

STUDIES IN QUALITATIVE SEPARATIONS ON A MICRO SCALE.

II. SEPARATIONS IN THE AMMONIUM SULFIDE GROUP.

By

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This paper deals with the elements which are ordinarily included in the third analytical group. The methods very closely follow the scheme of A. A. NOYES and W. C. BRAY² except in the chromium group. As to the working technique, it will be necessary to make frequent reference to our recently published text³.

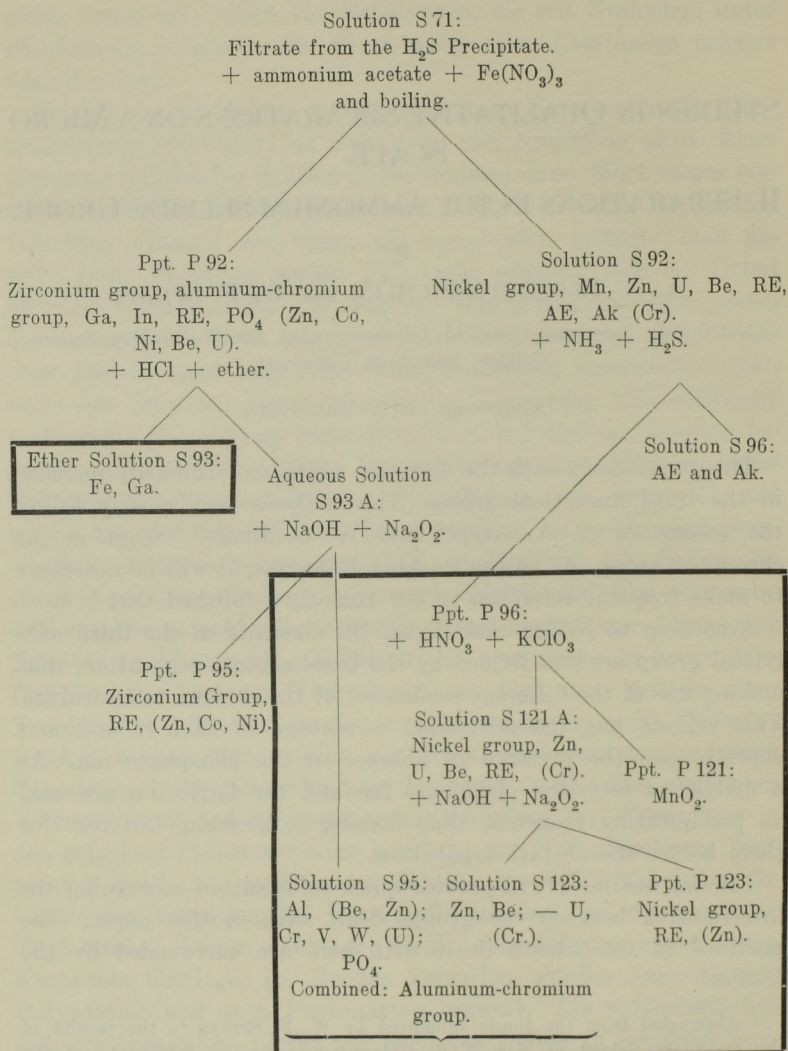
According to NOYES and BRAY, the elements of the third analytical group are sub-divided by the basic acetate separation, thus making use of the different tendencies of the cations to hydrolyze. This scheme has the additional advantage in that it does not depend upon the presence or absence of the phosphate ion. As a matter of fact, the phosphate ion and the ferric ion are used as precipitating reagents, thus making it necessary to test for them before the acetate separation.

Tabular outline I will provide quick information concerning the interrelation between the groups dealt with in this paper. The portions of the scheme dealt with here are surrounded by the frames.

¹ Abstracted from the thesis submitted by W. F. SPIKES to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy, April 1, 1936.

² Qualitative Analysis for the Rare Elements, New York 1927.

³ A. A. BENEDETTI-PICHLER and W. F. SPIKES, *Microtechnique of Inorganic Qualitative Analysis*, New York 1935, in future referred to as P.-S.

Tabular Outline I⁴.

⁴ RE, AE and Ak stand for rare earths, alkaline earths, and alkalis respectively. Parentheses indicate that the principal part of the element will be found elsewhere.

The numbers of the precipitates and solutions are given as far as possible in accordance with the paragraph numbers of NOYES and BRAY, *ibid*.

The discussions which follow will be shortened if a brief description of certain general procedures and apparatus is given at this point.

Centrifuge Cones: Capillary cones as shown in Fig. 1 were used throughout the experimental work. They vary from the micro cones (EMICH type) in that the lower half of the cone is made from tubing of *uniform* bore. The bore of this half may vary from 1 to 4 mm., and should be 2.5 to 3 cm. long. The upper half is made from tubing 6 to 8 mm. in bore. These capillary cones have capacities of 0.6 to 0.9 cc. They prove advantageous for working with small precipitates and for the *estimation of the volumes* of precipitates.

Evaporation: In the work reported here, all evaporations were carried out in centrifuge cones unless otherwise specifically stated. The cones were placed in a boiling steam bath and a stream of filtered air was directed from a capillary on the surfaces of the solutions. When solutions other than aqueous solutions were evaporated to dryness, the cones were placed in aluminum heating blocks. In addition to the hole for the cone, there should be one sufficiently large to hold a 360° thermometer. A stream of air was blown on the surfaces of non-aqueous solutions, also. In this way, solutions containing perchloric or sulfuric acids can be rapidly and safely evaporated.

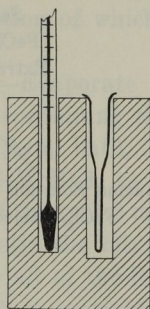


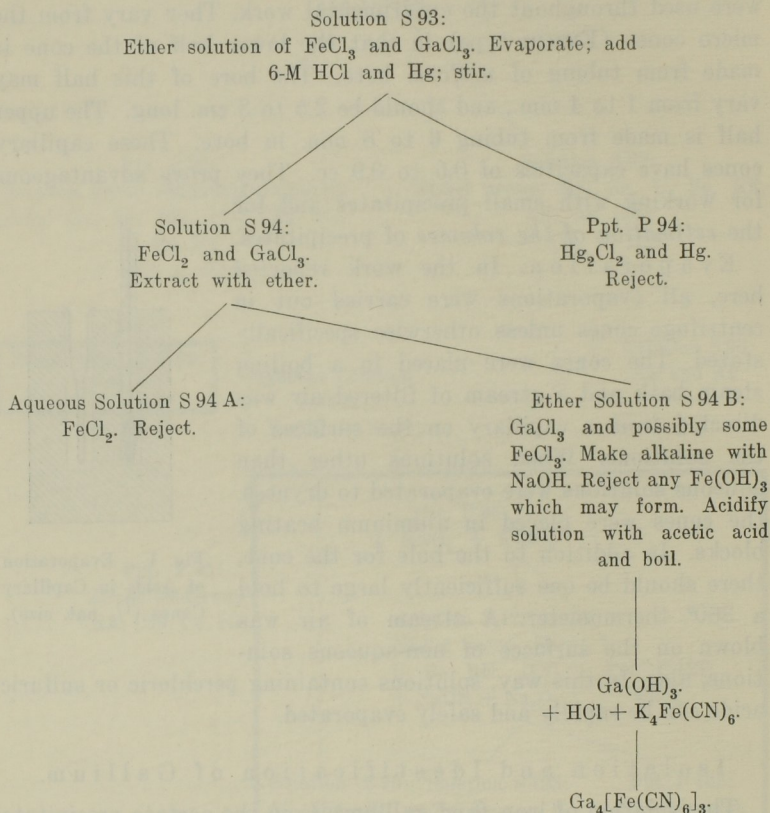
Fig. 1. Evaporation of Acids in Capillary Cones ($\frac{1}{3}$ nat. size).

Isolation and Identification of Gallium.

The isolation of iron (and gallium) from the acetate precipitate becomes necessary before further separations are carried out. Otherwise, the large amount of ferric hydroxide (ferric nitrate being added in the basic acetate separation) produced by the sodium hydroxide-sodium peroxide precipitation has a tendency to carry down considerable quantities of the ions of the aluminum-chromium group. Even though gallium is not considered in an analysis, the ether separation must be carried out at this point of the procedure in order to remove the iron present.

The diagram which immediately follows summarizes the separation of the gallium from the iron and the identification of the former.

