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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.

PART IV.—ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS.[1]

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Introduction.

The earlier parts of this system of analysis have dealt with the "Preparation of the Solution,"[2] the "Analysis of the Silver, Copper, and Tin Groups,"[2] and the "Analysis of the Aluminum and Iron Groups."[3] The present part treats of the analysis of the two remaining groups of metallic elements, which include barium, strontium, calcium, magnesium, sodium, potassium, and the rarer element, lithium. The general purposes of the investigation, the method of presentation, and the meaning of the abbreviations used have been described in the introduction to the first paper.[2]

General Discussion.

In the method of analysis here presented, magnesium is precipitated by ammonium carbonate together with the other alkaline earth elements, barium, strontium, and calcium, instead of being separated from them by this reagent. This somewhat radical modification of the usual process was made possible by the knowledge that magnesium separates out completely as a double ammonium magnesium carbonate, when the solution is cold and is concentrated with respect to both ammonium carbonate and ammonium hydroxide (the effect of the latter substance

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[2] A. A. Noyes and W. C. Bray, THIS JOURNAL, **29**, 137–205 (1907).

[3] A. A. Noyes, W. C. Bray and E. B. Spear, *Ibid.*, **30**, 481–563 (1908).

being to drive back the hydrolysis of the ammonium carbonate). Some time is, to be sure, required for complete precipitation, but this may be reduced from several hours to less than half an hour by the addition of alcohol. This method was developed in connection with experiments that were made to determine the proper conditions for precipitating calcium, strontium, and barium completely, in the course of which it was found not possible to attain this result by increasing the concentration of the ammonium carbonate, without at the same time causing the precipitation of magnesium when much was present. It was, however, afterwards found that Schaffgotsch,[1] as early as 1858, had recommended this method of separating magnesium quantitatively from the alkali elements, and an improved process has been recently described by Gooch and Eddy[2] which is almost identical with that devised in the present work.

One of the great advantages of this process is that the precipitation of calcium, strontium, and barium as carbonates is much more complete than in the usual process where only a small quantity of ammonium carbonate is added; and where, to detect and remove them, it is necessary to add ammonium sulphate and ammonium oxalate to the filtrate. The process also makes unnecessary the lengthy operation of removing magnesium before testing for the alkali elements, which involves ignition to remove ammonium salts, precipitation of magnesium hydroxide by barium hydroxide, and subsequent removal of the barium. The only disadvantages of the process are that about half an hour is required to complete the precipitation of magnesium and that a somewhat longer time is required for filtration than when the carbonates are precipitated from a hot solution. These, however, seem slight in comparison with the lack of delicacy of the ordinary process of precipitation and the difficulty of subsequently removing magnesium.

In the analysis of the alkaline earth group, the ammonium carbonate precipitate is dissolved in acetic acid; and barium and strontium are precipitated as chromates, the former from an acetic acid solution of known concentration, the latter by making the filtrate alkaline with ammonia and adding alcohol. This method of precipitating barium has been adopted in nearly all text books in qualitative analysis, and the precipitation of strontium as chromate has been recommended by a few authors.[3] It was, however, found necessary to carry out a large number of experiments to determine the conditions under which a small amount of either element is easily detected, and a large amount com-

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[1] *Ann Physik*, 104, 482 (1858).

[2] *Am. J. Sci.* [4], **25**, 444 (1908). *Z. anorg. Chem.*, **59**, 427 (1908).

[3] W. Fresenius and F. Ruppert, *Z. analyt. Chem.*, **30**, 677 (1891). Caron and Raquet, *Bull. soc. chim.* [3], **35**, 1061 (1906).

pletely precipitated; and under which a large quantity of strontium when present alone does not interfere with the test for barium, and a large quantity of calcium does not interfere with that for strontium. This portion of the investigation was carried out by Dr. E. B. Spear in this laboratory.

After barium and strontium have been thus removed, calcium is precipitated as calcium oxalate, the filtrate is made strongly ammoniacal, and the magnesium precipitated by adding sodium phosphate and alcohol. In order to prevent the precipitation of some magnesium as oxalate when much of it is present, it is necessary to dilute the solution to about 300 cc. before making the test for calcium, but this large volume does not prevent the detection of even less than 1 mg. of magnesium. It may seem remarkable that the precipitation of magnesium ammonium phosphate is such a delicate test under these conditions, especially in view of the fact that it is usually directed to make the precipitation in as small a volume as possible. The difference is brought about by the presence in the solution of a moderate amount (about 20 per cent.) of alcohol, which doubtless greatly decreases the tendency of the solution to remain supersaturated.

The filtrate from the ammonium carbonate precipitate, which should now contain only salts of the alkali elements, is evaporated to dryness; the ammonium salts are expelled by ignition, and the residue dissolved in a little water. This solution is divided into two parts: the smaller one is tested for lithium and potassium, and the larger for sodium. Lithium is precipitated as phosphate from a hot, slightly alkaline solution, the delicacy of the test being greatly increased by the addition of a little alcohol. The potassium is tested for in the filtrate, after expelling the alcohol completely, by adding sodium cobaltinitrite, which gives a precipitate of $K_2NaCo(NO_2)_6.H_2O$. This reaction has been used as a quantitative method of determining potassium;[1] it is delicate enough to enable 0.2–0.3 mg. of potassium to be detected in 5 cc. of solution. In order to detect sodium the second portion of solution is evaporated and treated with an alkaline potassium pyroantimonate solution.[2] When the reagent is properly prepared this test is satisfactory and reliable on account of the characteristic appearance of the crystals of sodium pyroantimonate formed, and it is delicate enough to detect 1 or 2 mg. of sodium in the portion of solution tested. It is seldom that a more delicate test for this abundant element is necessary; indeed, if a much more sensitive one be employed, the sodium introduced in the process of analyses from the reagents, the glass vessels, and the dust of the air would prevent a blank

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[1] Adie and Wood, *J. Chem. Soc.*, **77**, 1076 (1900). Drushel, *Am. J. Sci.* [4], **24**, 433 (1907); **26**, 329 (1908).

[2] Cf. Boettger, Qualitative Analyse, Zweite Auflage, 232.

being obtained in the absence of this element. For this reason and because it gives no idea of the quantity present, the flame test relied upon in some schemes of analyses is unsatisfactory. Unfortunately, however, the presence of a large amount of a potassium salt presents the precipitation of even several milligrams of sodium; moreover, even a small amount of lithium gives a similar precipitate. In these cases, lithium is precipitated as fluoride, and a large part of the potassium as sulphate, before making the test for sodium.

An as yet unpublished scheme of analysis for the alkali elements, which included also rubidium and caesium, was worked out a few years ago in this laboratory by A. A. Noyes and J. E. Ober. In the first step of the process, following the method in common use, sufficient chlorplatinic acid was added to convert all the elements into the corresponding chlorplatinates; the sodium and lithium salts were washed out by means of alcohol, and the potassium, rubidium, and caesium salts left undissolved. In the present scheme, in which the detection of the common elements is of primary importance, this process has not been adopted on account of the time required to make this separation and to remove the platinum before testing for sodium and lithium, and also because of the expense involved in the use of the large amount of chlorplatinic acid required.

A final confirmatory test has been given for each element except magnesium. These will be omitted by the experienced analyst except when a small precipitate or one of doubtful character is obtained. The test for calcium is made by treating the oxalate precipitate with dilute sulphuric acid and precipitating the calcium sulphate from the solution by the addition of alcohol. The test for strontium depends on the transformation of the strontium chromate into carbonate at 100° in a solution containing sodium carbonate and sufficient oxalate to transform any calcium salt present into oxalate; the strontium is dissolved in acetic acid and precipitated by adding ammonium hydroxide and carbonate and boiling. The presence of the remaining elements is confirmed by the usual flame tests. The confirmatory tests for calcium, strontium, barium and lithium can be made in a still more satisfactory manner by the use of a small "pocket" spectroscope, comparative experiments being made with known solutions. A small instrument of this kind, which costs less than a platinum dish, should be available in every laboratory of qualitative analysis, because of the educational value to the student.

