruding end by clamps held on ring stands is lifted bodily from the furnace. After the boat inside the tube has ceased to glow, that is, within two or three minutes, a slow stream of hydrogen is led through the tube until most of the air is displaced. The gas currents should never be so violent as to produce loss of the fustuary material from the boat. The tube is then placed back in the furnace which has not been allowed to cool and heated at the full heat of the furnace for twelve or fifteen minutes, after which it is removed and allowed to cool with hydrogen still passing through it. When the tube and boat have become cool the boat is removed and weighed forthwith.

Miles and Wex, loc. cit., found that the accuracy of the method for zinc decreased with rising pH values. The same was not found true for cobalt. The complete set of values for the range of acidity investigated in this research is given in the following table:
<table>
<thead>
<tr>
<th>Altitude (°)</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
<th>1.8</th>
<th>2.0</th>
<th>2.2</th>
<th>2.4</th>
<th>2.6</th>
<th>2.8</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mm Hg)</td>
<td>760</td>
<td>767</td>
<td>773</td>
<td>779</td>
<td>786</td>
<td>792</td>
<td>798</td>
<td>804</td>
<td>810</td>
<td>816</td>
<td>823</td>
<td>829</td>
<td>836</td>
<td>842</td>
<td>849</td>
<td>855</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Density (g/L)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Note: The table above provides the density of air in liters per gram at various altitudes. The data is rounded to the nearest hundredth.
the initial ph value. the error in parts per thousand was plotted as

the complete set of results had been obtained a given time.

case

in the absence of caustic the primary-charge was complete in each

hypochlorite solution. the degree of hypochlorite added is not shown

in excess of hypochlorite and the extent of the reaction to the hypochlorite

that the hypochlorite added is not shown to affect the results of the reaction and one mole of

hypochlorite is added by the partial hypochlorite of the caustic hypochlorite solution

the results to some hypochlorite added from the caustic solution. this

effects the hypochlorite present in the proportion of excess to the

exceeded by the errors of the reagents

effects a deviation of value were subject to some variation. this in

affected. the degree of added caustic added to each sample

determined the final ph values of the hypochlorite added. to

because it was found impossible by reason of electrolyte poisoning to

given error in parts per thousand. only the initial ph values were given

give the ph values in the field conditions, the hypochlorite added and the

the next column gives the weight found, the initial ph value of

the next column gives the weight in grams of caustic fresh taken.
Graph III.
Relation between Completeness of Precipitation and Initial pH.
ordinates and the pH values as abscissae. The curve is here shown
(Graph III). The point of greatest accuracy was selected from the curve
while taking into account various other factors. The acidity selected
must provide for desirable filtering properties in the precipitate and
reasonable ease in obtaining complete precipitation. A pH value of
3.35 was found to fulfill all of these requirements. The precipitate
was so compact and granular as to permit washing with little or no
danger of loss by oxidation even when washed very thoroughly. A
series of three determinations involving six samples were made in
solutions of this acidity and the results are given below:

Table Showing Accuracy of Determination Under
Optimum Conditions for Precipitation
as the Sulfide

<table>
<thead>
<tr>
<th>St. Taken</th>
<th>Wt. Found</th>
<th>pH</th>
<th>Cubic Centimeters Acid Added</th>
<th>Error in Parts per 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2013</td>
<td>0.2034</td>
<td>3.222</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.2006</td>
<td>0.2016</td>
<td>3.222</td>
<td>4.9</td>
<td>-1.0</td>
</tr>
<tr>
<td>0.2066</td>
<td>0.2065</td>
<td>3.929</td>
<td>4.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>0.2044</td>
<td>0.2046</td>
<td>3.920</td>
<td>4.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>0.2027</td>
<td>0.2027</td>
<td>3.946</td>
<td>4.5</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2035</td>
<td>0.2036</td>
<td>3.914</td>
<td>4.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
The text seems to be describing a scientific experiment or calculation. It mentions parameters and calculations involving exponents. The text also appears to contain a table with values and calculations. However, the text is not entirely legible due to the quality of the image.
entirely correct. There are highly undesirable features involved in using a greater volume for precipitation. In the first place a longer filtering time is required. It becomes extremely difficult to obtain complete precipitation. A much greater time must be allowed for passing of hydrogen sulfide, and greater care exercised in general. It will also be noted that the amount of acid required to give the desired pH value is greater in the case of the larger volume.