Tabular Outline II.



Procedure.

§ 93.—The Extraction of Gallium and Iron.—Dissolve the washed precipitate P 92 in 10 cmm. of 6-M HCl, and evaporate the solution to about 1 cmm. Then add 10 cmm. of 6-M HCl, stir the mixture with a glass thread, and by means of a capillary pipet transfer the solution to an ether extraction cone⁵.

⁵ P.-S., p. 148.

Extract the solution with three 10 cmm. portions of ether which has been shaken with twice its volume of 6-M HCl immediately before use. The ether extracts (when combined are considered as solution S 93) are transferred to a micro cone. The transfer is effected by means of a rather wide capillary pipet (0.6 to 0.7 mm. in bore) having a wide point (0.2 to 0.3 mm.), care being exercised in the removal of the ether. If the ether solution comes too close to the fingers holding the capillary pipet, rapid and almost explosive evaporation ensues, and much of the liquid will be blown out and lost. Frequent immersions of the extraction cone in an ice bath will help to prevent such occurrences. The ether may be transferred by a contraction pipet, also, a description of which is found in P.-S., p. 81.

§ 94.—The Detection of Gallium.—Evaporate the combined ether extracts S 93 by holding the cone containing them in the steam issuing from a rapidly boiling steam bath, and stirring with a glass thread. Add 10 cmm. of 6-M HCl, to the residue. Heat to about 70° in a hot-water bath, add 0.5 to 1.0 cmm. of metallic mercury with a capillary pipet, and stir the mixture for about five minutes at 70° C. During this time all of the ferric chloride will be reduced to ferrous chloride, which is insoluble in ether-hydrochloric acid solutions, thus affording a separation of the iron from the gallium in the subsequent ether extraction. Cool the cone containing the mixture in an ice bath, centrifuge, and quickly transfer solution S 94 to an ether extraction cone containing 0.1 cmm. of mercury and 10 cmm. of ether which has been shaken immediately before use with two volumes of 6-M HCl; wash precipitate P 94 in the first cone with 2 to 3 cmm. of 6-M HCl, centrifuge, and combine the wash liquid with solution S 94. Reject precipitate P 94 which consists of metallic mercury and mercurous chloride. Stir the mixture in the extraction cone for a half minute, and then centrifuge. Remove the ether solution S 94 B by means of a capillary pipet as described above, or by means of a contraction pipet. Reject solution S 94 A which is an aqueous solution of FeCl_2 .

Wash the ether solution S 94 B by transferring it to an extraction cone containing 3 cmm. of 6-M HCl and 0.1 cmm. of metallic mercury, stirring the mixture, centrifuging, and then

transferring the ether solution to a micro cone. Since ferrous chloride is rapidly oxidized in contact with air, some of the iron will be contained in solution S 94 B. Hence, the procedure of washing solution S 94 B with 6-M HCl in the presence of metallic mercury is advisable in order to obtain a more quantitative separation of the gallium from the iron.

Evaporate the ether extract S 94 B just to dryness by holding the cone in the steam issuing from a vigorously boiling steam bath and stirring with a glass thread. Then add 5 cmm. of water to the residue obtained. To this solution add just 2 cmm. of 6-M NaOH, heat to boiling, and cool. Add a 15 cmm. portion of water, centrifuge, and reject any precipitate which consists of ferric hydroxide. Next add 6-M acetic acid until the solution is just acid to litmus, and then add 1 cmm. more. Dilute the mixture to 100 cmm., place in a gently boiling steam bath, heat for ten minutes, and then cool. The formation of a white precipitate indicates the presence of gallium. The precipitate will consist of $\text{Ga}(\text{OH})_3$. Centrifuge and estimate the quantity of gallium present by comparison with a $\text{Ga}(\text{OH})_3$ precipitate of known gallium content.

The presence of gallium is further confirmed as follows: Separate the solution from the $\text{Ga}(\text{OH})_3$ obtained above. Transfer 3 cmm. of 6-M HCl to the white precipitate, and stir with a glass thread until solution is complete. Add 5 cmm. of water, stir again, and then add 3 cmm. of 0.3-M $\text{K}_4\text{Fe}(\text{CN})_6$. The $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$ will be a white or bluish-white precipitate.

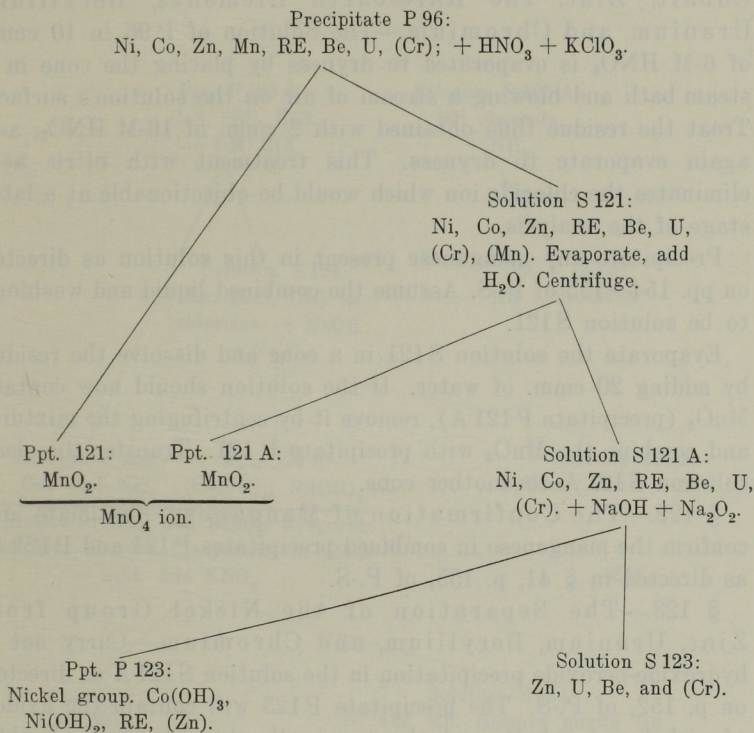
Experimental Results: By the scheme just described, it is possible to separate one part of gallium from one thousand parts of iron. Since in the complete procedure (tabular outline I) 0.5 mg. of iron as ferric nitrate is added at the most, it can be expected that 1 μg . of gallium may be detected in the course of an analysis of a 1 mg. sample.

The Analysis of the Ammonium Sulfide Precipitate.

The first step in this procedure consists in separating the manganese from the rest of the ions; then the zinc, beryllium,

chromium, and uranium are separated from the nickel group and the rare-earth elements; finally, the nickel group and the rare-earth elements are divided. The procedure may be briefly summarized as follows:

Tabular Outline III.



In the analysis of this group we have decided to deviate from the NOYES and BRAY scheme by eliminating the manganese before the sodium hydroxide-sodium peroxide treatment⁶. Of the hydroxides Ni(OH)₂, Co(OH)₃, and MnO₂·H₂O, precipitated by the hydroxide-peroxide treatment, the last named has the greatest tendency to carry down zinc, thus preventing the quantitative transfer of this element to the aluminum group. Since the

⁶ P.-S., p. 153.

elimination of manganese previous to this step is carried out in strongly acid solution, there is little danger of co-precipitation of the zinc.

Procedure.

§ 121.—The Separation of Manganese from Nickel, Cobalt, Zinc, the Rare-earth Elements, Beryllium, Uranium, and Chromium.—The Solution of P 96 in 10 cmm. of 6-M HNO_3 is evaporated to dryness by placing the cone in a steam bath and blowing a stream of air on the solution's surface. Treat the residue thus obtained with 2 cmm. of 16-M HNO_3 , and again evaporate to dryness. This treatment with nitric acid eliminates the chloride ion which would be objectionable at a later stage of the analysis.

Precipitate any manganese present in this solution as directed on pp. 154—155 of P.-S. Assume the combined liquid and washings to be solution S121.

Evaporate the solution S121 in a cone and dissolve the residue by adding 20 cmm. of water. If the solution should now contain MnO_2 (precipitate P121 A), remove it by centrifuging the mixture, and combine the MnO_2 with precipitate P 121. Transfer the clear solution S121 A to another cone.

§ 122.—The Confirmation of Manganese.—Estimate and confirm the manganese in combined precipitates P 121 and P121 A, as directed in § 41, p. 155, of P.-S.