Tabular Outline.

In Table X an outline of the process is given, the confirmatory tests being, however, omitted. The symbols of the anhydrous substances are given without reference to the actual state of hydration of the precipitates. When lithium is not to be tested for, the directions enclosed within brackets are to be omitted. No attempt should be made to carry out an analysis without consulting the detailed directions given in the procedures.

TABLE X.—ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS.

Solution containing Ba, Sr, Ca, Mg; Li, K, Na.

Evaporate to a small volume, add $(NH_4)_2CO_3$ *reagent and alcohol, filter after 1/2 hour (P. 81).*

<table>
<tr><td colspan="4">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $(NH_4)_2CO_3$. *Dissolve in acetic acid, add* K_2CrO_4 *(P. 82).*</td><td colspan="3">Filtrate: *Evaporate, ignite, add* 5–10 *cc. water (P. 91).*</td></tr>
<tr><td rowspan="4">Precipitate: $BaCrO_4$.</td><td colspan="3">Filtrate: *Add* NH_4OH *and alcohol (P. 84).*</td><td colspan="2">*To 1/3 of solution [add* $NaOH$ *and* Na_2HPO_4, *heat, add alcohol (*P. 91 a)].*</td><td>Remainder: [Precipitate Li as LiF (*P. 93*)].</td></tr>
<tr><td rowspan="3">Precipitate: $SrCrO_4$.</td><td colspan="2">Filtrate: *Dilute, add* $(NH_4)_2C_2O_4$ *(P. 86).*</td><td rowspan="3">Precipitate: Li_3PO_4.</td><td>Solution: *Add* $Na_3Co(NO_2)_6$ *(P. 92).*</td><td>*Evaporate to 1 cc., add* $K_2H_2Sb_2O_7$ *reagent (P. 94).*</td></tr>
<tr><td rowspan="2">Precipitate: CaC_2O_4.</td><td>Filtrate: *Add* NH_4OH *and* Na_2HPO_4 *(P. 88).*</td><td rowspan="2">Precipitate: $K_2NaCo(NO_2)_6$.</td><td rowspan="2">White crystalline precipitate: $Na_2H_2Sb_2O_7$.</td></tr>
<tr><td>Precipitate: $MgNH_4PO_4$.</td></tr>
</table>

Procedures and Notes.

Procedure 81.—Evaporate the filtrate from the NH_4OH and $(NH_4)_2S$ precipitate (P. 51) to a volume of about 10 cc., and filter off any sulphur that may have precipitated. To the cold solution add 30 cc. of the $(NH_4)_2CO_3$ reagent (see N. 2) and 30 cc. 95 per cent. alcohol; let the mixture stand for at least half an hour, shaking frequently. (Precipitate, presence of *alkaline-earth elements.*) Filter and wash the precipitate with a little of the $(NH_4)_2CO_3$ reagent; if the precipitate is large dry it by suction. (Precipitate, P. 82; filtrate, P. 91.)

Notes.—1. The filtrate from the $(NH_4)_2S$ precipitate should be colorless or light yellow (see P. 51, N. 12). It is evaporated in order that the elements of the alkaline earth group may be precipitated more quickly and more completely. The volume to which the $(NH_4)_2CO_3$ reagent is added should not exceed 20 cc. The evaporation also serves to destroy $(NH_4)_2S$ and to coagulate any sulphur that may separate.

2. The reagent used in precipitating the elements of this group is conveniently prepared by dissolving 100 grams freshly powdered ammonium carbonate in 300 cc. NH_4OH (0.96), filtering, if there is any precipitate, and adding 100 cc. NH_4OH (0.90). The solid carbonate contains a large proportion of ammonium carbamate, $NH_2CO_2NH_4$, but, on dissolving, the latter is rapidly converted into ammonium carbonate.

3. In an ammoniacal ammonium carbonate solution, calcium, strontium, and barium

are precipitated as carbonates. If the ammonium carbonate and hydroxide were added in only small excess, the precipitation would not be complete, and additional tests for these elements would have to be made (for example, by adding to the filtrate $(NH_4)_2C_2O_4$ and $(NH_4)_2SO_4$). But, by the use of a concentrated solution of $(NH_4)_2CO_3$ and the addition of a large excess of NH_4OH to diminish the hydrolysis of the carbonate into $(NH_4)^+HCO_3^-$ and NH_4OH, the precipitation may be made practically complete, owing to the greatly increased concentration of the carbonate ion $(CO_3^{=})$.

4. When the concentrations of $(NH_4)_2CO_3$ and NH_4OH are sufficiently great, magnesium is in the cold also quantitatively precipitated as a double carbonate $MgCO_3.(NH_4)_2CO_3.4H_2O$. This substance is, however, fairly soluble in water and the solubility increases rapidly with the temperature.

5. In an aqueous solution in the cold, the precipitation of these elements takes place slowly, especially in the case of magnesium and calcium, but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure, not more than 0.1–0.3 mg. of any of the four elements remain in solution after half an hour, and even 0.5 mg. is easily detected within this time.

6. Li_2CO_3 is by far the least soluble carbonate of the alkali elements but under the conditions of the procedure no precipitate is obtained even when 150 mg. of lithium are present. Larger amounts of lithium yield a precipitate; but this case will seldom, if ever, occur if the weight of the original substance taken for analysis did not exceed 1 gram. The presence of the alkali elements does not interfere in the analysis of the alkaline earth group, and it is therefore not necessary to wash the $(NH_4)_2CO_3$ precipitate.

Procedure 82.—Dissolve the $(NH_4)_2CO_3$ precipitate (P. 81) by pouring repeatedly through the filter a portion of hot dilute acetic acid (10–25 cc.) 30 per cent. acid. Make the solution slightly alkaline with NH_4OH; add 30 per cent. acetic acid, drop by drop, until the solution after shaking is just acid to litmus, and then add 3 cc. more. Dilute to 40 cc., heat to boiling in a flask; measure out 10 cc. 20 per cent. K_2CrO_4 solution and add it a few drops at a time; if a precipitate forms heat the mixture just to boiling and shake it after each addition; finally heat the mixture at 90–100° for 1 or 2 minutes, shaking it frequently. Filter, even though the solution appears clear; remove the filtrate, and wash the precipitate thoroughly with cold water. (Pale yellow precipitate, presence of *barium.*) (Precipitate, P. 83; filtrate, P. 84.)

Notes.—1. The solubility in water of the chromates of the alkaline earth elements increases rapidly in the order, Ba, Sr, Ca, Mg. The difference in solubility of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the procedure 0.5 mg. Ba can be detected, while even 400 mg. Sr give no precipitate. The amount of K_2CrO_4 added is sufficient to precipitate completely more than 500 mg. of barium.

2. Acetic acid is added to prevent the precipitation of $SrCrO_4$. By its action the concentration of the chromate ion is reduced, owing to its conversion into hydrochromate ion and bichromate ion according to the reactions:

$$2CrO_4^{--} + 2H^+ = HCrO_4^- = H_2O + Cr_2O_7^{--}.$$

The relative amounts of these two ions present in the acid solution depends upon the dilution; in the fairly concentrated solution used in this procedure $Cr_2O_7^{--}$ predominates, but this would be reversed in a much more dilute solution. Since $HCrO_4^-$ is a weaker acid than acetic acid, the CrO_4^{--} concentration in the acid solution is very small. It is evident that the CrO_4^{--} concentration decreases as the H^+ concentration increases. For this reason the presence of excess of a strong acid (such as HCl or HNO_3 in the absence of acetate) prevents the precipitation of $BaCrO_4$; but owing to the fact that acetic acid is itself a weak acid and that a large amount of acetate is present the addition of a considerable excess of acetic acid has but little effect. The most satisfactory separation of barium and strontium is obtained when a small excess of acetic acid is present; 2 cc. 50 per cent. acetic acid are nearly equivalent to 10 cc. 20 per cent. K_2CrO_4 solution.