It was also thought advisable to ascertain the effect of ammonium salts on the accuracy of the method. While using the usual volume of approximately ninety-five cubic centimeters, twenty-five grains of ammonium chloride were added. The following table gives the results:

<table>
<thead>
<tr>
<th>No. Taken</th>
<th>No. Found</th>
<th>pH</th>
<th>Cubic Centimeters</th>
<th>Acid Added</th>
<th>Error in Parts per 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2060</td>
<td>.2057</td>
<td>3.864</td>
<td>4.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>.2019</td>
<td>.2017</td>
<td>3.866</td>
<td>4.5</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

No decrease in accuracy was noted but it was not apparent that the ammonium salt exerted a salting out effect as is supposed to be the case with zinc, Treadwell and Hall (22a). It will be seen that the pH values obtained are lower than usual with the amount of acid added. This is possibly due to the neutral salt effect or hydrolysis of the ammonium chloride.

It seemed likely that cobalt and nickel could be determined together by precipitation as the sulfides and nickel subsequently reprecipitated from the dissolved metals by dimethyl glyoxime after the combined weights had been determined. This would give the weight of cobalt by difference. Experimental work with nickel alone disclosed
apparently insuperable difficulties in the way of this plan. Nickel is
said to be more difficult to precipitate completely as the sulfide than is cobalt, Fresenius (23). Nickel precipitated at the most favorable
pH for cobalt did show a trace of residual nickel in the filtrate when
the latter was tested with dimethyl glyoxime. This reagent produced a
slight coloration in the solution but it was not until the solution
had stood for some time that any definite precipitate of nickel dimethyl
glyoxime was formed. It may be said therefore that nickel is completely
precipitated under the same conditions as is cobalt. Moreover, when
nickel sulfide is roasted and reduced under the same conditions as those used
for cobalt the reduced metal exhibits extremely pyrophoric properties.
This apparently absolutely prevents the determination of nickel in this
way. Work is about to be conducted in the catalyst laboratory of the
Fixed Nitrogen Research Laboratory to determine whether flushing out
the hydrogen from the hot tube after the reduction by some inert gas
such as nitrogen will destroy this pyrophoric nature of nickel, Dr.
P. B. Amott (24).
Separation from Interfering Metals

A method is of greater value if provision is made for separation from interfering metals. The materials used for studying this problem were synthetic solutions containing cobalt, nickel, aluminium, iron, zinc and manganese. The barium carbonate method, Treadwell and Hall (25) was investigated first as a means of removing aluminium and iron. The method is apparently satisfactory but involves manipulative details and addition of certain materials which should be avoided. Consequently the ammonium hydroxide-ammonium chloride method was substituted and found to be more satisfactory.

Zinc can be removed after iron and aluminium by the ammonium thiocyanate method, Treadwell and Hall (25). However, the pH value of the solution must be more carefully controlled than is provided for by the usual directions for the method because cobalt and nickel will be precipitated in the presence of ammonium thiocyanate, at least at the pH furnished by sodium bicarbonate solutions. In order to avoid any doubt the solution must be adjusted to a pH of two to three before the addition of the thiocyanate because the latter exerts a poisoning effect upon the electrode. The zinc sulfide is precipitated from a hot solution and filtered when cold. The precipitate must be washed with hydrogen sulfide water containing ammonium thiocyanate and not with water containing some other ammonium salt as suggested by Treadwell. If washed with an ammonium chloride solution, for example, any cobalt or nickel contained on the paper will be precipitated. When the zinc
has been removed, the hydrogen sulfide remaining in the solution can be very readily removed by drawing air through the solution for several hours. This is a method which eliminates any danger of loss such as might arise from evaporation if the solution is boiled to expel hydrogen sulfide.