§ 123.—The Separation of the Nickel Group from Zinc, Uranium, Beryllium, and Chromium.—Carry out a hydroxide-peroxide precipitation in the solution S121 A as directed on p. 152, of P.-S. The precipitate P123 will contain the oxides of nickel and cobalt, and the rare-earth elements, and possibly some zinc. The solution S123 will contain the uranium, beryllium, chromium, and the greater part of the zinc, and is analyzed by the procedures outlined in parts of this paper dealing with the analysis of the aluminum and chromium groups.

The Analysis of the Nickel Group.

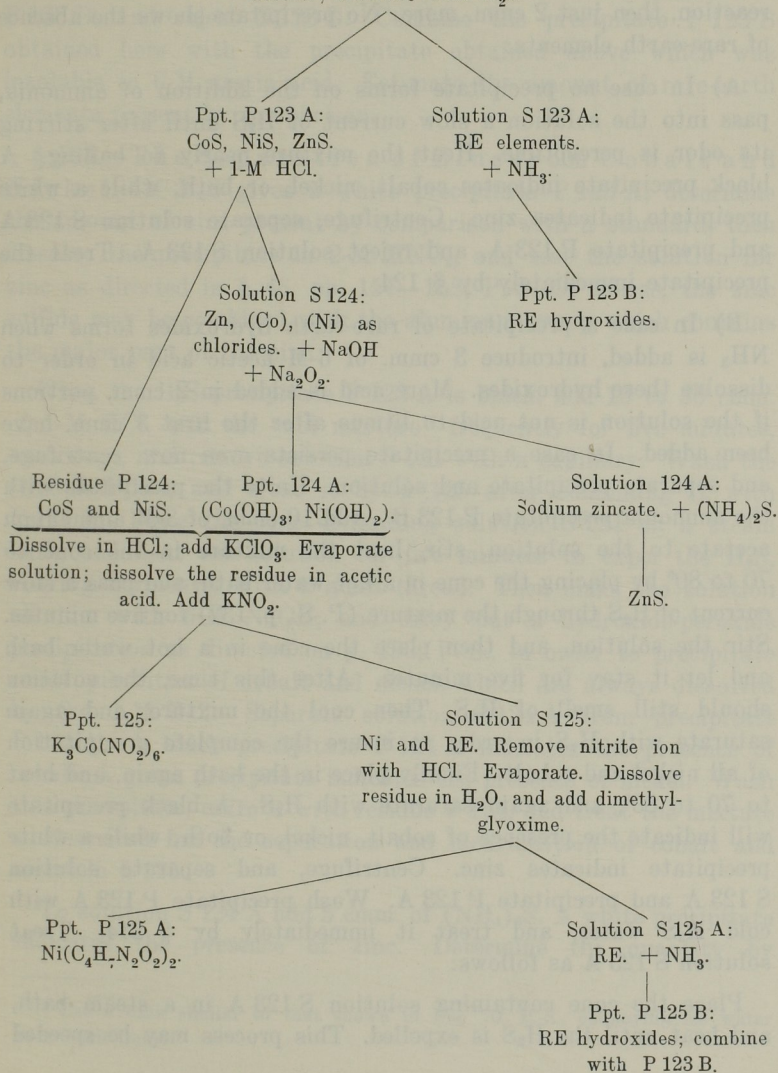
Procedure.

The treatment of the nickel group may be summarized as follows:

Tabular Outline IV.

Ppt. 123:

Nickel group and rare-earth elements: Oxides of Ni, Co, and RE, and possibly some Zn. Dissolve in HCl; evaporate, dissolve the residue thus obtained in H_2O ; add NH_3 , acetic acid, and ammonium acetate; saturate with H_2S .



§ 123 (Cont.—).—To precipitate P123 add 5 to 20 cmm. of 6-M HCl, and heat the mixture on a boiling steam bath. Centrifuge and evaporate the solution in the cone almost to dryness by blowing a stream of air on the solution's surface. Add 30 cmm. of cold water and 1 cmm. portions of 6-M NH_3 to a slight alkaline reaction, then just 2 cmm. more. No precipitate shows the absence of rare-earth elements:

A) In case no precipitate forms on the addition of ammonia, pass into the solution a slow current of H_2S until after stirring its odor is perceptible. Heat the mixture nearly to boiling. A black precipitate indicates cobalt, nickel, or both; while a white precipitate indicates zinc. Centrifuge, separate solution S 123 A and precipitate P 123 A, and reject solution S 123 A. Treat the precipitate immediately by § 124.

B) In case a precipitate of rare-earth hydroxides forms when NH_3 is added, introduce 3 cmm. of 6-M acetic acid in order to dissolve these hydroxides. More acid is added in 2 cmm. portions if the solution is not acid to litmus after the first 3 cmm. have been added. In case a precipitate persists even now, centrifuge, and separate precipitate and solution. Unite the precipitate with the ammonia precipitate P 123 B. Add 10 cmm. of 3-M ammonium acetate to the solution, stir, heat the mixture in the cone to 70 to 80° by placing the cone in a hot water bath, and pass a slow current of H_2S through the mixture (P.-S., p. 132) for five minutes. Stir the solution, and then place the cone in a hot water bath and let it stay for five minutes. After this time, the solution should still smell of H_2S . Then cool the mixture, and again saturate with H_2S in order to insure the complete precipitation of all nickel and cobalt. Finally place in the bath again, and heat to 70 to 80°, and again saturate with H_2S . A black precipitate will indicate the presence of cobalt, nickel, or both; while a white precipitate indicates zinc. Centrifuge, and separate solution S 123 A and precipitate P 123 A. Wash precipitate P 123 A with cold H_2S water, and treat it immediately by § 214. Treat solution S 123 A as follows:

Place the cone containing solution S 123 A in a steam bath, and heat until the H_2S is expelled. This process may be speeded

up by stirring the solution with a glass thread having a bead fused on its end. Centrifuge, reject any precipitate, add 6-M NH_3 until solution S 123 A smells of it, and then add 2 cmm. more. A white precipitate indicates the presence of the rare-earth elements. Centrifuge, separate the solution from precipitate P 123 B, and reject S 123 B. Combine the precipitate P 123 B obtained here with the precipitate obtained above which was insoluble in 6-M acetic acid. Estimate the amount of rare-earth elements present by comparison.

§ 124.—The Separation of Zinc from Cobalt and Nickel.—If H_2S gives a white precipitate P 123 A, determine the amount of zinc present by comparison with a standard, then dissolve the precipitate in 2-M HNO_3 , and test the solution for zinc as directed in § 46, pp. 157—158, P.-S. Of course, the zinc sulfide may be combined with the aluminum group which contains the major part of the zinc.

When the H_2S precipitate P 123 A is black, add 10 to 30 cmm. of 1-M HCl , stir the cold mixture⁷ frequently for five minutes, centrifuge, and remove solution S 124 with a capillary. Wash the residue P 124, and treat it by § 125 after combining it with P 124 A. Place the cone containing solution S 124 on a steam bath, and heat the solution for five minutes to expel the H_2S , stirring frequently with a glass thread. Then make the solution alkaline with 6-M NaOH , and carry out a hydroxide-peroxide precipitation as directed on p. 152, P.-S., in order to precipitate small quantities of cobalt and nickel, which are always dissolved by the 1-M HCl . Separate solution S 124 A from precipitate P 124 A. A black precipitate P 124 A indicates the presence of cobalt; a green precipitate indicates the presence of nickel. Wash this precipitate, unite it with residue P 124, and treat the mixture as described for the separation and identification of cobalt and nickel in § 125.

To solution S 124 A add 5 cmm. of $(\text{NH}_4)_2\text{S}$. A white precipitate indicates the presence of zinc. Determine the quantity by

⁷ Use a bath similar to that shown in Fig. 70, P.-S., employing ice water as a bath liquid.

comparison, and add the amount thus determined to that found in the aluminum group.

§ 125.—The Detection of Cobalt and Nickel.—Add 5 to 15 cmm. of 13-M HCl to the combined precipitates P 124 and P 124 A, heat nearly to boiling, and treat with 0,1 to 0,3 cmm. of powdered KClO_3 . Centrifuge and separate the clear solution from the sulfur precipitate. Evaporate the solution to dryness, and dissolve the residue thus obtained in 5 cmm. of 6-M acetic acid. Add 3 cmm. of 6-M KNO_2 solution, and let stand with occasional stirring for at least 15 minutes. If a considerable amount of precipitate forms, add to the mixture 10 cmm. more of the 6-M KNO_2 solution and 4 cmm. of powdered KCl, and let the mixture stand with frequent stirring for another fifteen minutes. Centrifuge and determine the quantity of cobalt present by comparison. Remove solution S 125 from precipitate P 125.

