The above results indicate that a little zirconium is carried down. They could probably be lowered by adding the mixed chlorides to the boiling solution of oxalic acid, since this would prevent the formation of the insoluble zirconium oxalate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ALLEGHENY COLLEGE.]

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.

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CONTENTS.—Introduction: Outline of Investigation. Part I, Precipitation of Group. Part II, Analysis of Group. Part III, Summary.

Introduction.

The investigation reported in this paper is a continuation of the work reported in a previous paper[1] in which it was pointed out that "although it is well known that many of the methods which are generally used in qualitative analysis need revision, apparently very little time has been devoted to the systematic study of their relative effectiveness. It would seem, therefore, that any investigation which comprehended a detailed study of qualitative methods with particular reference to their accuracy in detecting small amounts of the elements in the presence of large amounts of any or all of the elements, and for the purpose of developing and formulating more reliable procedures, would be of considerable value to the analytical chemist."

The purpose of this investigation, however, was the experimental survey of only those methods which are most frequently employed in the precipitation and separation of the metals of the zinc group, namely, zinc, manganese, nickel and cobalt.

As in the investigation to which reference has been made, "it was hoped that the result of such an examination would render possible the selection of the best of the proposed methods and enable the formulation of the conditions best adapted to securing the desired end. As the work progressed, however, and larger discrepancies among the recommended procedures than had been anticipated were noted, it became obvious that although some methods ought to be revised, others ought to be rejected and new ones substituted, if possible."

Although an effort has been made to formulate such methods as will enable the analyst to estimate the approximate amount of the elements present, care has been exercised in the selection of the final procedures

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[1] "A Method for the Qualitative Analysis of the Calcium Group," Richard Edwin Lee and F. L. Mickle, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 257–278; *Chem. Abstr.*, 6, 20, 3240 (1912); *Chem. Ztg.*, 36, 1302 (1912).

to adopt only those which may be executed with facility by the average worker.

The results of the investigation are reported in the order of their dependence. For convenience in presenting data, the paper has been divided into three parts: "Precipitation of the Group," "Analysis of the Group," and "Summary." Under each of the first two parts there is first presented a "General Discussion" in which the reasons for rejecting certain procedures, and adopting others, are given. This is followed by a record of the "Test Experiments" which were performed to test the accuracy of a given process. Next there is presented the "Procedure and Notes" in which the various details of the adopted procedure are submitted and briefly discussed.

The abbreviations used in the cross references may be explained as follows: G. D. is used for General Discussion; P. for Procedure; N. for Notes; T. E. for Test Experiments.

Part I. Precipitation of the Group: (a) General Discussion; (b) Test Experiments; (c) Adopted Procedure; Notes.

(*a*) *General Discussion.*—With respect to the original precipitation of the members of this group, schemes of qualitative analysis differ as to whether this group and the preceding group (the Iron Group) should be precipitated separately by the successive addition of ammonium hydroxide, and ammonium sulfide, or whether these reagents should be added together so that all the elements of the two groups may be obtained in a single precipitate. Authors[1] are about evenly divided on this question of procedure. Either method has its advantages as well as its disadvantages. When the two groups are precipitated simultaneously, the problem of the analyst is exceedingly difficult, if large quantities of many of the metals of the two groups are present, and especially so, if but traces of only one or two of the members are present. Again, zinc, aluminum, and chromium cannot be completely separated from manganese and iron by alkali hydroxide,[2] the reagent usually employed for this separation when the two groups are precipitated together. Finally, the color changes which occur during the precipitation of either group and which frequently

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[1] Those in Group I suggest the precipitation of the Iron Group with the Zinc Group; those in Group II, a separate precipitation for each group.

Group I: "Qual. Chem Anal.," Noyes, A. A.; "Qual. Anal.," Dennis and Whittlesey; "Qual. Chem. Anal.," Noyes, Wm. A.; "Qual. Chem. Anal.," Treadwell, F. P.; "Qual. Chem. Anal.," Stieglitz, Julius; "Qual. Anal.," Baskerville and Curtman; "Anal. Chem.," Menschutkin, N.; "Qual. Chem. Anal.," Perkin, F. M.

Group II: "Qual. Anal.," Böttger, W.; "Qual. Chem. Anal.," Tower, O. F.; "Qual. Chem. Anal.," Newth, C.; "Qual. Chem. Anal.," Bailey and Cady; "Qual. Anal.," Morgan, W. C.; "Qual. Anal.," Gooch and Walker; "Qual. Anal.," Hill, Arthur E.; "Anal. Chem.," Long, J. H.; "Qual. Chem. Anal.," McGregory, J. F.

[2] Ebler, E., *Z. anal. Chem.*, **47**, 665–667; cf. *Chem. Abs.*, **3**, 294–5 (1909).

supply indications as to the presence or absence of certain metals, are partially or wholly obscured when the two groups are precipitated simultaneously.

The objections usually urged against the precipitation of each group separately is that it is difficult to effect a complete separation of the two groups. This difficulty may be nearly overcome by avoiding the use of an unnecessary excess of ammonium hydroxide when precipitating the iron group; or the more elaborate formate, benzoate, or basic acetate methods may be used. If the latter method is employed, phosphates are removed during the regular course of the analysis. Finally, the separate precipitation of the groups renders the analytical problem less complex.

It has seemed advisable, therefore, to adopt the method of precipitating the iron and zinc groups separately.