3. The K_2CrO_4 is added slowly to a hot solution, the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of K_2CrO_4 is added; this is of special importance when much barium is present, since as much as 3 mg. Sr may then be carried down completely if the K_2CrO_4 reagent is added quickly. If for any reason the filtrate is turbid after two or three filtrations, the precipitate ($BaCrO_4$) may be coagulated by boiling gently for 1 or 2 minutes. Vigorous or long-continued boiling is to be avoided, since, owing to loss of acetic acid, $SrCrO_4$ may then separate if much strontium is present. The presence of 1 mg. or more of barium is indicated by a distinct turbidity or the formation of a precipitate; when the amount is smaller than 1 mg. it is very difficult to distinguish the faint turbidity in the colored solution, and the pale yellow precipitate can be seen only after filtering and washing the K_2CrO_4 out of the filter. The precipitate must always be washed thoroughly in order to remove strontium as completely as possible, which otherwise would obscure the confirmatory test for barium in P. 83.

Procedure 83.—To confirm the presence of barium, dissolve the K_2CrO_4 precipitate (P. 82), or a portion of it, in HCl (1.12) and evaporate the solution to a few drops. Dip a clean platinum wire into the solution and introduce the wire into a colorless flame. (Green flame, presence of *barium.*)

Notes.—1 HCl is used, instead of HNO_3, in dissolving the precipitate because the flame test for barium is then somewhat more delicate, owing to the greater volatility of the chloride. When the amount of barium is very small, only a momentary green color is seen as the yellow (sodium) color which first appears fades away. The presence of chromium does not interfere with the test.

Procedure 84.—To the filtrate (P. 82), after cooling it, add NH_4OH (0.90) slowly until the color of the solution changes from orange to yellow, and then 3 cc. more. Dilute the solution to 60 cc., and add slowly, with constant shaking, 50 cc. 95 per cent. alcohol. (Pale yellow precipitate, presence of *strontium.*) Filter after several minutes, using suction if filtration is slow; do not wash the precipitate. (To insure the complete precipitation of strontium, when much strontium or barium has been found, add to the filtrate 5 cc. 20 per cent. K_2CrO_4 solution and 10 cc. alcohol; filter off any precipitate that separates, and reject it if a precipitate has already been obtained in this procedure.) (Precipitate, P. 85; filtrate, P. 86.)

Note.—Under the conditions of the procedure 0.5 mg. of strontium is detected almost at once, and a smaller amount on standing, while even 400–500 mg. of calcium or magnesium give no precipitate. A moderate change in the conditions will not affect this result, but, if the concentration of alcohol or K_2CrO_4 is much less than is recommended, the precipitation of strontium may be incomplete, while the addition of larger amounts of alcohol and K_2CrO_4 may cause the precipitation of chromate of calcium or magnesium, if much of these elements is present, or of K_2CrO_4 itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore be tried. The precipitate is not washed because $SrCrO_4$ is a fairly soluble substance.

Procedure 85.—To confirm the presence of strontium, transfer the precipitate (P. 84) (or a portion of it if the precipitate is large), with the filter if necessary, to a casserole; add a mixture of 30–35 cc. 3 per cent. $Na_2C_2O_4$, 2 cc. 10 per cent. Na_2CO_3 (both measured out in graduates), and about 0.5 cc. 20 per cent. K_2CrO_4; cover the casserole with a watch glass, heat to boiling, and boil gently for 3–5 minutes. Filter, wash the precipitate thoroughly with water, pour repeatedly through the filter about 5 cc. of 5 per cent. acetic acid; add to this solution NH_4OH in excess and 3–5 cc. of the $(NH_4)_2CO_3$ reagent; heat to boiling in a small flask and set aside for 5–10 minutes. (White precipitate, presence of *strontium.*)

Notes.—1. In a boiling solution containing oxalate and carbonate in the proportions recommended in the procedure small quantities of calcium and strontium are converted in a few minutes almost quantitatively into oxalate and carbonate respectively. At 100° the solubility product of calcium oxalate is not more than 1.5 times as great as that of calcium carbonate; and therefore the carbonate will be converted into the oxalate when the ratio of the concentrations of $Na_2C_2O_4$ and Na_2CO_3 is greater than this amount. The ratio adopted in the procedure is about 4 to 1. In the case of strontium, however, the oxalate is so much more soluble than the carbonate that even when this ratio is as great as 8 to 1 no strontium oxalate is formed. To provide for the very rare case that barium is present, a small amount of K_2CrO_4 is added; the barium then remains as $BaCrO_4$, the yellow color of which is easily seen on the filter after washing out the K_2CrO_4. In this procedure it will usually be more convenient to prepare a special reagent by dissolving 30 grams $Na_2C_2O_4$, 6 grams Na_2CO_3, and about 3 grams K_2CrO_4, and diluting the mixture to 1 liter.

2. In the treatment with dilute acetic acid the strontium is dissolved, but not enough calcium to give a test with ammonium carbonate. If barium is present a little $BaCrO_4$ dissolves, giving a yellow solution; it may, however, be easily removed by adding excess of K_2CrO_4 and boiling the acid solution (see P. 82).

3. In this procedure the presence of 0.5 mg. of strontium may be detected, and a perfect blank is obtained even with 30 mg. of calcium or magnesium. With larger amounts of calcium, however, a very small precipitate may be obtained with ammonium carbonate.

4. If a spectroscope is available the presence of strontium in the precipitate obtained in P. 84 may be quickly detected after dissolving the precipitate in a little nitric acid and evaporating the solution to a few drops. Comparative tests with pure strontium and calcium solutions should be made.

Procedure 86.—To the filtrate (P. 84) add 200 cc. water, heat to boiling, and add slowly to the boiling solution 20–50 cc. 4 per cent. $(NH_4)_2C_2O_4.H_2O$ solution, shake, and let the mixture stand for several minutes. (White precipitate, presence of *calcium.*) Filter and wash the precipitate once with water. (Precipitate, P. 87; filtrate, P. 88.)

Note.—The solution is heated to boiling, the ammonium oxalate is added slowly, and the mixture is allowed to stand a few minutes, since otherwise the filtration is slow and calcium oxalate may pass through the filter. Moreover, since small amounts of calcium do not precipitate rapidly in the cold, 2 or 3 mg. may escape detection if the mixture is not heated. Under the conditions of the procedure, *i. e.*, in a volume of about 300 cc., 0.5 mg. of calcium can be detected within 5 minutes, while 400 mg. of magnesium give no precipitate. If, however, the volume of the solution is much less than 300 cc. and much magnesium is present, some may precipitate, especially if the mixture be allowed to cool to room temperature.

Procedure 87.—Dissolve the $(NH_4)_2C_2O_4$ precipitate (P. 86), or a portion of it, in 5 cc. cold dilute H_2SO_4 (1.20); filter, if necessary; add 10–15 cc. 95 per cent. alcohol, and let the mixture stand for several minutes. (White precipitate, presence of *calcium.*)

Notes.—1. $CaC_2O_4.H_2O$ is very difficultly soluble in water, but dissolves in dilute solutions of highly ionized acids, owing to the formation by metathesis of unionized $HC_2O_4^-$. $CaSO_4$ is somewhat soluble in dilute H_2SO_4 but is completely thrown out as a flocculent precipitate by the addition of two or three volumes of alcohol. One mg. of calcium gives a distinct turbidity at once, 0.5 mg. in 1–3 minutes, and 0.2 mg. within 10 minutes.

2. Moderate amounts of magnesium and of K_2CrO_4 do not interfere with this test, and it is therefore unnecessary to wash the precipitate thoroughly in P. 86. If strontium is present, however, a small amount of it dissolves in the H_2SO_4 and gives a slight turbidity at once on the addition of alcohol corresponding to that given by only 0.2–0.3 mg. of calcium after standing a few minutes. Therefore, anything more than a slight turbidity is a conclusive proof of the presence of calcium.