Confirm the presence of cobalt in precipitate P 125 by the procedure described in § 53, p. 160, of P.-S.

To solution S 125 add 10 cmm. of 13-M HCl, and heat for three minutes on a steam bath. Centrifuge and evaporate to dryness on a steam bath. Treat the residue with 5 cmm. of 13-M HCl, and evaporate the solution to dryness again. Dissolve this residue in 20 cmm. of water. Add to the solution in the cone 4 cmm. of 6-M NH_3 and then 2 cmm. portions of a saturated solution of dimethylglyoxime in alcohol. Mix and centrifuge after each addition. Continue this procedure until the precipitation of the nickel is complete. Centrifuge and compare the volume of precipitate with the amount of nickel dimethylglyoxime obtained from a known quantity of nickel.

Confirm the presence of nickel by the procedure outlined on p. 160, § 54, of P.-S.

Experimental Results. Experiments were carried out to determine the applicability of the above scheme, and it has been found that the smallest amounts of the elements which can be safely detected with the unaided eye in the cone are as follows:

Mn as MnO ₂ . Vol. of 15 cmm.	0,5 μg.
Co as K ₃ Co(NO ₂) ₆ . Vol. of 10 cmm.	0,5 μg.
Ni as dimethylglyoxime. Vol. of 25 cmm.	0,5 μg.
RE as La(OH) ₃ . Vol. of 40 cmm.	5,0 μg.
Co as CoS. Vol. of 35 cmm.	1,0 μg.
Ni as NiS. Vol. of 35 cmm.	1,0 μg.

The following limiting proportions are either reported in the literature or have been determined during the course of this research:

Co : Mn	= 1 : 1000.
Co : Ni	= 1 : 500 ⁸ .
(Co, Ni) : Zn	= 1 : 1000.
La : (Co, Ni)	= 1 : 50 (probably better).
Mn : Zn	= 1 : 1000 (probably better).
Mn : Co	= 1 : 1000 (certainly better).
Ni : Co	= 1 : 100 ⁹ .
Zn : Co	= 1 : 100 ⁹ .
Zn : Ni	= 1 : 100 ⁹ .

Thirty-five solutions containing zinc, cobalt, nickel, and manganese in varying proportions were analyzed, and the few results listed in table I may be considered representative.

Table I.

	306-a		307-a	
	ADDED	RECOVERED	ADDED	RECOVERED
Mn	10 μg	15 μg	100 μg	100 μg
Zn	25 „	30 „	10 „	2 „
Co	8 „	15 „	100 „	75 „
Ni	4 „	5 „	0 „	0 „
RE	30 „	15 „	50 „	not tested

⁸ A. A. NOYES, W. C. BRAY and E. B. SPEAR, J. Am. Chem. Soc. **30**, 561 (1908).

⁹ NOYES, BRAY, and SPEAR, *ibid.*, p. 522.

Separation of the Aluminum and Chromium Groups.

In order to obtain all of the uranium and most of the zinc together, it is necessary to combine the solutions from the sodium hydroxide-sodium peroxide precipitations. These solutions are S 95 and S 123. The combination is then treated with NaHCO_3 as directed below in order to obtain the division of the elements Al, Be, Zn and Cr, U, V, W into the aluminum and chromium groups.

Procedure.

§ 101.—The Separation of Chromium, Uranium, Vanadium, and Tungsten from Aluminum, Zinc, and Beryllium.—Carefully acidify the solution by adding 3 cmm. portions of 2-M HNO_3 until the solution has an acid reaction to Congo red paper. Then carry out a sodium bicarbonate precipitation as directed in § 43, pp. 156—157, of P.-S.

Finally centrifuge the special centrifuge cone in which the precipitation was carried out, cut it open, and separate the solution S 101 from the precipitate P 101.

Experimental Results. The limits for this separation were not determined, but the analyses of a dozen or more solutions containing the ions of the aluminum and chromium subgroups in varying proportions indicate that this separation will be satisfactory. These analyses were carried out by the procedures described in this paper. A few of the results are listed in table II.

Table II.

No. of Sample	516		517		520	
	ADDED RECOVERED		ADDED RECOVERED		ADDED RECOVERED	
Be	50 μg	45 μg	10 μg	6 μg	15 μg	10 μg
Cr	100 "	90 "	10 "	10 "	10 "	10 "
U	10 "	10 "	100 "	100 "	50 "	45 "
V	10 "	8 "	50 "	35 "	10 "	5 "
Al	10 "	10 "	25 "	25 "	100 "	95 "
Zn	30 "	25 "	10 "	5 "	50 "	45 "

Analysis of the Aluminum Group.

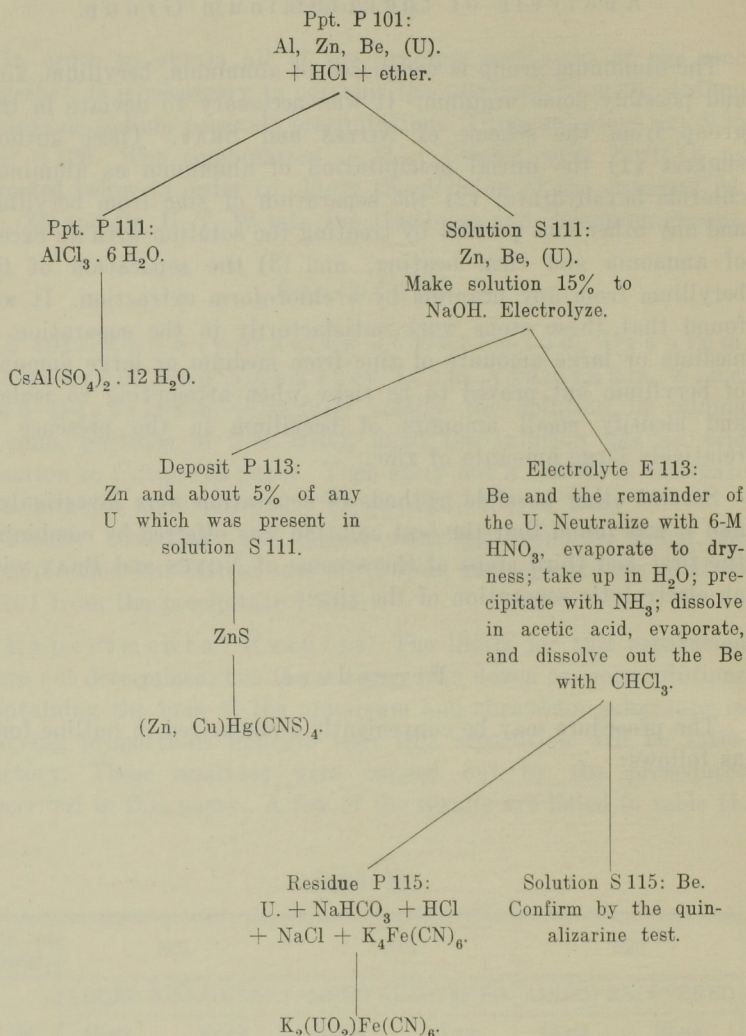
The aluminum group is comprised of aluminum, beryllium, zinc, and possibly some uranium. It was necessary to deviate in this group from the scheme of NOYES and BRAY. These authors suggest (1) the initial precipitation of aluminum as aluminum chloride hexahydrate; (2) the separation of zinc from beryllium and any other ions present by treating the solution with an excess of ammonia and then heating; and (3) the separation of the beryllium from any uranium by a chloroform extraction. It was found that these steps work satisfactorily in the separation of medium or large amounts of zinc from medium or large amounts of beryllium but proved to be risky when attempting to isolate and identify small amounts of beryllium in the presence of relatively large amounts of zinc.

Several other possible methods of separation were investigated, and it was found that the best solution was offered by combining the first and third steps of the scheme of NOYES and BRAY with an electrolytic separation of the zinc.

Procedure.

The procedure may be conveniently summarized in outline form as follows:

Tabular Outline V.



§ 111.—The Separation of Aluminum from Zinc and Beryllium.—Dissolve the sodium bicarbonate precipitate P 101 in the special cone by adding 5 to 10 cmm. of 6-M HCl

and stirring. Transfer the solution to a centrifuge cone, rinse out the special cone with 5 cmm. of 6-M HCl, and transfer the wash liquid to the cone containing the main portion of the solution. Then place the centrifuge cone in a steam bath, and evaporate the solution by blowing a stream of air on its surface.