The next problem presented was the determination of the most reliable group precipitant, *i. e.*, whether ammonium polysulfide, ammonium monosulfide, or hydrogen sulfide should be used. An examination of many of the recommended schemes of analysis revealed the fact that the majority of authors prefer to precipitate the group by use of the reagent "ammonium sulfide." The work conducted in this laboratory, however, indicates that precipitation is most satisfactorily accomplished by hydrogen sulfide. Ammonium polysulfide, $(NH_4)_2S_x$, was rejected for two reasons: First, the sulfides of some of the members of the group, especially nickel sulfide, are markedly soluble in this reagent; second, its presence in the filtrate (from this group) imparts a deep yellow color and in the subsequent analysis results in the separation of sulfur on standing or heating.

Ammonium monosulfide, $(NH_4)_2S$, as the group precipitant yielded fairly satisfactory results. However, the following objections may be offered to its use: First, nickel is very frequently precipitated in the colloidal condition; second, the shelf reagent, unless freshly made, is a constant source of difficulty, as the monosulfide is readily oxidized in the presence of air to the polysulfide, thus:

$$2(NH_4)_2S + O \longrightarrow (NH_4)_2S_x + 2NH_3 + H_2O.$$

Therefore, if a large excess of the reagent is used it is practically equivalent to using the polysulfide.

The method of passing hydrogen sulfide, H_2S, into a weak ammoniacal solution containing the metals of this group presented no new difficulties and practically eliminated the difficulties attendant upon the use of either one of the two other precipitants. The dissolving of the nickel sulfide is entirely prevented and nickel is seldom precipitated in the colloidal condition.

It would seem, therefore, that the method of precipitating the group with hydrogen sulfide is to be preferred, especially so when nickel is likely to be present. By the procedure outlined in this paper (see Procedure I) it is easily possible to precipitate as well as detect 0.0005 gram of any of the metals of this group.

(*b*) *Test Experiments.*[1] *Series I.*—Difficulties Encountered in Attempting to Precipitate Nickel by Ammonium Polysulfide or Monosulfide.

After a few trial experiments with $(NH_4)_2S_x$ this reagent was rejected as a possible group precipitant because of its solvent action on nickel sulfide.

When large or small amounts of the pure salts of nickel were used in the test experiments, the complete precipitation of the nickel by the use of ammonium sulfide was found to be almost impossible. The filtrate invariably had a brown color in each case. When it was boiled for five or six minutes, shaken thoroughly and then filtered, it usually came through colorless. The amount of nickel in the filtrate apparently increased with the amount of $(NH_4)_2S$ used and the length of exposure to the air.

Lecrenier (*Chem. Ztg.*, **13**, 431–449 (1889)) and Villiers (*Compt. rend.*, **119**, 1263 (1894)) have shown, however, that nickel can be completely precipitated as NiS—the filtrate remaining colorless—with freshly prepared $(NH_4)_2S$ in the absence of air. The results obtained by these men indicate that, in those cases to which reference has been made, the brown colored filtrate is due to the presence of a polysulfide. The composition of this brown colored filtrate, however, is probably not definitly known. It may be colloidal nickel polysulfide or it may be ammonium sulfonickelate, $(NH_4)_2NiS_3$. Antony and Magri (*Gazz. chim. ital.*, **31**, II, 265 (1901)) prepared NiS_4 by evaporating the brown colored filtrate in the absence of air.

All the experimental work relating to precipitation of the group with ammonium polysulfide or monosulfide showed that these reagents as possible group precipitants should be rejected.

Series II.—Completeness of Precipitation of Zinc, Manganese, Nickel, and Cobalt in an Ammoniacal Solution with Hydrogen Sulfide.

In the following series of experiments the amount of the metal in the form of a chloride was dissolved in distilled water and diluted to 25 cc., 5 cc. of 5 *N* HCl was added, after which the solution was made *slightly* alkaline with 5 *N* NH_4OH. Precipitation from both cold and hot solution was tried.

A. Zinc.

0.0003 gram Zn (as $ZnCl_2$) gave no precipitate.
0.0004 gram Zn (as $ZnCl_2$) gave no precipitate but the solution became turbid.
0.0005 gram Zn (as $ZnCl_2$) gave a distinct precipitate after 1–2 minutes which coagulated perceptibly.
0.001 gram Zn (as $ZnCl_2$) gave heavy flocculent precipitate.
0.200 gram Zn (as $ZnCl_2$) gave large precipitate at once and precipitation was complete in 2–3 minutes.

B. Manganese.

0.0003 gram Mn (as $MnCl_2.4H_2O$) gave no precipitate.
0.0004 gram Mn (as $MnCl_2.4H_2O$) gave no precipitate but the solution became turbid.
0.0005 gram Mn (as $MnCl_2.4H_2O$) gave a distinct precipitate.

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[1] Authors Note.—The record of the "test experiments and references" is presented before the adopted procedure is reported. Conclusions drawn from the results obtained in the test experiments are incorporated in the "procedure and notes."

0.001 gram Mn (as $MnCl_2.4H_2O$)	a distinct precipitate was obtained after 1–2 minutes.
0.200 gram Mn (as $MnCl_2.4H_2O$)	gave a heavy precipitate at once and precipitation was complete in 2–3 minutes.