The method as followed after aluminum, iron and zinc are removed is to precipitate nickel with dimethyl glyoxime, Bransk (27) filter and evaporate the solution until the addition of the buffer solution will not increase the volume beyond one hundred cubic centimeters. The pH value cannot be determined in the solution because the materials present poison the electrode. Hence it is necessary to know the amount of acetic acid that must be added to give a pH of approximately four. The acidity must not be decreased beyond this because of danger of precipitating manganese. If conditions are very carefully controlled cobalt is precipitated quantitatively in the presence of the various materials in the solution. Occasionally, in spite of precautions, cobalt appears to form complexes with organic residues in the solution and does not precipitate completely. If the acidity is kept at the optimum for cobalt precipitation, namely pH 3.83, the likelihood of loss from this cause is negligible.

A change in procedure from that described above which appears promising but which was not investigated is precipitation of cobalt and nickel together as the sulfides. In such a case sulfides and filter paper would be dissolved in aqua regia containing an excess of hydrochloric acid. The chloride solution would be evaporated to
completely made up and fails made with this solution. There are

some error in the determination of the tank. In order to see the results best in this way it was necessary to compute precipitation over movement. This plan was necessary only where corrective showed too much detail. the precipitation was determined and

be said to precipitation. This was done to save time. If the

(2) to determine whether or not an appreciable quantity of capable

emerald the anther was tested by the Ford tests. Treatments

suitable

end site punctate surfur killed with both hydrogen sulfide and copper

solution in the wants precipitation to show a peak or curve on the paper

solution containing copper and sulfur, if the precipitation of the products tested was successful is necessary. In this in-

presence of other metals whose sulfides are soluble

manganese sulfide was obtained. When copper is precipitated in the

doing was surrounded with hydrogen sulfide. No precipitation of

excessive amounts of precipitate of manganese sulfate as a precipitate was obtained. When manganese sulfate was added to the

differences is expected with manganese. As a precipitation of

The solubility product of manganese sulfate is large and no

be the same as precipitation described.

in excess of hydrogen sulfide. From this point on the procedure would
made in the literature for a test when only two hundredths of a milligram of cobalt is present. The tests carried out indicated that the test could be obtained with one hundredth of a milligram of cobalt or even less. The test was unmistakable with one hundredth of a milligram.
multifaceted solution is added. The solution is then placed just to
mixture of solution and granulated caustic soda to form a
transformed to an emulsion which is clear and slightly yellow. So,
the pH value is dropped to approximately 2.5. The solution is then
slowly poured into the hydroxylated cold is added drop by drop until
solution very close to hydroxylation cold is added. The precipitate was
expected in the solution is precipitated readily. The pH range of the
expected to about one hundred cubic centimeters by which time all sodium is
the mixture was concentrated filtrate is concentrated on the water bath.

A piece paper was saturated.

Only one modification of this procedure was necessary. The color
accuracy is obtained if the procedure is discussed and reported.

containing ferric, stannic, titanic, and strontium hydroxides. Center
enough mixture solution will free from chloride. The precipitate
both two minutes and filter properly. When one minute and filter properly
hydrochloric drop by drop until the color changes to a distinct yellow,
Bottom and heat just to boil. cool and normal emulsion
soilution, and a few drops of 0.2 percent solution of methyl red is
then 0.2 grams of iron and examination in 200 cubic centimeters of
mixture solution containing the series of monohydrate chloride and not more
of iron and examination as follows:

The method of twenty sides contained. First of the result.

Reported Values Obtained
To the electrodes.

determined in this case because of the particular process which are performed.

The method as already described. The result of the solution is not.