When the hydrochloric acid solution has evaporated to dryness, add 15 cmm. of 6-M HCl, and stir until all of the residue has dissolved. Cool the cone by placing it in an ice bath, and then add 10 cmm. of ether. The volumes of ether and acid will take care of quantities of aluminum up to 100 μ g. If this quantity is exceeded, correspondingly larger volumes of ether and 6-M HCl are used. Pass dry HCl into the liquids until one layer results. This occurs when the aqueous solution and the ether become sufficiently saturated with HCl to be completely miscible. Introduce the gas into the liquids in the centrifuge cone by means of the capillary shown in Fig. 69, p. 132, P.-S. When the two liquid phases have merged into one, place the cone in a saturation chamber (Fig. 2) filled with HCl gas, and leave it there for a half hour.

The HCl is generated in an apparatus similar to that suggested by O. R. SWEENEY¹⁰. However, the outlet from the generating chamber has been equipped with a ground glass joint, and connects to the saturation chamber. The inlet tube, which extends almost to the bottom of the saturation chamber, has four glass rings fused on it 5 cm. from its end. These rings support centrifuge cones during saturation periods. The saturation chamber is equipped with stop-cocks on the inlet and outlet tubes, thus making it possible to fill the chamber with gas, and allow saturation to proceed undisturbed for any desired length of time.

After the half hour in the atmosphere of HCl, centrifuge the cone with some two hundred turns of the centrifuge crank, and then place the cone in an ice bath again. Of course, the centrifuging required here can be done more conveniently by means of an electric centrifuge. The amount of aluminum present is estimated at this point of the procedure by comparing precipitate P 111 with a precipitate of known aluminum content. Precipitate P 111 and

¹⁰ J. Am. Chem. Soc. 39, 2186—88 (1917).

solution S 111 are then separated by means of a rather wide capillary pipet (0,6 to 0,7 mm. in bore) having a wide point (0,2 to 0,3 mm.), or by the aid of a contraction pipet (P.-S., p. 81). Too much ether must not be taken up in the capillary pipet at one time, since the ether is apt to become warm, and to begin to evaporate so violently that the solution is blown out of the capillary, thus resulting in serious losses. Furthermore, the cone

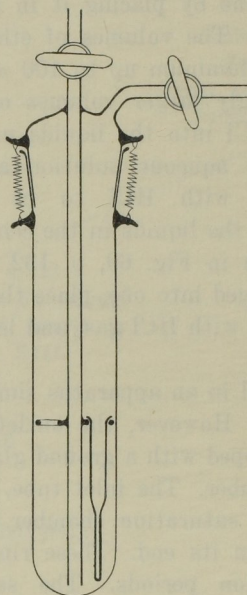


Fig. 2. Saturation Chamber ($\frac{1}{3}$ nat. size).

must be kept in the ice bath as much as possible, and should not be removed except during the time required for actual manipulations. This precaution has to be observed, else the ether becomes warm, HCl escapes from it, and the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ goes into solution. Furthermore, one should not attempt to remove all of the HCl-ether solution from precipitate P 111, but should only separate most of the liquid from the precipitate. It is very advisable to add another 10 cmm. portion of ether to the solution S 111, and to repeat the saturation with HCl gas in order to insure complete removal of the aluminum from solution. It was found

that it is possible to separate 990 $\mu\text{g.}$ of aluminum out of 1000 $\mu\text{g.}$ (or 99%) by the first HCl precipitation.

§ 112.—The Confirmation of Aluminum.—Dissolve the $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ (precipitate P 111) in enough 2-M HNO_3 to give a 10 $\mu\text{g./cmm.}$ Al solution, and transfer a portion of this solution to a slide. In this drop carry out the alum test for aluminum as described on pp. 101—102, in P.-S.

§ 113.—The Separation of Zinc and Beryllium.—Solution S 111 is now treated in the following way: First carefully remove the ether from the solution by holding the cone 5 to 6 cm. above the top of a vigorously boiling steam bath and stirring with a glass thread. When the bubbles of ether vapor and of HCl cease to form in the solution, place the cone in the steam bath, and direct a stream of air on the surface of the solution until complete evaporation is accomplished. Add a 30 cmm. portion of 15% NaOH solution to the cone by means of a calibrated capillary pipet, and stir the mixture of residue and solution. This procedure causes the formation of uranate, beryllate, and zincate. Electrolyze in an micro cone, such as suggested by EMICH (capacity 0.7 ml.), through the bottom of which is sealed a platinum wire having a diameter of 0,1 to 0,3 mm¹¹. This wire extends about 2 mm. into the cone, and has a length of 2 cm. outside the cone; this wire serves as the anode during the subsequent electrolysis. A platinum wire of the same diameter is employed for the cathode, and is inserted about 1 mm. below the surface of the solution. An E.M.F. of 10 volts is used.

After the electrolysis has proceeded for five minutes, quickly remove the cathode from the solution while the current is still flowing. The presence of a microgram of zinc will color the platinum wire gray or black, and will be quite visible to the unaided eye. Then dip the wire into 2-M HNO_3 contained in a cone, and heat on a steam bath until all of the electrolytically deposited zinc has dissolved. Again place the cathode in the electrolytic set-up, and electrolyze for another five minutes. Then remove the wire again, examine for a deposit of zinc, and finally dip into the same portion of 2-M HNO_3 used to dissolve the first

¹¹ BENEDETTI-PICHLER, A. A., *Ztschr. analyt. Chem.* **70**, 268—270 (1927).

electrolytic deposition product. Then evaporate the acid solution, and take up the residue in 20 cmm. of a solution prepared by mixing equal parts of 6-M ammonium acetate solution and 6-M acetic acid. Introduce H_2S into the solution by the usual method. If any ZnS forms, centrifuge it to the bottom of the cone, and estimate the amount present by comparison with a standard ZnS precipitate containing a known amount of zinc. The quantity of zinc estimated here is increased by the amount found in the nickel group (in solution S 124 A).

§ 114.—The Confirmation of Zinc.—It is now possible to dissolve the ZnS in 2-M HNO_3 , and to carry out the mercurithiocyanate test as described on pp. 103—104, of P.-S.

§ 115.—The Detection of Beryllium.—Neutralize the electrolyte E113 in the electrolytic cell with 6-M HNO_3 , and add enough of the acid to dissolve any precipitate which might be present.

Evaporate this solution to dryness on a steam bath. Then add a 20 cmm. portion of water along with enough 6-M NH_3 to give the solution a distinctly ammoniacal smell. Stir the mixture with a glass thread and heat nearly to boiling in the steam escaping from a vigorously boiling steam bath. Finally centrifuge the precipitate to the bottom of the cone, and remove and reject the solution.

Now add a 5 to 10 cmm. portion of 6-M acetic acid to the precipitate which remains in the cone, and evaporate the solution to dryness. Add another 10 cmm. portion of glacial acetic acid, and again evaporate the solution to dryness. Transfer 10 cmm. of dry $CHCl_3$ to the cone, and stir the residue and the chloroform. Carefully break up any large pieces of solid by means of a glass thread¹². Centrifuge and separate solution S115 and precipitate P115, transferring solution S115 to another centrifuge cone.

To solution S115 add 10 cmm. of water, and mix the two liquids thoroughly by means of a glass thread. Centrifuge, remove the upper aqueous layer, and reject it. Then evaporate the chloroform solution to dryness in the centrifuge cone. Dissolve the residue thus obtained in 3 cmm. of 6-M HNO_3 , and again evaporate to dryness. Now add a 10 cmm. portion of water, and make the

¹² F. HABER, and G. VAN OORDT, *Ztschr. anorgan. Chem.* **40**, 465—68 (1904).

solution distinctly alkaline with 6-M NH_3 . Place the cone in a steam bath, heat nearly to boiling, and then centrifuge the beryllium hydroxide to the bottom of the cone. Estimate the amount of beryllium present by comparison with a standard precipitate of known beryllium content.