C. Nickel.

0.0001 gram Ni (as $NiCl_2.6H_2O$)	gave only a slight coloration.
0.0002 gram Ni (as $NiCl_2.6H_2O$)	gave a distinct precipitate which coagulated perceptibly.
0.0003 gram Ni (as $NiCl_2.6H_2O$)	gave a distinct precipitate.
0.0004 gram Ni (as $NiCl_2.6H_2O$)	gave a distinct precipitate.
0.0005 gram Ni (as $NiCl_2.6H_2O$)	gave a distinct precipitate.
0.001 gram Ni (as $NiCl_2.6H_2O$)	gave a heavy precipitate at once.
0.200 gram Ni (as $NiCl_2.6H_2O$)	gave a heavy precipitate at once and precipitation was complete in 2–3 minutes.

D. Cobalt.

0.0001 gram Co (as $CoCl_2.6H_2O$)	gave no precipitate but solution became turbid.
0.0002 gram Co (as $CoCl_2.6H_2O$)	gave a distinct precipitate.
0.0003 gram Co (as $CoCl_2.6H_2O$)	gave a distinct precipitate.
0.0004 gram Co (as $CoCl_2.6H_2O$)	gave a distinct precipitate.
0.0005 gram Co (as $CoCl_2.6H_2O$)	gave a distinct precipitate.
0.001 gram Co (as $CoCl_2.6H_2O$)	gave a heavy precipitate at once.
0.200 gram Co (as $CoCl_2.6H_2O$)	gave a heavy precipitate at once. Precipitation was complete in 2–3 minutes.

This series of experiments shows that quantities as small as 0.0005 gram of either Zn, Mn, Ni, or Co are precipitated in 2–3 minutes. It is evident, therefore, that the method outlined in Procedure I provides for a practically complete precipitation of the members of the group.

(*c*) *Procedure Adopted and Notes. Procedure I.*—To the neutral acid solution (or the filtrate of Group III) containing the elements of the Zinc Group, add 5 *N* NH_4OH until the solution reacts slightly alkaline. Warm the solution, pass H_2S into it for 5 minutes, shake the mixture and again warm it. Filter at once. Test the filtrate with H_2S to ascertain whether precipitation is complete. If the filtrate has a dark brown color the presence of colloidal nickel sulfide is indicated. This difficulty may be overcome by boiling this filtrate for 5–10 minutes. This operation coagulates the precipitate, and therefore prevents it from passing through the filter. The nickel sulfide may then be filtered without further difficulty. Wash the group precipitate immediately and thoroughly with an aqueous solution of H_2S. Proceed with the analysis without delay, as the moist sulfides of nickel and cobalt are easily oxidized.

Notes.—(1) If $(NH_4)_2S$ is used to precipitate the group, it must be freshly prepared, as it oxidizes in the presence of air to ammonium polysulfide, in which it has been shown that NiS is soluble (see T. E., Series I). The use of a large excess of the reagent $(NH_4)_2S$, is equivalent to the use of ammonium polysulfide.

If hydrogen sulfide is passed into the solution which is made slightly alkaline with 5 *N* NH_4OH all of the difficulties enumerated are overcome and no new difficulties are presented.

(2) A large excess of ammonium hydroxide is to be avoided when the solution is made slightly alkaline preparatory to its treatment with H_2S, as the excess will be converted into $(NH_4)_2S$ and probably into $(NH_4)_2S_x$. On the other hand great care must be exercised to keep the solution slightly alkaline in reaction during the precipitation with H_2S.

(3) It has been shown (T. E., Series I) that the brown colored filtrate is duc to the presence of $(NH_4)_2S_x$, which exerts a solvent action upon NiS. This colloidal nickel salt may be coagulated by boiling, and shaking and then removed by filtration.

(4) Precipitations from cold ammoniacal solutions were as satisfactory as those from warm solutions if the amounts of the metals were greater than 0.001 gram.

(5) The precipitation of the metals of this group is practically complete (see T. E., Series II).

Part II. Analysis of the Group: (a) General Discussion; (b) Test Experiments; (c) Adopted Procedure; Notes.

(*a*) *General Discussion.*—In nearly all the schemes of qualitative analysis known to the authors the group precipitate is treated first with dilute hydrochloric acid in the effort to separate the readily soluble zinc and manganese sulfides from the more difficultly soluble sulfides of nickel and cobalt. Although this method is in very general use, the experiments conducted in this laboratory indicate that it does not meet the requirements of an accurate system of qualitative analysis. That others have experienced difficulties in endeavoring to make the separation is evidenced by the fact that the strength of the hydrochloric acid to be used in making the separation, as recommended by various authors[1] ranges from 0.5 *N* to 5 *N*. Our experiments, as well as those of others,[2] have shown that the sulfides of nickel and cobalt are moderately soluble in 1 *N* HCl, and that the presence of nickel and cobalt in the filtrate seriously interferes with the tests for zinc and manganese; if a weaker acid is used then the zinc frequently escapes detection by remaining in the residue, for it is known that zinc sulfide in the presence of nickel or manganese sulphide is not readily soluble in 0.1 *N* HCl. Again, there is evidence at hand which indicates that the rate at which different sulfides dissolve in an acid of given strength is variable, and depends apparently upon the state of aggregation. In view of these difficulties, this method has been abandoned, and instead, all the sulfides are brought into solution by the use of hydrochloric acid and (solid) potassium chlorate.