Procedure 88.—To the filtrate from the $(NH_4)_2C_2O_4$ precipitate (P. 86) add 10 cc. NH_4OH (0.90) and 20 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of *magnesium.*)

Note.—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate, $Mg^{++}(NH_4)^+PO_4^{---}$. This salt is somewhat soluble in water, owing chiefly to hydrolysis into NH_4OH and $Mg^{++}HPO_4^{=}$, and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature, the solution is cooled to the room temperature or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution; and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mg. of magnesium will give a distinct turbidity in this solution (containing 250 cc. water and 50 cc. alcohol) within half an hour, and the precipitate settles out on further standing. The presence of a small precipitate may then be detected by rotating the solution so as to cause the precipitate to collect in the centre. If calcium is present in this procedure, even as small an amount as 3 mg. will give a distinct precipitate of calcium phosphate; it is therefore very important to precipitate the calcium completely as oxalate in P. 86.

Analysis of the Alkali Group.

Procedure 91.—Evaporate the filtrate from the $(NH_4)_2CO_3$ precipitate (P. 81) almost to dryness in a casserole; acidify with HCl; evaporate to dryness and ignite the residue gently to a temperature below dull redness until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. Add about 10 cc. water, warm, filter, evaporate the filtrate to dryness, and ignite again (to insure complete removal of the ammonium salts). Add 5–10 cc. water and if necessary filter through a small filter. Test about one-third of the filtrate (first for lithium by *P. 91*a* and then) for potassium by P. 92; test the remainder of the filtrate for sodium by P. 93–4.

Notes.—1. Great care must be taken to remove the ammonium salts completely, since the presence of even 1–2 mg. of an ammonium salt would show the same reaction as potassium. The residue must not, however, be heated to redness, since the alkali elements might then be lost by the volatilization of their chlorides.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts used in the course of analysis and from the filter paper, usually remains upon treating the ignited residue with water. Sometimes, owing to the presence of this organic matter, the aqueous solution after the first ignition has a dark or yellow color, but it is usually clear after the residue is heated a second time.

3. The larger portion of the solution is used for the detection of sodium since the test for this element is less delicate than the tests for lithium and potassium.

***Procedure** 91a.—If lithium is to be tested for, evaporate one-third of the aqueous solution (P. 91) to 2 or 3 cc. Pour it into a large test-tube or small flask; add 0.3–0.5 cc. 10 per cent. NaOH solution, and filter if there is a precipitate. Add 1–2 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution, heat to boiling, add 1 cm. alcohol, shake, and boil gently for about one-half minute; add another portion of alcohol, and boil again for a few seconds. (White precipitate, presence of *lithium.*) Filter, remove the filtrate, and wash the precipitate thoroughly with NH_4OH (0.96).

Dissolve the precipitate in dilute HCl, evaporate the solution to a few drops, dip the loop of a clean platinum wire into it, and introduce the loop into a colorless gas flame. (Brilliant red flame, presence of *lithium.*)

To the filtrate from the Na_2HPO_4 precipitate add acetic acid until it is slightly acid, evaporate the solution to a few drops, and add 3–5 cc. water. Test the solution for potassium by P. 92.

Notes.—1. If magnesium was not completely removed in the $(NH_4)_2CO_3$ treatment, it precipitates upon the addition of NaOH, and should be filtered off, since otherwise it would be converted into phosphate and obscure the lithium test.

2. Li_3PO_4 is difficultly soluble in both hot and cold water, but the solubility is still less in an alkaline solution, since its hydrolysis into $(Li^+)_2HPO_4^{--}$ and Li^+OH^- is then diminished. The presence of NaOH is, moreover, necessary, in order to neutralize the acid formed in the reaction between the lithium salt and Na_2HPO_4. The tendency of Li_3PO_4 to form a supersaturated solution is overcome by heating the mixture, and by the addition of alcohol. Under the conditions of the procedure 0.3 mg. Li may be easily detected in the portion of solution used, and even 0.2 mg. when the second portion of alcohol is added and the mixture again boiled.

3. The alcohol is expelled before testing the filtrate for potassium because the presence of both alcohol and Na_2HPO_4 in a $Na_3Co(NO_2)_6$ solution causes the formation of a violet precipitate on standing. If a precipitate of lithium phosphate is formed by Na_2HPO_4 alone, the addition of alcohol, and the subsequent evaporation are unnecessary.

4. Before making the confirmatory test it is important to wash out the sodium salts as far as possible; otherwise the yellow color of the sodium flame may completely obscure the red color due to lithium. When the amount of lithium present is very small (0.2–0.3 mg.), there will always be sufficient sodium present to cause the brilliant red flame of lithium to appear reddish yellow.

5. If a small spectroscope is available time can often be saved by examining with it the solution before the addition of NaOH and Na_2HPO_4, for if the characteristic red line of lithium is absent, this procedure may be omitted. If present this procedure will serve to give an estimate of its quantity, which can hardly be formed from an ordinary spectroscopic examination.

Procedure 92.—To one-third of the solution (P. 91) (or to the filtrate from the Na_2HPO_4 precipitate (*P. 91*a*)), whose volume should not exceed 5 cc., add a few drops of acetic acid if the solution is not already acid, and an equal volume of $Na_3Co(NO_2)_6$ reagent. If no precipitate forms at once, let the mixture stand for at least fifteen minutes. Filter and wash the precipitate thoroughly with water. (Yellow precipitate, presence of *potassium.*)

Dissolve the precipitate or a portion of it in hot dilute HCl, evaporate to a few drops, dip a clean platinum into the solution, and introduce it into a colorless gas flame, viewing the flame through a sufficient thickness of blue cobalt glass to cut off sodium light. (Violet flame, presence of *potassium.*)

Notes.—1. To prepare the sodium cobaltinitrite reagent, dissolve 100 grams $NaNO_2$ in about 200 cc. water, add 60 cc. 30 per cent. acetic acid and 10 grams $Co(NO_3)_2.6H_2O$, let the mixture stand for a day or two, filter off any precipitate that is formed (such as $K_2NaCo(NO_2)_6.H_2O$ arising from the presence of potassium as an impurity in the reagents), and dilute the solution to 400 cc. For the chemical reactions involved, see Part III, P. 69, N. 1.

2. The presence of 0.3 mg. of potassium in 5 cc. of solution may be easily detected within 5 or 10 minutes and an even smaller amount on long standing. The yellow color of the precipitate is best seen on the filter after washing out the $Na_3Co(NO_2)_6$ thoroughly. The solution must not be alkaline when the $Na_3Co(NO_2)_6$ reagent is added, since $Co(OH)_3$ would then be precipitated. In the presence of an ammonium salt (containing even 0.5–1 mg. NH_4) a precipitate is obtained very similar in appearance to that obtained with potassium, but moderate amounts of the alkaline earth elements or of lithium do not interfere with the test. Ammonia may of course be tested for in the precipitate by warming a portion in a test with dilute NaOH solution, and noting the odor.

3. The flame test for sodium is so much more delicate than that for potassium that the yellow color due to a trace of sodium may completely obscure the color given by a moderate amount of potassium. A sufficient thickness of cobalt blue glass is used to absorb the yellow rays completely, and thus permit the violet rays due to potassium to be seen. Comparative experiments with known solutions ought always to be made unless the analyst is perfectly familiar with the appearance of the flames. If a spectroscope is used, the characteristic potassium line will be found near the red end of the spectrum.

Procedure 93.—In the absence of lithium (*P. 91*a*) or of much potassium (P. 92), test the remainder of the solution (P. 91) for sodium by P. 94.

If much potassium was found (and no lithium), add about 1 cc. H_2SO_4 (1.84), evaporate in a casserole and heat strongly until the white fumes cease to come off; let the mixture cool; add a few drops of water and 10 per cent. KOH solution until the solution is alkaline. Evaporate to about 2 cc., cool, filter or decant off the solution, wash the crystals with a few drops of water, and test the solution for sodium by P. 94.