Treat the beryllium hydroxide precipitate with enough M/5 or M/4 NaOH to form a 10 μg . Be/cmm. solution of beryllium, and take the alkaline solution up in a capillary having a bore of 0.6 to 0.8 mm. Confirm the presence of beryllium as follows:

A 3 cmm. portion of a solution of 0.05% quinalizarine in 0.2-N KOH is placed on a slide, and taken up in the capillary containing the beryllium solution. The solutions are then blown out on a slide, and taken back into the capillary in order to mix them thoroughly. The capillary's dry end is sealed, and the solution is centrifuged into the sealed end. A blank is prepared in exactly the same way as described above, the blank consisting of only the quinalizarine solution and NaOH solution of the concentration used to dissolve the beryllium hydroxide precipitate.

Both capillaries are then cut off at the same length, clamped in the axis of a microscope¹³, and the colors are compared. The blank should have a rich purple color, but the capillary containing the test solution will be blue if beryllium is present. This reaction may be used for the colorimetric estimation of beryllium as suggested by H. FISCHER¹⁴.

§ 116. — Detection of Uranium.—Add 20 to 50 cmm. of a freshly prepared 1% NaHCO_3 solution to the residue P115, and heat the mixture on a steam bath for two to three minutes, stirring from time to time with a glass thread. Centrifuge and separate the solution from any residue which is rejected. Acidify the solution with 6-M HCl, and add 2 to 5 cmm. in excess. Remove the carbon dioxide present by boiling, and make the solution alkaline with ammonia. Centrifuge the cone, and separate solution and precipitate. Reject the former. To confirm the presence of

¹³ The clamp described by EMICH (EMICH-SCHNEIDER, p. 93) or by ALBER (H. ALBER, *Mikrochemie* **14**, 223—227 [1934]) may be used satisfactorily for this purpose.

¹⁴ *Ztschr. analyt. Chem.* **73**, 54 (1928).

uranium, treat the precipitate by the procedure described in § 1106 B (below).

Experimental Results. Experiments to determine the limitations of the scheme suggested above were carried out, and are reported below. Since the results given are self-explanatory, they will not be discussed.

It has been found that the smallest amounts of the elements which give precipitates in the cone that can be safely detected with the unaided eye are as follows:

Al as $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$. Vol. of 15 cmm. . . .	0.5 μg .
Be as $\text{Be}(\text{OH})_2$. Vol. of 15 cmm. . . .	3.0 μg .
Zn (electrolysis). Vol. of 30 cmm. . . .	0.5 μg .

The following limiting proportions were determined:

$$\text{Be} : \text{Zn} = 1 : 1000.$$

$$\text{Be} : \text{Zn} = 1000 : 1.$$

$$\text{Al} : (\text{Be}, \text{Zn}) = 1 : 1000.$$

$$\text{Al} : (\text{Be}, \text{Zn}) = 1000 : 1.$$

Analyses were carried out on fifty solutions containing aluminum, beryllium, and zinc where the proportions varied from 1 : 100 to 100 : 1. The results obtained were satisfactory.

Analysis of the Chromium Group.

In addition to the phosphate ion which collects here, the chromium group consists of chromium, uranium, vanadium, and tungsten. The last named element is in the group only when the original material contains phosphate.

The analysis of this group presented extraordinary difficulties, and lead to a lengthy investigation, the results of which are presented in the following paper¹⁵.

Two alternative procedures suggest themselves, the first of which is to be used when tungsten is present.

Procedure I.

The first procedure for the analysis of the chromium group may be summarized as follows:

¹⁵ MOLISCH-Festschrift, p. 36.

Tabular Outline VI.

Solution S 101:

Cr, U, V, and W (as phosphotungstate); add 6-M HNO_3 until acid; evaporate to dryness; take up in 100 cmm. of H_2O ; divide into two parts.

1/6 of solution S 1102:
+ HNO_3 + $\text{Pb}(\text{NO}_3)_2$.

Precipitate P 1103:

PbCrO_4
+ 6-M HNO_3 + ether
+ H_2O_2 .

H_3CrO_7 .

5/6 of solution S 1102:
+ 5 cmm. of 5-M NaCl ;
evaporate; heat to 210°C ;
add 20 cmm. of 70–72%
 HClO_4 .

Residue R 1104:
+ H_2SO_4 . Centrifuge.

CrO_2Cl_2 .

P 1104 A:

White precipitate
probably silicic acid.
Wash with HCl ;
test for W with
 SnCl_2 .

S 1104 A:
Cool in ice bath;
add 3% aqueous
cupferron solution;
centrifuge.

P 1106:

Vanadium salt of cupferron; + H_2SO_4
+ HClO_4 ; destroy the cupferron; evap-
oration to dryness; + 6-M NH_3 + H_2S
+ HNO_3 .

S 1106:
+ HClO_4 ; to dryness;
+ H_2O + acetic
acid + Na_2HPO_4 .

P 1106 A: V_2S_5 .

S 1106 A: Reject.

P 1106 B:

$\text{UO}_2\text{NH}_4\text{PO}_4$ + HCl
+ NaCl + $\text{K}_4\text{Fe}(\text{CN})_6$.

$\text{K}_2(\text{UO}_2)\text{Fe}(\text{CN})_6$.

S 1106 B:
+ NH_3 + Mg reagent.

P 1107:

MgNH_4PO_4 ; Reject.

S 1107:
+ HNO_3 ; boil.

P 1107 A:
 H_2WO_4 + HCl + SnCl_2 .

Tungsten blue.

S 1107 A:
Reject.

§ 1102.—The Separation and Identification of Chromium.—To solution S 101 add 6-M HNO_3 until the solution is acid. Allow all of the carbon dioxide to escape from the acidified solution by stirring it with a glass thread while holding the cone in the steam issuing from a vigorously boiling steam bath. Then evaporate the solution in the cone to dryness, take up in 10 cmm. of 6-M HNO_3 , and again evaporate to dryness. Repeat the evaporation with HNO_3 , and finally dissolve in 100 cmm. of H_2O . By means of a calibrated capillary pipet transfer 15 to 17 cmm. of this solution S 1102 to another cone, and test it for chromium as described in the following paragraphs. Continue the analysis of the larger portion of solution S 1102 by § 1104.

To the smaller part of solution S 1101 add 0.1 to 0.3 cmm. of 6-M HNO_3 and 5 cmm. of 0.5-M $\text{Pb}(\text{NO}_3)_2$. Mix and allow to stand for fifteen to twenty minutes. Centrifuge and estimate the amount of chromium present by comparison. Finally remove and reject the supernatant solution.

§ 1103.—The confirmation of Chromium.—Add 10 cmm. of water to precipitate P 1103, stir, centrifuge, and discard the wash liquid. By means of a capillary pipet measure off 2 cmm. of 6-M HNO_3 and 8 cmm. of water, and transfer them to the lead chromate precipitate. Stir the mixture, and heat on a steam bath. Two alternatives are possible:

a) The yellow precipitate does not dissolve. This may occur when a large amount of lead sulfate is associated with a small amount of lead chromate. Under such conditions the latter salt is insoluble in 1.2-M HNO_3 .

Separate the dilute nitric acid from the lead chromate, add 15 to 30 cmm. of 3-M ammonium acetate, stir with a glass thread, and heat on a steam bath. Then cool, centrifuge, and reject the extract. Again treat the precipitate with 1.2-M HNO_3 and continue by the procedure outlined in "b".

b) The lead chromate dissolves on warming with the dilute nitric acid. In this case, cool the solution, and by means of calibrated capillary pipets add exactly 10 cmm. of water, about 2 cmm. of ether, and 1 cmm. of 3% H_2O_2 . Stir the mixture with a glass thread. When chromate is thus treated, it is oxidized to the blue H_3CrO_7 . This compound immediately concentrates

in the ether solution. Peroxychromic acid is quite unstable, decomposition being speeded up by too much peroxide or acid, or by a rise in temperature of the solution. If the blue fades and the solution remains yellow, another cubic millimeter of 3% H_2O_2 may be added.

§ 1104.—The Separation of the Chromium from the Major Portion of the Uranium, Vanadium, and Phosphotungstate.—By means of a capillary pipet add about 5 cmm. of 5-M NaCl solution to the main portion of solution S 1102, and stir with a glass thread.

Transfer the solution to a 1 cc. porcelain crucible, and heat slowly to 100° C. This heating may be done in an ordinary heating block such as is used in the sublimation of mercury in a capillary. (See P.-S., p. 82.) One of the three holes on its end should be reamed out so that the lower half of the 1 cc. porcelain crucible fits snugly. A 250° thermometer is fitted with a rubber stopper, and suspended so that its bulb is in the heating block on the same level as the part of the crucible being heated. The evaporation is speeded up by directing a stream of air on the surface of the solution.