The next step in the proposed method of analysis is the separation of zinc from manganese, nickel, and cobalt by the addition of sodium hy-

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[1] Dennis and Whittlesey recommend 1 *N* HCl; W. C. Morgan recommends 1 *N* HCl; J. Stieglitz recommends 1 *N* HCl (approx.); A. A. Noyes recommends 2 *N* HCl; O. F. Tower recommends 2 *N* HCl; J. H. Long recommends 2 *N* HCl; F. M. Perkin recommends 2 *N* HCl; F. P. Treadwell recommends 2.5 *N* HCl; W. Böttger recommends 0.5 *N* HCl; W. Segerblom recommends 5 *N* HCl. Gooch and Walker separate Mn from Zn, Co and Ni by the use of $HC_2H_3O_2$.

[2] Hertz, *Z. anorg. Chem.*, **27**, 390 (1901); **28**, 343 (1901).

droxide and sodium peroxide. One of the main problems of this investigation was the determination of conditions which would insure an accurate separation of zinc. It is believed that the method as worked out and described in this paper has not been applied by any other author. By the treatment just mentioned, the manganese, nickel, and cobalt are completely precipitated as hydroxides of these metals in the trivalent condition and the zinc remains in the solution as sodium zincate. In this separation, advantage is taken of the fact which seems to have been overlooked by the majority of authors, namely, that cobaltic hydroxide, $Co(OH)_3$, is much less soluble than cobaltous hydroxide, $Co(OH)_2$, in an excess of sodium hydroxide. The zinc is precipitated and confirmed by conventional processes.

The separation of the hydroxides of manganese, nickel, and cobalt presented one of the most difficult problems connected with this investigation. The reaction finally selected for the purpose of separating manganese from nickel and cobalt is known as "Ford's Reaction." This reaction is frequently employed in iron and steel analysis, and consists in the conversion of the manganese into manganese dioxide by the action of chloric acid in the presence of strong nitric acid. The method of separating the manganese consists in dissolving the three hydroxides in strong hydrochloric acid, evaporating to a small bulk with an excess of nitric acid (1.20), adding (solid) potassium chlorate, boiling, and finally filtering off the manganese dioxide on a glass-wool-asbestos filter. This method has an advantage over the usual color tests for manganese, in that an idea of the quantity of the element present may be obtained. Although a confirmatory test is unnecessary, the usual color tests have been worked out and fitted to the system. Objections may be offered to this method, as it involves the use of an asbestos filter. When the operation (see Procedure IV, Note 2) has been executed once the objections will, in all probability, be withdrawn.

The filtrate (from the chloric acid precipitate) containing the nickel and cobalt is evaporated to expel the excess of acid and then made neutral with sodium hydroxide. The solution is divided into two parts and a test is made for each metal in the presence of the other; the nickel is precipitated by the use of potassium cyanide, sodium hydroxide, and bromine water as nickelic hydroxide; and the cobalt as potassium cobaltic nitrite by the use of acetic acid and potassium nitrite. Provision is made for the usual borax-bead tests.

(*b*) *Test Experiments and References. Series III.*—Solubility of the Sulfides of Zinc, Manganese, Nickel and Cobalt in Hydrochloric Acid.

0.2 gram of Mn and 0.2 gram of Zn as sulfides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1 *N* HCl; after 5 minutes treatment the sulfides were completely dissolved.

0.2 gram of Ni and 0.2 gram of Co as sulfides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1 *N* HCl; after 10 minutes treatment the mixture was filtered and the filtrate tested for Ni and Co by adding NH_4OH and H_2S. A heavy, black precipitate appeared at once. Approximately 0.04 gram of Ni and Co had dissolved.

This series of experiments shows that sulfides of nickel and cobalt are moderately soluble in 1 *N* HCl. Therefore zinc and manganese cannot be completely separated from nickel and cobalt by the use of this reagent.

Series IV.—Action of Hydrochloric Acid on Various Mixtures of the Sulfides of the Group.

0.2 gram of Ni and 0.0005 gram of Zn as sulfides were treated with 25 cc. of 1 *N* HCl; after 10 minutes treatment the mixture was filtered and the filtrate tested for Zn by adding NH_4OH and H_2S. A heavy, black precipitate appeared at once, indicating that the NiS had dissolved. The *white* sulfide of zinc escaped detection, owing to the presence of a large mass of *black* nickel sulfide. Similar results were obtained when the experiment was repeated with quantities of Zn as ZnS varying in amount from 0.001 gram to 0.02 gram.

These experiments show that a quantity of Zn as large as 0.02 gram escaped detection, owing to the presence of the Ni dissolved by the 1 *N* HCl.

0.2 gram of Zn and 0.0002 gram of Ni as sulfides were treated with 25 cc. of 1 *N* HCl; after 10 minutes treatment the sulfides were completely dissolved. This experiment was repeated with quantities of Ni varying in amount from 0.0003 gram to 0.001 gram. Quantities of Ni smaller than 0.0005 gram were completely dissolved; on the other hand, it was found that ZnS in the presence of NiS, was not completely dissolved in 1 *N* HCl. Owing to these facts small amounts of Zn in the presence of relatively large amounts of Ni escaped detection.

Series V.—Action of Hydrochloric Acid and Potassium Chlorate on Mixtures of Sulfides.