*If lithium is present evaporate the solution to 2 cc. (or 5 cc. if much lithium is present); add 1 cc. NH_4OH (0.90) and 2–4 cc. 20 per cent. NH_4F solution; shake, and filter after a few minutes. To the filtrate add HCl, evaporate to dryness (in a platinum dish under a hood), heat to expel ammonium salts, add HCl and evaporate to dryness. Dissolve in a little water and treat the solution by P. 94, or by the preceding paragraph if much potassium is present.

Notes.—1. The presence of a large amount of potassium salt, as KCl or KNO_3, in P. 94 greatly decreases the delicacy of the test for sodium. The process here recommended for the removal of a large part of the potassium depends on the relatively slight solubility of K_2SO_4 (as compared with KCl or KNO_3), and on the fact that the saturated solution may be easily separated from the heavy crystals of K_2SO_4 either by decantation or by filtering through a small filter. In the presence of 300 mg. potassium as chloride 7 mg. of sodium may escape detection if the mixture is treated directly by P. 94, but the present process enables 2–3 mg. to be found. Unless the solution contains more than 50–100 mg. potassium, this treatment is unnecessary.

*2. Since even 2 mg. of lithium will interfere with the test for sodium in P. 94, the lithium must be removed before making this test. The precipitation as LiF is not complete, but if the directions are followed the filtrate will not contain more than 1 mg. of lithium. The process will not be satisfactory if the volume of the solution is too large or if too little NH_4F is used. If much sodium is present, some NaF will also be precipitated but the filtrate will contain 50–100 mg. of sodium if the volume is not less than 5 cc.

*3. As an alternative process for the separation of the alkali elements, the lithium may be first precipitated as fluoride and potassium and sodium tested for in separate portions of the filtrate. In this case, owing to the precipitation of NaF, a precipitate is almost always obtained with ammonium fluoride, which must be tested for lithium, *e. g.*, by dissolving in HCl, evaporating in a platinum dish, dissolving, and precipitating lithium as phosphate by *P. 91*a*. When LiF is precipitated as directed in the present procedure it is just possible to detect and confirm 1 mg. Li. If the volume is decreased in order to obtain a more delicate test, the amount of sodium that remains in solution is also greatly decreased. This alternative process has therefore no advantages over the one adopted.

*4. When only chlorides are present lithium may be conveniently separated from sodium (and potassium) by dissolving the lithium chloride in a mixture of equal volumes of absolute alcohol and ether. In this case the mixture is dissolved in HCl, evaporated to dryness, heated and cooled, and 5–10 cc. of the alcohol-ether solution added at once; the mixture is triturated with a pestle, filtered, and the residue washed with the alcohol-ether solution. By this process a small amount of lithium can be detected in the presence of a large amount of sodium and *vice versa*, but the method is not applicable in all cases, *e. g.*, when sulphates are present.

Procedure 94.—If the solution that is to be tested for sodium (P. 93) reacts acid with litmus paper, add 10 per cent. KOH solution drop by drop until it is neutral or slightly alkaline. Evaporate the solution to about 1 cc. and cool it. Add 1 to 2 cc. of the $K_2H_2Sb_2O_7$ reagent; pour the mixture at once into a test tube, and let it stand for at least half an hour, or better over night. (White crystalline precipitate, presence of *sodium.*)

Decant off the solution, wash the precipitate several times with water and dissolve it in a little HCl. Evaporate the solution to a few drops, and introduce a little of it on a platinum wire into a colorless gas flame. (Brilliant yellow flame, presence of *sodium.*)

Notes.—1. The dipotassium dihydrogen pyroantimonate reagent is prepared as follows: Add 2 grams of the best commercial salt to 100 cc. boiling water, boil for about one minute until nearly all the salt is dissolved, quickly cool the solution, add about 3 cc. 10 per cent. KOH solution, and filter. If a (flocculent) precipitate settles out on standing, decant off the clear solution. This reagent will usually keep for several months, but it should be tested frequently with a known solution of a pure sodium salt. When a pyroantimonate solution is made slightly acid, it decomposes rapidly with precipitation of metantimonic acid. The same reaction takes place slowly in neutral solutions, owing to hydrolysis.

2. In this test with the antimonate, if 2 cc. of the reagent are added to 1 cc. of solution, 2 mg. Na should give a distinct crystalline precipitate in less than 5 min., 1 mg. within 30 min., and a smaller amount on standing several hours. The precipitate is a heavy crystalline granular one and usually adheres in part to the glass, where it can be best seen by tilting the test tube. Although in a solution of a pure sodium salt 1 mg. of sodium is easily detected, yet in an actual analysis, owing to the presence of potassium salt and of certain substances that obscure the test, it is often difficult to detect less than 2 or 3 mg. Thus a distinct turbidity is produced by even 0.1 to 0.2 mg. of calcium, barium, or magnesium and by 1 to 2 mg. of aluminum. These light flocculent precipitates are, however, very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. These crystals may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle and decanting off the suspended, flocculent precipitate.

3. In the flame test the yellow color is to be regarded as a confirmation of the presence of an appreciable amount of sodium in the sample only when a brilliant, large, spreading flame is obtained. Owing to the delicacy of the test there is always sufficient sodium present to give a slight yellow color. The chief value of this test is in proving the absence of lithium, since the precipitate due to lithium alone is very similar in appearance to sodium pyroantimonate.

Test Analyses.

The following analyses were made to test the efficiency of the process. Analyses 184, 185, 187, 189, 193, 195 were made by Mr. A. B. Babcock, almost all of them as unknowns.

Analyses 182–205 were begun at P. 81.

T. A. No.	182.	183.	184.	185.	186-7.	188-9.
Ba............	500 S	500 S	500 S	500 S	500 S	500 S
Sr............	0 S	1 F[1]	3 F[1]	5 S–[1]	1 S	0 S
Ca............	0 S[2]	1 S	...	...	...	...
Mg............	0 S	1 S	...	...	...	...

T. A. No.	190.	191.	192.	193.	194-5.	196.
Ba	1 S	0 S	0 S	1 S	0 S	1 S
Sr	400 S	400 S	0 S	0 F^{3}	0 S	1 S
Ca	0 S^{2}	1 S	500 S	500 S	0 S^{2}	1 S
Mg	0 S	1 S	0 S	1 S	400 S	400 S

T. A. No.	197.	198.	199.	200-1.	202.	203.	204.	205.
Sr	...	...	...	...	...	...	200	200
Mg	400	400	400	5	5	5	...	...
Li	0 S	1 S–^{6}	1 S–^{6}	...	...	...	0 S	1 S
K	0 S	1 F^{5}	1 S–	0 S	2 S	1 S	0 S	1 S
Na	0 S^{4}	2 F^{5}	2 D	0 S^{4}	4 S	2 S^{7}	0 S	2 F^{6}

Analyses 206–213 were begun at *P. 91*a*. In each case the whole solution was used in making each test, instead of only one-third as directed in P. 91.

T. A. No.	206.	207.	208.	209.	210.	211.	212.	213.
Li	0 S	0 S	1 S	0.3 S^{9}	0 S	0.3 S^{9}	100 S	100 S
K	0 S^{8}	0.5 S	0 S^{8}	...	170 S	170	0 S	0.5 S
Na	300	300	200	300	...	...	....	...

Analyses 214–221 were begun at P. 93. The whole solution was used in testing for sodium, instead of two-thirds as directed in P. 91.

T. A. No.	214.	215.	216.	217.	218.	219.	220.	221.
Li	...	...	...	...	...	100	100	100
K	300	300	200	300	300	...	...	...
Na	0 S	3 S	2 S^{7}	2 F	1 F	0 S	2 S	1 F

Notes.—1. In analyses 183–5 strontium was carried down with $BaCrO_4$ in P. 82 because the K_2CrO_4 reagent was added all at once in precipitating $BaCrO_4$, instead of slowly as directed.