Now heat the block so that the temperature rises at a rate of about twenty degrees a minute. By means of a capillary of rather wide bore (0.7 to 1 mm.) drop 20 cmm. of 70 to 72% $HClO_4$ onto the center of the residue in the crucible when a temperature of 210° has been reached. In this case the acid covers the entire precipitate at the same instant. The brown fumes of CrO_2Cl_2 come off immediately being displaced by the heavier vapor of the $HClO_4$. The latter is eliminated by maintaining the temperature of 210° C. until the white fumes cease to appear.

If one follows the directions just given, all of the chromium will be eliminated as chromyl chloride (unless unusually large amounts of this element are present), since the perchloric acid reacts instantaneously with the chromate and chloride ions with the formation of the chromyl chloride, and then it drives this compound off as the temperature is above the boiling point of the chromyl chloride (117°) and the boiling point of the perchloric acid (203°).

If the temperature is below 190° , the perchloric acid liberates

HCl from the sodium chloride and the chromate ion is reduced to chromium ion. Naturally, the complete elimination of the chromium is prevented when this occurs. The dark red color of vanadium pentoxide (appearing when large amounts of vanadium are present) should not be confused with chromium which has not been eliminated.

To repeat the separation of the chromium, which is necessary when large quantities of this element are present, add 3 cmm. of 5-M NaCl to the residue from the first treatment, and evaporate to dryness. Again heat on the block. When the temperature has reached 210°, add another 20 cmm. portion of 70 to 72% HClO₄.

After the removal of the chromium, cool the crucible, and transfer the residue to a centrifuge cone by using four 10 cmm. portions of 10% H₂SO₄. If large amounts of vanadium are present, all of the vanadium pentoxide formed by the oxidizing action of the hot perchloric acid will not go into solution. However, this may be accomplished by adding about 5 cmm. of 3% H₂O₂, stirring and heating in the steam issuing from a steam bath. Finally centrifuge, and separate the solution S 1104 A from precipitate P 1104 A.

Precipitate P 1104 A will usually consist of white dehydrated silica. However, it should be washed with a 10 cmm. portion of 13-M HCl, and tested for tungsten with stannous chloride and hydrochloric acid as directed in § 1107.

§ 1106.—The Separation and Identification of Vanadium.—Place the cone containing solution S 1104 A in an ice bath, and cool it for five minutes. Then add 1 cmm. portions of a 3% aqueous cupferron solution until an excess of the precipitant is present. This point is indicated by the simultaneous occurrence of two phenomena: a permanent precipitate of white cupferron forms, and the brick-red vanadium cupferronate suddenly coagulates. Again place the cone in the ice bath for five minutes. The centrifuge cone should now be centrifuged with a couple of hundred turns of the crank (an electric centrifuge is quite handy at this point of the procedure). Separate solution S 1106 from precipitate P 1106.

Wash precipitate P 1106 with 10 cmm. of a cold 10% sulfuric acid solution containing 1.5 g. of cupferron per 100 cc. Centrifuge and reject the wash liquid.

To the washed precipitate P 1106 add 5 cmm. of 18-M H_2SO_4 and 5 cmm. of 70 to 72% HClO_4 , and evaporate to dryness. This procedure is designed to destroy the cupferron.

Evaporate by placing the cone in an aluminum heating block, and heating to 205° . When dryness has been reached, remove the cone from the block, and allow it to cool to room temperature. Add about 30 cmm. of 6-M NH_3 , stir until solution is complete, and then introduce H_2S by the usual method for 15 minutes. The appearance of a brilliant red coloration indicates the presence of vanadium. This color appears only after the ammoniacal solution has been saturated with H_2S . Ammonium salts tend to interfere with the formation of the color. However, all ammonium salts will have been volatilized during the decomposition of the cupferron by heating. The red color seems to be due to the formation of thiovanadate.

Now add 6-M HNO_3 in 3 cmm. portions to the solution until distinctly acid, and then heat the cone in steam issuing from a boiling steam bath.

Stir constantly with a glass thread. Centrifuge and estimate the amount of vanadium present by comparison.

§ 1106 A.—The Separation of Uranium from Phosphotungstate.—Destroy the excess of cupferron in solution S 1106 by the method outlined in § 1106. After evaporating to dryness, take up the residue in 40 cmm. of water, and neutralize with 6-M NH_3 . By means of a calibrated capillary pipet add 5 cmm. of 6-M acetic acid and 15 cmm. of 0,5-M Na_2HPO_4 . Heat the mixture nearly to boiling by placing the cone in a steam bath. A white precipitate P 1106 B is $\text{UO}_2\text{NH}_4\text{PO}_4$. Let the mixture stand for fifteen minutes, centrifuge, and estimate the amount of uranium present by comparison.

Finally wash the precipitate P 1106 B of $\text{UO}_2\text{NH}_4\text{PO}_4$ with 10 cmm. of 1-M NH_4NO_3 , and confirm the presence of uranium as outlined in § 1106 B.

§ 1106 B.—The Confirmation of Uranium.—Add 10 to 20 cmm. of 6-M HCl to precipitate P 1106 B, and heat in a steam bath, stirring until solution is complete. Then evaporate the solution to a volume of about 0,2 cmm., and add 5 cmm. of 1-M $\text{K}_4\text{Fe}(\text{CN})_6$. Let stand for fifteen minutes. The formation

of a reddish-brown precipitate indicates the presence of uranium, and consists of $K_2(UO_2)Fe(CN)_6$. The presence of 1 $\mu g.$ of ferric iron in 10 $\mu g.$ of uranium will result in the formation of a black precipitate which masks the characteristic reddish-brown color of the $K_2(UO_2)Fe(CN)_6$. When the ratios become greater than this, the well-known Prussian blue color appears. Vanadium may interfere with the identification of the uranium as ferrocyanide, since it gives a greenish colored precipitate.

§ 1107.—The Separation of Tungsten from Phosphate and the Identification of Tungsten.—Place the cone containing solution S 1106 B in a steam bath, and evaporate the solution to dryness. Transfer 50 to 60 cmm. of water to the cone, and stir the mixture until the solution is complete. Then add 2 cmm. of 15-M NH_3 , or more if the solution is not alkaline. Stir with a glass thread, add 20 cmm. of 0,5-M $Mg(NO_3)_2$ reagent, heat the mixture by placing the cone in a steam bath, and gradually add 5 cmm. of 15-M NH_3 . Then cool the mixture, and let it stand for an hour with occasional stirring. Centrifuge and reject the $MgNH_4PO_4$ precipitate P 1107.

Now place the cone containing the filtrate S 1107 in a boiling steam bath, and heat and stir until no more ammonia escapes from the solution. Add 3 cmm. of 16-M HNO_3 , evaporate the solution to about 10 cmm. Cool, add 1 cmm. of 16-M HNO_3 and 5 cmm. of H_2O , and heat in a steam bath until all of the crystalline salts have dissolved. Centrifuge and reject solution S 1107 A. Estimate the amount of tungsten present in P 1107 A by comparison.

Dissolve residue P 1107 A in 10 cmm. of 15-M NH_3 , evaporate the solution to dryness, and then add about 3 cmm. of 0,5-M $SnCl_2$. Stir, heat the mixture, and add 3 cmm. of 12-M HCl . Heat to boiling again, and let it cool. A blue color or a blue precipitate indicate the presence of tungsten.

Experimental Results. Experiments were carried out to determine the applicability of the above scheme, and it has been found that the smallest amounts of the elements which can be safely detected in cones with the unaided eye are as follows:

Cr as $PbCrO_4$. Vol. of 75 cmm.	0,3 $\mu g.$
Cr as H_3CrO_7 . Vol. of 25 cmm.	0,5 $\mu g.$
U as $UO_2NH_4PO_4$. Vol. of 60 cmm.	1,0 $\mu g.$

U as $K_2UO_2Fe(CN)_6$. Vol. of 10 cmm.	0,1 μg .
V as Cupferronate. Vol. of 10 cmm.	1,0 μg .
V as Thiovanadate. Vol. of 30 cmm.	2,0 μg .
W as H_2WO_4 . Vol. of 40 cmm.	1,0 μg .
W as Tungsten blue. Vol. of 7 cmm.	1,0 μg .
W (Separation from phosphate and identification as tungsten blue as outlined in §. 1107)	20,0 μg .