0.2 gram of Mn, 0.2 gram of Zn, 0.2 gram of Ni, and 0.2 gram of Co as sulfides were treated with 25 cc. of HCl (1 : 12), and the mixture boiled for 5 minutes. A black residue proved to be a mixture of NiS and CoS. A few crystals of $KClO_3$ were added to the mixture. The residue dissolved at once.

Series VI.—Behavior of Sodium Hydroxide and Sodium Peroxide towards Zinc, Manganese, and Nickel Hydroxides.

A solution containing 0.3 gram of Zn as $ZnCl_2$ was made slightly alkaline with 5 *N* NaOH. A white precipitate of $Zn(OH)_2$ appeared at once. The mixture was divided into two equal portions. When NaOH was added in moderate excess to one portion the $Zn(OH)_2$ dissolved, forming a clear solution of sodium zincate. A few grains of Na_2O_2 were added to the other portion—the $Zn(OH)_2$ was readily dissolved.

Similar results were obtained when the above experiments were repeated with hot solutions.

The composition of sodium zincate is probably not definitly known. Kunchert (*Z. anorg. Chem.*, 41, 343–348 (1904)) using Bodländer's electromotive-force method proved that solutions of sodium zincate contain chiefly ZnO_2^{--} and some $HZnO_2^-$. Forster (*Z. Elektrochem.*, 6, 301 (1899)) has prepared solid $NaHZnO_2$. Hantzsch (*Z. anorg. Chem.*, 30, 298–303 (1902)) from conductivity measurements, and Fisher and Hertz (*Z. anorg. Chem.*, 31, 355 (1902)) from dialysis experiments concluded that sodium zincate is almost completely hydrolyzed into NaOH and $Zn(OH)_2$, and that the latter is present as a colloid.

0.2 gram of Mn as $MnCl_2$ was completely precipitated by NaOH as flesh-colored

$Mn(OH)_2$, which turned brown owing to its oxidation (in the presence of air) to $MnO(OH)_2$. $Mn(OH)_2$ was found to be insoluble in excess of NaOH. $Mn(OH)_2$ is converted by Na_2O_2 into the brown hydrated MnO_2, probably $MnO(OH)_2$. The precipitation of Mn as $MnO(OH)_2$ by the use of NaOH and Na_2O_2 was complete.

From a solution containing 0.03 gram of Ni as $NiCl_2$, NaOH, when added to alkaline reaction, completely precipitated the Ni as $Ni(OH)_2$. The precipitate was insoluble in excess of the precipitant. The precipitate was converted into black $Ni(OH)_3$ when treated with Na_2O_2. The filtrate gave negative results when tested for Ni.

Series VII.—Behavior of Cobalt Salts towards Sodium Hydroxide and Sodium Peroxide.

0.03 gram of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made just alkaline with 5 *N* NaOH, then *10 cc. excess* were added and the mixture heated to boiling. The precipitate was filtered off, and the blue-colored solution was acidified, then made just alkaline, and saturated with H_2S. A precipitate of CoS separated. This experiment was repeated but 4 grams of Na_2O_2 was added *before* the mixture was heated to boiling. The precipitate was converted into black $Co(OH)_3$, which was removed by filtration. The filtrate possessed a blue color, which indicated that some of the cobalt had dissolved in the alkaline solution, forming a soluble salt, probably Na_2CoO_2, and when tested, as in the previous experiment, CoS separated.

0.03 gram of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made *slightly* alkaline with 5 *N* NaOH. *No excess* of this reagent was added. 0.4 gram of Na_2O_2 was added and the mixture heated to boiling. The dark colored precipitate of $Co(OH)_3$ was filtered off; the filtrate was colorless and yielded no test for Co. This experiment was repeated many times with quantities of Co varying in amount from 0.0003 gram to 0.5 gram; in each experiment the precipitation was complete, the filtrate being colorless.

This series of experiments indicate that cobalt*ous* salts dissolve in excess of NaOH forming a blue solution; but if the cobaltous salts are first oxidized to the "-ic" condition by such agents as Na_2O_2 in NaOH solution, they are insoluble and therefore may be completely precipitated as $Co(OH)_3$. See Donath, *Z. anal. Chem.*, 40, 137 (1901).

Series VIII.—Precipitation of Manganese Peroxide by Chloric and Nitric Acids.

See "Ford's Method," Olsen's "Quant. Chem. Anal.," p. 385, 3rd Rev. Ed., and Ford, *Trans. Am. Inst. Min. Eng.*, 9, 397 and 100. Experiments were conducted to prove that the presence of Ni and Co do not interfere with the reaction formulated as follows:

$$KClO_3 + HNO_3 \longrightarrow HClO_3 + KNO_3$$
$$Mn(NO_3)_2 + 2HClO_3 \longrightarrow \mathit{MnO_2} + 2HNO_3 + 2ClO_2.$$

Small pieces of filter paper were placed in the casserole with MnO_2 and boiled with HNO_3 (1 : 20); all of the MnO_2 dissolved in 10 minutes. 0.0003 gram of Mn as $MnCl_2$ in 25 cc. of water yielded a comparatively voluminous precipitate.

Series IX.—Confirmatory Color Test for Manganese.

Following the directions outlined in Procedure IV, it was found that 0.0002 gram of Mn could be easily detected. The violet color due to the presence of the MnO_4 ion is very distinct.

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O.$$

Series X.—Precipitation of Cobalt with Potassium Nitrite. Sensitiveness of Test.