2. In testing for calcium in T. A. 182, 190, 194, and 195, very small precipitates of calcium oxalate were obtained, which were estimated to contain only 0.1 to 0.2 mg. Ca. The precipitates obtained in T. A. 183, 191, and 196 when 1 mg. Ca was present were much larger.

3. In T. A. 193 several mg. Ca were precipitated as chromate in P. 84, probably because a little too much alcohol was added. The precipitate was filtered off and dissolved in HNO_3; 10 cc. 30 per cent. acetic acid were added, and NH_4OH to precipitate $Cr(OH)_3$; P. 84 was repeated. Less than 0.5 mg. Sr was found, which was present as impurity in the calcium salt. The calcium used in T. A. 192 was first freed from strontium by means of P. 84.

4. In the test for sodium in T. A. 197 and 200, small flocculent precipitates were obtained corresponding to 0.2–0.3 mg. Mg. In T. A. 201 a perfect blank was obtained.

5. The $Na_3Co(NO_2)_6$ reagent used in testing for potassium in T. A. 198, and the $K_2H_2Sb_2O_7$ reagent used in testing for sodium in T. A. 198 (and possibly 205), were not properly made, and were not used in the other experiments.

6. In T. A. 198–9 lithium was confirmed by means of a small spectroscope.

7. The sodium tests in T. A. 203 and 216 were distinct after standing several hours.

8. In T. A. 206 and 208 small precipitates corresponding to 0.1 to 0.2 mg. K separated, owing to presence of potassium in the NaOH reagent used in *P. 91*a*.

9. In T. A. 209 and 211 the precipitate of Li_3PO_4 did not form until the second portion of alcohol was added and the solution boiled, but the precipitate was then very distinct.

These analyses, together with the experiments on the delicacy of the separate tests, show that 1 mg. of each element except sodium can be detected in any combination; also that 2 mg. of sodium (in the sample) can be found in most simple combinations, and 3 mg. in every case except in the presence of a very large amount of potassium (T. A. 217).

Confirmatory Experiments and References.

P. 81, N. 3-5: *Precipitation of Alkaline Earth Elements by Ammonium Carbonate.*—For the precipitation of $MgCO_3.(NH_4)_2CO_3.4H_2O$ see Gooch and Eddy.[1]

Varying small amounts of Ca, Sr, Ba and Mg as nitrates, in separate experiments, were dissolved in 4 cc. HCl (1.12); the solutions were neutralized with NH_4OH and diluted (or evaporated) to 10 cc.; 30 cc. of the $(NH_4)_2CO_3$ reagent (Note 2), and finally 30 cc. alcohol were added; the mixtures were shaken frequently and examined at intervals, with the following results:

0.5 mg.	Ca.	Sr.	Ba.	Mg.
Solution distinctly turbid in	5	5	5–10	15–20 min.
Very distinct test in..................	10	15–20	20–30	30 min.

With 1 mg. the same results were obtained more quickly in each case; with 2 mg. a distinct test was obtained in less than 5 min. in each case. Even with 0.3 mg. a better test was obtained in half an hour than in a blank experiment (with no magnesium) over night.

The above experiments were repeated with 500 mg. of each element; the precipitates were thick and gelatinous but became more crystalline when the mixtures were shaken. The precipitates were filtered off after half an hour, and the filtrates allowed to stand; no precipitate separated in any case. Each filtrate was finally evaporated almost to dryness and tested—in the case of calcium, with NH_4OH and $(NH_4)_2C_2O_4$, strontium and barium with H_2SO_4, and magnesium with NH_4OH, Na_2HPO_4 and alcohol: no calcium was found, less than 0.1 mg. Ba or Mg and less than 0.2 mg. Sr^-. The experiment with 500 mg. Mg was repeated, except that the mixture was filtered after 15 minutes; a small precipitate separated in the filtrate on standing which was estimated to contain 1 to 2 mg. Mg.

To determine the effect of shaking, the experiment with 500 mg. Mg was repeated, except that the mixture was shaken only once at the beginning of the experiment; the mixture was filtered after half an hour, and the filtrate allowed to stand: a precipitate separated corresponding to 2 or 3 mg. Mg. It was also observed in the case of each element that the precipitates became crystalline more rapidly and were much more easily filtered off if the mixtures were shaken frequently.

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[1] *Am. J. Sci.* [4], **25**, 444 (1908). *Z. anorg. Chem.*, **59**, 427 (1908).

To determine the effect of the addition of alcohol, the experiment, with 500 mg. Mg, was repeated several times except that 10 to 20 cc. alcohol were added instead of 30 cc. On filtering after half an hour and allowing the filtrates to stand over night, precipitates formed corresponding to several mg. Mg, the amounts increasing rapidly as the amount of alcohol decreased.—The experiments with 0.5 to 2 mg. of each element were repeated, except that no alcohol was added. With barium the precipitates formed as quickly as in the presence of alcohol, and with strontium almost as quickly, but in the experiments with 0.5 and 1.0 mg. Ca or Mg no precipitates were obtained.

Experiments with 0.5 and 1.0 mg. of each element to determine the effect of dilution showed that the solutions became turbid somewhat less quickly when the volume of the solution before adding the $(NH_4)_2CO_3$ reagent was 20 cc. instead of 10 cc. The difference was most marked in the case of magnesium and 0.5 mg. might easily escape detection if the volume were still greater.

A large number of experiments similar to those described above were performed with another $(NH_4)_2CO_3$ reagent containing in 30 cc. about 5 g. ammonium carbonate and 20 cc. NH_4OH (0.90), *i. e.*, less $(NH_4)_2CO_3$ and more NH_4OH than the regular reagent: the results were almost identical.

The following experiments were performed to determine the effect of heating. 20 mg. Mg as $MgCl_2$ were dissolved in 4 cc. HCl (1.12); the solution was neutralized with NH_4OH and diluted to 10 cc.; 30 cc. of a solution containing 10 cc. NH_4OH (0.90) and 3 g. $(NH_4)_2CO_3$ were added. A large precipitate appeared quickly. After several minutes the mixture was heated gently; the precipitate dissolved and a clear solution resulted at 60°-70°. The mixture was cooled rapidly to room temperature, a large precipitate separated, showing that the magnesium is much more completely precipitated at low temperatures. After half an hour the precipitate was filtered off, and Na_2HPO_4 and alcohol added to the filtrate. A precipitate separated that was estimated to contain about 4 mg. Mg.—In separate experiments 1 and 2 mg. of Ca, Sr, and Ba as chlorides were dissolved in HCl (1.12); the solutions were neutralized with NH_4OH (0.90) and an excess of 10 cc. added; the solutions were diluted to 40 cc. and 3 g. powdered $(NH_4)CO_3$ were added. The mixtures were heated just to boiling, and filtered after 10 minutes; the amount of unprecipitated metal in the filtrate was estimated as described above. In each case distinct precipitates of the carbonates were obtained which filtered readily, and the filtrates were estimated to contain less than 0.1 mg. Ba, 0.2 mg. Sr, and 0.1 mg. Ca.—These experiments were repeated except that to 10 cc. of each solution were added 30 cc. of a solution containing 20 cc. NH_4OH (0.90) and 5 g. $(NH_4)_2CO_3$; no alcohol was added, and the mixtures were boiled vigorously in flasks for 1 minute. The results were almost the same as before.—The last experiment was repeated with 500 mg. Ca and with 500 mg. Ba. In each case the filtrate contained not more than 0.1 mg. of the element, and the precipitate was more granular and more readily filtered than when the carbonate was precipitated in the cold in the presence of alcohol.