100 cubic centimeters end equals precipitated immediately according to
the precipitation of buffer mixture added, the volume adjusted to

The mixture is evaporated almost to dryness on the water bath.

extraction. The precipitation is filtered off and washed with hot water.

evaporated to the hot mixture and solution end evaporate to dryness

Next, is the mass precipitated and dried & reconstitute solution or distillation

is for some hours and if the volume is not greater than 50 cc are concentrated

The mixture is freed of hydroxide & by adding and heating

dissolved with hydroxide solution

d and washed thoroughly with care to the same & concentrated solution

Until to room temperature. The precipitated from solution is filtered

pouting and hydroxide solution passed into the solution which is to

31
Analysis of Cobalt Oxide

An attempt was made to obtain a cobalt ore from the United States Bureau of Standards but none was available. A request of the Oxford-Cobalt Silver Mining Company of Cobalt, Ontario, yielded the reply that cobalt ores varied so much in composition that a sample of definite cobalt content would be very difficult to obtain. Finally a sample of cobalt oxide was obtained from the Deloro Smelting and Refining Company, Ltd. of Deloro, Ontario. This was concentrated black oxide and contained 70.88% of cobalt. The percentage of nickel was given as 0.76. This left roughly seven percent of the sample to be taken up with siliceous matter, zinc, copper, aluminium, iron, etc.

The sample taken for analysis was three-tenths gram as it was desired to have a cobalt residue of approximately two-thirds that amount. The oxide was dissolved in hydrochloric acid containing a little nitric acid. A small amount of siliceous matter remained undissolved. Enough additional hydrochloric acid was added so that when the solution was diluted to one hundred cubic centimeters, five to seven cubic centimeters of concentrated acid would be present. Scott (38).

Hydrogen sulfide was then bubbled through the hot solution until it had cooled to room temperature. A small amount of second group metals precipitated and were filtered off with the siliceous matter. The hydrogen sulfide was then removed by bubbling air through the solution and iron and aluminium removed as above described. Zinc and nickel were next removed in order named.
Cobalt was last removed. One of the samples failed to precipitate completely presumably because of the formation of an undissociated organic cobalt complex. The solution retained an extremely deep red color. The other solution became clear when the cobalt precipitated. When the precipitates were filtered, washed and finally reduced to the metal, the weight of the sample which failed to decolorise was found to be, according to the stated percentage, 1.32% low.

The following table gives the results for the other sample:

<table>
<thead>
<tr>
<th>Wt. Taken</th>
<th>Wt. Found</th>
<th>ERROR in Parts per 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2145</td>
<td>.2140</td>
<td></td>
</tr>
<tr>
<td>70.88%</td>
<td>70.70%</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Lack of time prevented the running of further samples but it may be said that of all the several samples analyzed in developing the method for the separation, none failed to precipitate completely in the presence of whatever products were present as derivatives of dimethyl glycine, ammonium thiocyanate and traces of alcohol. However, because of this danger of incomplete precipitation it might be advisable to eliminate organic materials as described above.
A method has been developed for the quantitative precipitation of cobalt as the sulfide and subsequent determination of cobalt as the metal.

The completeness of precipitation of cobalt as the sulfide has been studied as a function of pH.

The effect of ammonium salts, temperature and concentration on completeness of precipitation has been investigated.

The completeness of precipitation of nickel as the sulfide under conditions optimum for cobalt precipitation has been investigated.

Methods have been developed for the separation of cobalt from interfering metals e.g. nickel, zinc, aluminium, iron and manganese.

A sample of crude cobalt oxide has been analysed by the method developed.

The error of the method when cobalt alone is present has been found to be less than one-tenth of one percent and in the presence of interfering metals less than two-tenths of one percent.
11. Landolt-Bornstein-Roth Tabellen, 4 Auflage, Page 1200.
15. Chapin, Second Year College Chemistry, Page 266.


   Scott, Standard Methods of Chemical Analysis, Page 488.
   Acid Separation of Zinc.


34. Dr. F. H. Remitt, Fixed Nitrogen Research Laboratory,
    Private Communication.


    Vogel's Reaction.

39. Trendall and Hall, Revised Edition Vol. II.

40. Scott, Standard Methods of Chemical Analysis.