0.0003 gram of Co as $CoCl_2$ was treated according to Procedure VII; the solution became turbid in 15 minutes. The experiment was repeated, using Ni instead of Co; the solution remained clear.

The above experiments were repeated, using 0.5 gram of Co, and 0.5 gram of Ni; results were the same.

See Procedure VII and notes for further report.

Series XI.—Test for Nickel in Presence of Cobalt.

Following the directions given in Procedure VIII, 0.0003 gram of Ni as $NiCl_2$ could be detected. A black precipitate, $Ni(OH)_3$ was obtained.

The experiment was repeated, except that 0.3 gram of Co as $Co(NO_3)_2$ was used; no precipitate was observed.

Series XII.—Relative to the Accuracy and General Utility of the Proposed Method.

More than 100 students doing work in this laboratory in Qualitative Analysis during the past two years have used the methods proposed in this paper, and apparently have encountered no difficulties in following the procedures. Unknown mixtures particularly difficult of analysis have been given to the students in order to test the accuracy and utility of the methods. The instructor in charge of the work reports an unusually small percentage of failures. This is probably due to the fact that a moderate change in the conditions of precipitation does not greatly alter the accuracy of the methods.

(*c*) *Procedure and Notes. Procedure II.*—The group precipitate (P. 1) which consists of ZnS, MnS, CoS, and NiS is transferred to a casserole and treated wtlh 10–20 cc. of HCl (1 : 12). Stir the mixture thoroughly for 2–3 minutes; if a black residue remains the presence of Ni and Co are indicated and a few crystals of $KClO_3$ should be added. Boil the mixture for a few minutes, dilute with a little water and filter off the yellow residue of sulfur. Evaporate the filtrate to a few cc. to remove excess of acid; add 10–20 cc. of water and make slightly alkaline with 5 *N* NaOH. If the precipitate which forms is so large that the mixture becomes gelatinous, add 10–20 cc. of water, cool the mixture and add solid Na_2O_2 in very *small* portions until a steady evolution of gas continues after the mixture has been well stirred. Heat to incipient boiling and filter (Precipitate, P. 4; Filtrate, P. 3.)

Notes.—(1) The MnS and ZnS usually dissolve readily in cold HCl (1.12); the NiS and CoS are quite soluble in concentrated HCl but dissolve very slowly (see T. E., Series III). If a black residue remains after the treatment with HCl the presence of Co and Ni is indicated. The absence of a black residue does not prove, however, that Ni and Co are not present in the precipitate.

All the sulfides of this group are readily soluble in HCl (1.12) and $KClO_3$. The group precipitate is first treated with HCl in order to obtain indications as to the presence of Ni and Co. HCl and $KClO_3$ are used to dissolve the precipitate in preference to *aqua regia*, since much free sulfur is formed at the start if the latter is used.

(2) NaOH completely precipitates Mn and Ni as $Mn(OH)_2$ and $Ni(OH)_2$; these substances do not dissolve in a moderate excess of this reagent. The $Zn(OH)_2$ dissolves readily, however, in an excess because it is an amphoteric substance. The product of the reaction is sodium zincate, $Na_2Zn_2O_2$ (see T. E., Series VI). If an excess of NaOH be added to $Co(OH)_2$ a portion, of the latter dissolves forming a blue solution,

the color of which is due, probably, to Na_2CoO_2. Therefore, great care must be exercised to avoid an excess until the cobalt is oxidized to the "-ic" condition.

The Na_2O_2 converts the $Zn(OH)_2$ into soluble Na_2ZnO_2, $Mn(OH)_2$ into a brown $MnO(OH)_2$, $Ni(OH)_2$ into black $Ni(OH)_3$, and $Co(OH)_2$ into black $Co(OH)_3$.

(3) The Na_2O_2 is added to a cold solution, as it decomposes with explosive violence when the solution is hot. Oxygen is liberated during the decomposition. Boiling decomposes excess of sodium peroxide.

(4) The separation of zinc by this method is very satisfactory. When the directions have been followed carefully the filtrate is free from Ni and Co, which usually interfere with the later tests for Zn.

Procedure III.—The filtrate obtained from P. 2 contains sodium zincate. Acidify the solution with acetic acid, $HC_2H_2O_2$, warm to about 70°, and saturate with H_2S. A white, flocculent precipitate, ZnS, confirms the presence of Zn. If results are doubtful, the confirmatory tests may be continued as follows: Filter, wash the precipitate of ZnS, then dissolve it in the least amount of HNO_3. Evaporate nearly to dryness to expel excess of acid, neutralize with a few cc. of Na_2CO_3 solution. Add a volume of $Co(NO_3)_2$ equal to that of one-sixth the solution in the casserole, evaporate to dryness and ignite gently. A green residue, ZnO.CoO, or $CoZnO_2$, confirms Zn.

Notes.—(1) Zn is precipitated readily from warm dilute $HC_2H_3O_2$. If but fractions of a milligram are present the precipitate coagulates slowly; therefore care must be exercised or the precipitate will be missed.

(2) If a white flocculent precipitate forms at once when the $HC_2H_3O_2$ solution is treated with H_2S, a confirmatory test is unnecessary as the action is highly characteristic of Zn. Mn is the only other element of the group which forms a light colored sulfide and it is not precipitated in the presence of acetic acid.