1 mg. Ba as chloride was dissolved in 4 cc. HCl (1.12), the solution was neutralized with NH_4OH (0.96), and an excess of only 4 cc. added; after dilution to 40 cc., 3 g. powdered $(NH_4)_2CO_3$ were added, the mixture was heated to boiling and allowed to stand. The solutions remained clear for at least half an hour.—The experiment was repeated with 2 mg. Ba. The solution remained clear for a minute or two after boiling, and then a very small precipitate formed. On standing for a day or two, however, nearly all the barium precipitated.—These results, together with those in the preceding section, show that the precipitation of barium is greatly accelerated by the presence of a large excess of NH_4OH.

1, 2, 3, and 5 mg. Mg as $MgCl_2$ were dissolved separately in 4 cc. HCl (1.12); the solutions were neutralized with NH_4OH and diluted to 10 cc.; 30 cc. of a solution containing 10 cc. NH_4OH (0.90) and 5 grams $(NH_4)_2CO_3$ were added; the mixtures were shaken frequently. The experiments were repeated with twice as much free NH_4OH in the same volume. The results showed that precipitates formed more quickly in the solutions containing more magnesium, but that there was very little difference between the two series of experiments. In another series of experiments with much less NH_4OH, the magnesium precipitates formed much less rapidly. In a series of experiments with 20 cc. NH_4OH (0.90) and 3 g. $(NH_4)_2CO_3$ the precipitation of the magnesium took place much more slowly than in the experiments with 5 g. $(NH_4)_2CO_3$ and the filtrates after 16 hours contained 0.5 to 1.0 mg. Mg instead of 0.1 to 0.2 mg. Therefore, the most favorable conditions for the complete and rapid precipitation of magnesium are to have the solution very concentrated with respect to both NH_4OH and $(NH_4)_2CO_3$. As shown above, the addition of alcohol enables 0.5 mg. Mg to be detected in half an hour, but this result depends also upon the presence of large amounts of NH_4OH and of $(NH_4)_2CO_3$.

P. 81, N. 6. *Precipitation of Lithium by Ammonium Carbonate.*—150 mg. Li as chloride were treated by P. 81 exactly as described in the first experiments under N. 3–4 above. After half an hour the solution was perfectly clear and there was no precipitate; after 5 hours there was a precipitate, which, however, was smaller than that obtained with 0.5 mg. magnesium. The experiment was repeated with 200 mg. Li. A granular precipitate separated very slowly; it was very small in 30 min., but after 24 hours it was estimated to contain 20 to 40 mg. Li.

Behavior of Lithium in the Analysis of the Alkaline Earth Group.—100 mg. Li as LiCl were dissolved in acetic acid and treated by P. 82–8. No precipitate whatever was obtained in the procedures for the detection of Ba, Sr, and Mg, and only a very small one in that for the detection of Ca, which corresponded to 0.2–0.4 mg. Ca, and was doubtless due to the presence of calcium as an impurity.

P. 82, N. 1-3. *Solubility of Barium and Strontium Chromates in Water.*—According to the conductivity measurements of Kohlrausch and Rose,[1] the solubility of $BaCrO_4$ is 1.5×10^{-5} mols per liter at 18° and 2.0×10^{-5} at 25°. Meschezerski[2] found that its solubility at the boiling point of water is 1.7×10^{-4} mols per liter; also that in the precipitation of $BaCrO_4$ foreign substances are carried down with the precipitate. R. Fresenius[3] collected earlier data, and also showed experimentally that the solubility of $BaCrO_4$ is somewhat increased by ammonium salts, and in a marked degree by acetic acid. He described a method of separating barium and strontium by precipitating $BaCrO_4$, but found that two precipitations were necessary in order to obtain the barium free from strontium.

R. Fresenius[4] determined the solubility of $SrCrO_4$ at 15° to be 5.9×10^{-3} mols per liter; he found that the presence of ammonium salts increased the solubility, but to a much less extent than dilute acetic acid.

The Separation of Barium and Strontium.—400 mg. Sr as nitrate and a mixture of 400 mg. Sr and 1 mg. Ba as nitrates were dissolved separately in 10 cc. 30 per cent. acetic acid, and treated by P. 82. With strontium alone a perfect blank was obtained in the K_2CrO_4 test for barium, while in the experiment with 1 mg. Ba a distinct precipitate was obtained. In the latter case the confirmatory flame test showed the presence of a little strontium with the barium, but it was possible to distinguish the green color due to barium; the presence of barium was more easily proved by means of a small spectroscope.

[1] *Z. physik. Chem.*, **12,** 241 (1893).

[2] *Z. anal. Chem.*, **21,** 399 (1882).

[3] *Ibid.*, **29,** 413–9 (1890).

[4] *Loc. cit.*, *p.* 419.

To determine the effect of long-continued boiling, the experiment with 400 mg. Sr was repeated; the clear solution that resulted was boiled vigorously for two minutes; a granular precipitate of $SrCrO_4$ began to separate and increased somewhat on continued boiling. The experiment was repeated with 200 mg. Sr. No precipitate separated even on boiling for 10 minutes.

A mixture of 500 mg. Ba and 1 mg. Sr was dissolved in 10 cc. 30 per cent. acetic acid and treated by P. 82, the first 2 to 3 cc. K_2CrO_4 solution were added a few drops at a time, and the mixture was heated and shaken frequently; the remainder of the K_2CrO_4 solution was added quickly; the filtrate was tested for strontium by P. 84; a distinct precipitate of $SrCrO_4$ was obtained, which was estimated to contain at least 0.5 mg. Sr.—The experiment was repeated with 500 mg. Ba mixed with 1.3, and 5 mg. Sr, respectively, but the 10 cc. portion of K_2CrO_4 solution was added all at once instead of very slowly; the $BaCrO_4$ ran through the filter in each experiment, and to obtain a clear filtrate it was necessary to filter several times through the same filter, or to boil the turbid filtrate for a minute or two. The clear filtrates were finally tested for strontium by P. 84. In each of several experiments with 1 mg. Sr no precipitate of $SrCrO_4$ formed; in the experiments with 3 mg., the $SrCrO_4$ precipitate was estimated to contain from 0.1 to 0.5 mg. Sr; and in the case of 5 mg. the precipitate contained about 1.5 mg. Sr.—Therefore, if the K_2CrO_4 reagent is added quickly in precipitating barium, the $BaCrO_4$ precipitate runs through the filter, and as much as 3 mg. Sr may be carried down almost completely by 500 mg. Ba in P. 82.

Effect of Varying the Excess of Acetic Acid and of Chromate.—In each of a series of experiments, 0.5 mg. Ba as nitrate was dissolved in 10 cc. 30 per cent. acetic acid, and treated by P. 82 and 83, except that the excess of 30 per cent. acetic acid added to the neutral solution in P. 82 was varied. With 2 cc. and 4 cc. acetic acid the tests on the filter after washing out the K_2CrO_4 were similar to that obtained with 3 cc. acid, and the flame tests were distinct; with 6 cc. acetic acid the yellow precipitate on the filter could scarcely be distinguished but a small flame test was obtained; with a larger amount of acetic acid the tests failed.—The experiments were repeated with 1 mg. Ba. With 10 cc. acetic acid faint tests for barium were obtained; with 15 cc. the tests failed.—A few quantitative experiments were performed with acetic acid alone, without neutralizing with NH_4OH as in the preceding experiments: the precipitation of barium was quantitative with 2 or 3 cc. acetic acid, *i. e.*, with the amount equivalent to the K_2CrO_4 present, but the solubility of $BaCrO_4$ increased rapidly when more acetic acid was used.

The above series of experiments with 1 mg. Ba was repeated, except that 5 cc. 20 per cent. K_2CrO_4 (instead of 10 cc.) were used: distinct tests for barium were obtained when 3 cc. acetic acid were added after neutralization, but the precipitation was not quite complete; the tests were very poor with 5 cc. excess acetic acid and failed with 6 cc., showing that the precipitation is less complete and that acetic acid has a greater influence when the amount of chromate is decreased.