The limiting proportions for the separations are not entirely satisfactory, especially when one attempts to isolate and identify the tungsten after carrying out the entire procedure as outlined above. It is not possible to find tungsten when less than 50 μg . are present in the original material.

(U, V) : Cr (removed as CrO_2Cl_2) = 1 : 1000 (certainly better).

U : (Cr, V) = 100 : 1 (or better).

V : (Cr, U) = 100 : 1 (or better).

A series of analyses was run on mixtures containning chromium, uranium, vanadium, and tungsten in order to determine the applicability of the scheme. Some of the results are reported below:

Table III.

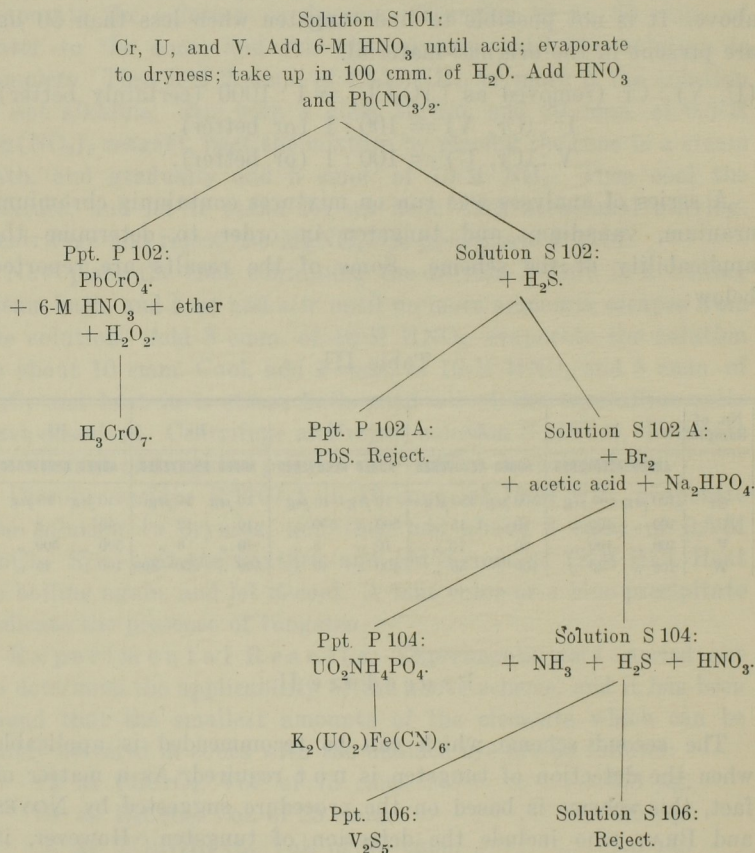
No. of Sample	Ar		Bh		Bi		Bk		Bj	
	ADDED	RECOVERED	ADDED	RECOVERED	ADDED	RECOVERED	ADDED	RECOVERED	ADDED	RECOVERED
Cr	100 μg	90 μg	500 μg	450 μg	10 μg	10 μg	10 μg	10 μg	10 μg	10 μg
U	100 "	100 "	10 "	15 "	500 "	500 "	10 "	12 "	10 "	8 "
V	100 "	100 "	10 "	10 "	10 "	8 "	10 "	8 "	500 "	500 "
W	100 "	40 "	100 "	50 "	100 "	40 "	500 "	250-300	100 "	45 "

Procedure II.

The second scheme which can be recommended is applicable when the detection of tungsten is not required. As a matter of fact, this scheme is based on the procedure suggested by NOYES and BRAY who include the detection of tungsten. However, it

was found that it is impossible to isolate and identify even 100 μg . of tungsten when present with similar amounts of chromium, uranium, and vanadium. Consequently, the scheme was adapted to a micro scale with the omission of provisions for the identification of tungsten. Of course, the cupferron procedure works under these conditions, too, and it is probably preferable, since the use of cupferron gives a faster and a more complete separation of the vanadium. The scheme may be summarized as follows:

Tabular Outline VII.



§ 102.—The Separation and Identification of Chromium.—Carry out the acidification of solution S 102 as directed in § 1102. Then, without dividing the solution, proceed to carry out the precipitation of the chromate ion with lead nitrate. Of course, six times the volumes of reagents have to be employed as the whole solution is being treated. Centrifuge and estimate the amount of chromium in P 102 by comparison. Finally confirm the presence of chromium in P 102 as directed in § 1103. Treat solution S 102 as follows:

Saturate with H_2S in the usual way. Centrifuge and separate solution S 102 A from the lead sulfide. Then heat S 102 A in a steam bath until all of the H_2S has been eliminated. Stirring with a glass thread will speed up the elimination of the gas. Then place the cone in a water bath heated to 50 to 60°, add 1 to 2 cmm. of liquid bromine to the solution, and leave the cone in the hot water bath for five minutes. This procedure insures the oxidation of any vanadyl salts to vanadic acid, and prevents the precipitation of $VONH_4PO_4$ with the $UO_2NH_4PO_4$ in the subsequent procedure. Finally place the cone on a steam bath and evaporate the solution S 102 A to dryness.

§ 104.—The Separation of Uranium from Vanadium.—To the residue obtained in the last paragraph, add 40 cmm. of water, and stir with a glass thread. The solution at this point may contain a white turbidity of sulfur which must be removed by centrifuging. The clear solution S 102 A should be neutral to litmus. If it is not, add 6-M NH_3 in 1 cmm. portions until the solution is barely alkaline to litmus. Then by means of a calibrated capillary pipet add 5 cmm. of 6-M acetic acid and 15 cmm. of 0.3-M Na_2HPO_4 solution. Heat the solution to boiling. A white precipitate P 104 is $UO_2NH_4PO_4$. Place the cone in a wooden block, and allow it to stand for 10 to 15 minutes in order to coagulate the phosphate precipitate. Then centrifuge, by comparison estimate the amount of uranium present, and separate precipitate P 104 from solution S 104. After washing P 104 with 1-M NH_4NO_3 , confirm the presence of uranium by the procedure outlined in § 1106 B of the preceding scheme.

§ 106.—The Detection of Vanadium.—Evaporate solution S 104 to dryness, and then take up the residue thus

obtained in 40 to 50 cmm. of 6-M NH_3 . Then proceed to the identification of vanadium by introducing H_2S into the solution, and by the addition of HNO_3 as directed in § 1106 of the preceding scheme. Estimate the amount of vanadium present by comparing the V_2S_5 precipitate with a similar precipitate of known vanadium content.

Experimental Results: It was found that the following limiting proportion holds for the separation of chromium from uranium and vanadium:

$$(\text{U}, \text{V}) : \text{Cr (removed as PbCrO}_4) = 1 : 100.$$

A series of analyses were run to determine the applicability of the above scheme, and the following are a few of the results obtained.

Table V.

No. of Sample	CD		CF		CG	
	ADDED	RECOVERED	ADDED	RECOVERED	ADDED	RECOVERED
Cr	100 μg	95 μg	25 μg	25 μg	10 μg	10 μg
U	10 "	10 "	100 "	90 "	50 "	45 "
V	25 "	20 "	10 "	6 "	100 "	70-80 "

Summary.

An attempt has been made to develop a milligram procedure for the qualitative analysis of the aluminum-chromium, nickel and rare earths groups of A. A. NOYES and BRAY. In the aluminum group proper the electrolytic isolation of zinc had to be adopted to obtain better limiting proportions for the detection of zinc and beryllium. In the analysis of the nickel group, the manganese is separated by precipitation of MnO_2 from nitric acid solution before proceeding to the treatment with sodium peroxide; a cleaner separation of the zinc is expected due to the absence of manganese in the sodium peroxide treatment. The rare earths are isolated as a group. The isolation of gallium according to NOYES and BRAY was transposed to a small scale without change in the chemical procedure.

Unusual difficulties were met with in the analysis of the chromium group. The scheme of NOYES and BRAY does not permit the detection of tungsten in mixtures of chromium, uranium, vanadium, and phosphate. A scheme was developed in which the chromium is eliminated as chromyl chloride by treatment of the dry residue with 72% perchloric acid (and NaCl) at 210° C. Even this scheme does not permit the detection of smaller quantities than 50 μg . of tungsten in milligram-samples. The actual evaporation of the chromyl chloride requires only a few seconds, and is certainly one of the least time consuming operations of qualitative analysis.

Directions for the estimation and identification of the elements are included, the limitations of the methods have been determined for most of the procedures.