(3) The composition of the green salt obtained in the confirmatory test for Zn is probably represented by the formula $CoZnO_2$. A large excess of Co salt should be avoided, as the black color of CoO obscures the green color.

Procedure IV.—The Na_2O_2 precipitate (P. 2) which contains $MnO(OH)_2$, $Ni(OH)_2$, and $Co(OH)_3$ should be washed thoroughly to insure the removal of the soluble adhering zinc salt, then transferred to a casserole and dissolved in the least quantity of warm HCl (1 : 12). Filter to remove paper and evaporate filtrate to about 2 cc. Add 5 cc. of HNO_3 (1 : 20), boil until the reddish brown fumes cease to be given off, then add 10–20 cc. of HNO_3 (1.20), heat to boiling and add several crystals of $KClO_3$, continue to boil gently for several minutes. Cool the mixture and allow any suspended matter (probably a precipitate of MnO_2, if it has a brown color) to settle. Decant the liquid through an asbestos filter in such a manner that most of the precipitate (if there is one) remains in the casserole. Test the filtrate by boiling it with a crystal of $KClO_3$. Filter if more precipitate forms (Precipitate, P. 5; Filtrate, P. 6).

Notes.—(1) Manganous salts of the type of $MnCl_2$ are rapidly oxidized to MnO_2 by $KClO_3$ in the presence of HNO_3 (see T. E., Series VIII). As MnO_2 is readily soluble in the presence of reducing agents all fragments of filter paper must be removed from the HNO_3 solution. The HCl must be removed previously by evaporation, since it reacts with HNO_3 to form oxides of nitrogen in which MnO_2 is readily soluble. The separation of manganese by this method is very satisfactory; small fractions of a milligram of the metal are easily detected.

(2) The MnO_2 is filtered off by means of an asbestos filter. This filter is easily prepared by placing a small loose plug of glass wool well down in the apex of the ordinary glass funnel, and spreading a large layer of asbestos over it. If filtration is slow, suction may be used.

Students in this laboratory have experienced no trouble whatever in executing the various steps described in this procedure.

Procedure V.—Place the $HClO_3$ precipitate (P. 4) in a casserole, add 20 cc. of HNO_3 (1 : 40), boil for a few minutes, add 1 gram of PbO_2, and boil again for 2–3 minutes. Pour the mixture into a test tube and allow any suspended matter to settle. A pink or violet colored solution confirms manganese.

Notes.—(1) When Mn is precipitated as MnO_2 by $KClO_3$ in HNO_3 solution, the confirmatory tests are really superfluous, as this reaction is highly characteristic of Mn.

Procedure VI.—Evaporate the filtrate from the $HClO_3$ treatment (P. 4) to about 5 cc. to expel excess of acid, add 10–15 cc. of water, filter, if turbid, then add NaOH solution, drop by drop, until the solution is neutral or until a permanent precipitate begains to form. Divide the mixture into two equal parts. Test one for Co by Procedure VII, and the other for Ni by Procedure VIII.

Procedure VII.—Add $HC_2H_3O_2$ to one-half the neutral solution obtained in P. 6 until it is barely acid in reaction, then add an equal volume of a saturated solution of KNO_3. Warm the mixture and allow to stand for an hour if a precipitate does not form sooner. A yellow pulverulent precipitate, $K_3Co(NO_2)_3$, indicates Co. Filter, wash the precipitate with KNO_2 solution and test it with a borax bead. A blue color confirms Co.

Notes. — (1) The yellow pulverulent precipitate, potassium cobaltic nitrite, $K_3Co(NO_2)_6$, forms slowly. Therefore, it is advisable to allow the precipitate to stand for an hour. However, distinct tests are obtained in 20 minutes when 0.0003 gram of Co are present, although precipitation is not complete after four hours. The yellow precipitate is slightly soluble in water, but not in a strong solution of KNO_2, owing to the presence of the common ion, K^+.

(2) The theory of the formation of the salt is indicated by the following equations:

$$K^+NO_2^- + H^+C_2H_3O_2^- \rightleftarrows H^+NO_2^- + K^+C_2H_3O_2^-$$

$$Co^{++}(C_2H_3O_2^-)_2 + 2K^+NO_2^- \rightleftarrows CO^{++}(NO_2^-)_2 + 2K^+C_2H_3O_2^-$$

$$CO^{++}(NO_2^-)_2 + 2H^+NO_2^- \rightleftarrows Co^{+++}(NO_2^-)_3 + H_2O + NO$$

$$Co^{+++}(NO_2^-)_3 + 3K^+NO_2^- \longrightarrow K_3Co(NO_2)_6.$$

(3) Nickelous salts are not oxidized by nitrous acid, HNO_2, and are not precipitated by KNO_2, except in very concentrated solutions. By diluting the solutions as directed the precipitation of Ni is avoided. Potassium nickelous nitrite, $K_4Ni(NO_2)_6$, is dark yellow to red in color.

See Lang, *J. prakt. Chem.*, **86**, 299 (1862); Hampe, *Ann.*, **125**, 346 (1863); and Richards, *Chem. Ztg.*, **28**, 479, 885, 912 (1904).

Procedure VIII.—Add KCN to the other portion of the neutral solution (P. 6) until the precipitated cyanides just redissolve. Heat the solution (do not boil) with frequent stirring for two or three minutes. Filter off any residue that may be present. Add a relatively large amount of NaOH solution, then bromine water until the reddish brown color of the bromine water persists. A black precipitate, $Ni(OH)_3$, indicates Ni. The borax bead test may be used to confirm Ni.

Notes.—(1) The addition of KCN to the neutral solution containing Ni and Co salts results in the precipitation of green $Ni(CN)_2$ and brown $Co(CN)_2$. These cyanides dissolve readily in excess of KCN, forming the soluble complex cyanides, $K_2Ni(CN)_4$, and $K_4Co(CN)_6$. The cobalt salt readily undergoes oxidation when in the presence of air, and tends to pass from the cobalto-cyanide to the cobalti-cyanide, thus:

$$2K_4{}^+[Co(CN)_6]^{==} + O + H_2O \rightleftarrows 2K_3{}^+[Co(CN)_6]^{\equiv} + 2K^+OH^-.$$

The complex nickel salt is more stable in the air, and moreover forms no compound corresponding to the cobalticyanide. However, in the presence of strong oxidizing agents like chlorine, bromine, or the hypochlorites in alkaline solution, the complex nickelous salt is oxidized to the nickelic state, in the form of a simple salt, which is then precipitated as black $Ni(OH)_3$. The final results of the reaction may be formulated as follows:

$$2K_2Ni(CN)_4 + NaClO + 5H_2O \longrightarrow 2Ni(OH)_3 + NaCl + 4KCN + 4HCN.$$

Hence, under the same oxidizing treatment the potassium cobalto-cyanide is converted into the soluble potassium cobalti-cyanide, while the potassium nickelous-cyanide is converted into the insoluble $Ni(OH)_3$, and may be separated by filtration.

The cobalt is not precipitated, probably because the complex ion $[Co(CN)_6]^{==}$ is so slightly dissociated into Co^{+++} and CN^- ions.

Summary.

(1) Attention has been directed again to the well-known fact that the methods which are generally used in qualitative chemical analysis have received but little systematic study and are in need of revision.

(2) A comparison of a large number of methods for the precipitation and analysis of the Zinc Group as outlined by the respective authors has been made, and the inaccuracies and discrepancies of the procedures noted.

(3) A method has been formulated by which the difficulties usually encountered in attempting the complete precipitation of zinc, manganese, nickel, and cobalt have been overcome without introducing intricate procedures. By a series of test experiments it has been shown that a quantity as small as 0.0005 gram of any one of the metals in the presence of large amounts of any or all of the other metals may be readily detected.

(4) In the second part of the paper, which relates to the subsequent analysis of the group precipitate, it has been shown that the usual methods of procedure are entirely inadequate for making an accurate analysis, and that the methods proposed in this paper are adequate for confirming even 0.0005 gram of any of the metals of the group.

(5) The accuracy and general utility of the proposed methods have been proven, as shown by Series XII of the Test Experiments.

MEADVILLE, PA.

THE INFLUENCE OF CHLORINE ON THE DETERMINATION OF NITRATES BY THE PHENOL DISULPHONIC ACID METHOD.

BY ROBERT STEWART AND J. E. GREAVES.

Received March 22, 1913.

The question involved in this study is of fundamental importance in the determination of nitrates in cultivated soils of the arid west, which may be impregnated with alkali. Earlier work[1] at this laboratory on this question demonstrated a marked influence of chlorine upon the amount of nitrates found. Thus, it was found that if the soil solution contained even as low a concentration as 2.6 parts per million of chlorine in the soil extract less nitrates were found by this method than were actually present.

The experimental data recently presented by Lipman and Sharp,[2] although they are apparently not aware of this fact, confirm this conclusion. This may be seen by converting the results obtained in both cases to the same basis in order to make a comparison, since our results are reported as parts per million of chlorine in the *soil extract*, while Lipman and Sharp's results are reported as milligrams of sodium chloride present.

The results converted to the same basis, *i. e.*, milligrams of sodium chloride actually present in the portion of the solution used are compared in Table I.

TABLE I.—INFLUENCE OF IONIC CHLORINE ON THE DETERMINATION OF NITRATES IN SOLUTION.

By Stewart and Greaves.				By Lipman and Sharp.			
Mg. NaCl.	N. N. added.	N. N. found.	% N. N. found.	NaCl.	N. N. added.	N. N. found.	% N. found.
0.04	0.01	0.01	100	0.01	0.05	0.051	102
0.09	0.01	0.01	100	0.05	0.05	0.051	102
0.13	0.01	0.01	100	0.10	0.05	0.049	98
0.27	0.01	0.009	90	0.25	0.05	0.045	90
0.52	0.01	0.0094	94	0.50	0.05	0.041	82
0.79	0.01	0.0086	86	1.00	0.05	0.035	70

Thus, it may be readily seen that when only 0.1 mg. of sodium chloride was present in both cases all of the nitrates present could be easily determined. Lipman and Sharp, however, found that when 0.25 mg. of sodium chloride was present that only 90% of the nitrates actually present could be determined while we found that when 0.27 mg. of sodium chloride was present, only 90% of the nitrates could be found. With a concentration of 1 mg., Lipman and Sharp found only 70% of the nitrate, while we, with 0.79 mg. of sodium chloride, found only 86%

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[1] Stewart and Greaves, THIS JOURNAL, **32**, 756 (1910).

[2] *Univ. of Cal. Publication in Agr. Sci.*, **1**, 12 (1912).