200 mg. Sr as nitrate and 10 cc. 30 per cent. acetic acid were treated by P. 82, except that only 1 cc. acetic acid was added after neutralizing with NH_4OH: a precipitate of $SrCrO_4$ separated corresponding to about 20 mg. Sr. The experiment was repeated with 400 mg. Sr: a very large precipitate separated—400 mg. Sr as nitrate and 10 cc. 30 per cent. acetic acid were treated by P. 82, except that an excess of only 2 cc. acetic acid was added. A precipitate of $SrCrO_4$ separated which was estimated to contain about 10 mg. Sr.—The experiments with 400 mg. Sr were repeated with 3 and with 4 cc. excess acetic acid. No precipitate separated in either experiment (except on boiling the solutions for a minute or two).—Therefore strontium, when present alone, will precipitate in this procedure if too little acetic acid is added.

State of Chromic Acid in Solution.—See article by Sherrill.[1]

P. 84, N. 1. *Solubility of $SrCrO_4$, $CaCrO_4$, and $MgCrO_4$ in Water and in Mixtures of Alcohol and Water.*—W. Fresenius and F. Ruppert[2] found the solubility of $SrCrO_4$ in 29 and 53 volume per cent. alcohol at room temperature to be 0.5×10^{-4} and 1.0×10^{-4} mols per liter. The solubility of calcium chromate in 29 and 53 volume per cent. alcohol was found to be 7.8×10^{-2} and 5.6×10^{-2} mols per liter.

Mylius and Wrachem[3] prepared several different chromates, $CaCrO_4$, $CaCrO_4.1/2H_2O$, $CaCrO_4.H_2O$, $\alpha CaCrO_4.2H_2O$, and $\beta CaCrO_4.2H_2O$; and found their solubilities in water to increase in the order given, and to decrease with rising temperature. Since the solubility of $SrCrO_4$ increases with rising temperature, the separation of calcium and strontium will be more satisfactory at room temperature, as recommended in P. 84, than at 70°, as recommended by W. Fresenius and F. Ruppert. We have found that a precipitate sometimes separates in P. 84 when a very large amount of calcium is present, and increases in amount on standing; this indicates that the solution first obtained was supersaturated with respect to one or more of these chromates.

According to Mylius and Funk,[4] the solubility of $MgCrO_4.7H_2O$ at 18° is 42.0 grams $MgCrO_4$ in 100 grams of solution (sp. gr. 1.422). Schweitzer[5] found the solubility of the double salt $MgCrO_4.K_2CrO_4.2H_2O$ to be 28.2 grams in 100 grams water at 20°, which seems to indicate that the double salt is more likely to separate in P. 84, than is $MgCrO_4.7H_2O$.

Separation of $SrCrO_4$ and $CaCrO_4$ by Means of Chromate and Alcohol.—W. Fresenius and F. Ruppert determined the difference in solubility of $SrCrO_4$ and $CaCrO_4$ in water and on adding alcohol (see preceding section) and first suggested a method based on it for use in qualitative analysis: they add K_2CrO_4 to a fairly dilute solution of the chlorides, free from HCl, heat to about 70°, and then add a quantity of alcohol equal to 1/3 the volume of the solution. The authors state that the precipitation of strontium is not quite complete even at the point where a moderately large amount of calcium begins to precipitate. They did not introduce ammonium salts because the solubility of $SrCrO_4$ was then somewhat increased and they worked at 70° because the precipitation of $SrCrO_4$ was more rapid than at room temperature.

The method of separation adopted by us is essentially the same as that described by Caron and Raquet.[6] A large number of experiments were performed, however, to determine the best conditions for making the separation. The presence of ammonia and ammonium salts appears to have a greater influence on the solubility of $CaCrO_4$ than on that of $SrCrO_4$, and thus makes the separation more satisfactory.

Precipitation of $SrCrO_4$ in P. 84.—1, 0.5, 0.3 and 0.2 mg. Sr as nitrate were treated in separate experiments by P. 84, 10 cc. 20 per cent. K_2CrO_4 and 10 cc. 30 per cent. acetic acid being first added in each case: in the experiments with 1 and 0.5 mg. the mixture became turbid at once on adding 50 cc. alcohol to the ammoniacal solution; in the two remaining experiments the mixtures became distinctly turbid on standing several minutes. Therefore, the test is a delicate one, and the precipitation must be nearly complete.

To 500 mg. Sr as nitrate were added 10 cc. 30 per cent. acetic acid and 10 cc. 20 per cent. K_2CrO_4 solutions (*i. e.*, an excess of about 3.7 cc.) and the mixture was treated by the first paragraph of P. 84: a very large precipitate of $SrCrO_4$ separated. This

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[1] *J. Am. Chem. Soc.*, **29**, 1641 (1907)

[2] *Z. anal. Chem.*, **30**, 677 (1891).

[3] Cf. Seidell, *Solubilities*, 90.

[4] *Ber.*, **30**, 1718 (1897).

[5] Cf. Seidell, *Solubilities*, 181.

[6] *Bull. soc. chim.* [3], **35**, 1061–9 (1906).

was filtered off and the filtrate treated by the second paragraph of the procedure, 5 cc. more K_2CrO_4 solution and 10 cc. alcohol being added: a precipitate separated at once which was estimated to contain about 20 mg. of strontium. The filtrate was treated again in the same way: no precipitate separated on long standing, showing that even 500 mg. of strontium are completely precipitated in the procedure.

Precipitation of K_2CrO_4 in P. 84.—A mixture of 10 cc. 20 per cent. K_2CrO_4 solution and 10 cc. 30 per cent. acetic acid was treated by P. 84, the alcohol being added slowly: 50 cc. alcohol produced no precipitate and the solution was perfectly clear after the addition of 20 cc. more alcohol and shaking; 5 cc. more produced a small precipitate and on the addition of another 5 cc. portion, making 80 cc. in all, the precipitate was large. It dissolved readily on washing.—The experiment was repeated except that the alcohol (50 cc.) was added quickly: a precipitate appeared as the alcohol was poured into the solution, but disappeared on shaking the mixture.—The experiment was repeated with 20 cc. K_2CrO_4 solution instead of 10 cc., a permanent precipitate of K_2CrO_4 formed with 40 cc. alcohol, but not with 35 cc.

Behavior of Calcium and Magnesium towards Potassium Chromate.—500 mg. Ca as pure $Ca(NO_3)_2$, 10 cc. 20 per cent. K_2CrO_4 solution, and 10 cc. 30 per cent. acetic acid were treated by P. 84, 50 cc. alcohol being added; no precipitate separated in half an hour, and only an insignificant one on standing over night. After pouring through a filter, 5 cc. more K_2CrO_4 solution and 10 cc. alcohol were added: a precipitate separated slowly, which after standing several hours corresponded to only several milligrams of calcium.—The experiment was repeated, except that after the addition of the extra K_2CrO_4 and alcohol the mixture was allowed to stand several days: the precipitate separated slowly as before, but was large after several days.

400 mg. Mg as nitrate, 10 cc. 20 per cent. K_2CrO_4 solution, and 10 cc. 30 per cent. acetic acid were treated by P. 84: the solution remained clear on adding 50 cc. alcohol, but a very small crystalline precipitate separated out on standing several hours, which was very different in appearance from $SrCrO_4$.

P. 85, N. 1–2. *Action of a Mixture of Sodium Oxalate and Carbonate on Calcium and Strontium Solutions.*—In a series of experiments 5 mg. Ca as nitrate were added to varying amounts of a 10 per cent. Na_2CO_3 solution; 30 cc. 3 per cent. $Na_2C_2O_4$ solution were added, and the mixture boiled for 5 minutes. The precipitate was filtered off, washed well, and a 5 cc. portion of dilute acetic acid was poured three times through the filter; the residue was dissolved in dilute HCl. The amount of calcium in each solution was estimated by adding NH_4OH and $(NH_4)_2C_2O_4$ and boiling. The results are given in the following table:

Amount of 10 per cent. Na_2CO_3 used. . .	2	4	5	6 cc.
Amount of calcium in $C_2H_4O_2$	0.05–0.2	$<$0.1	1	4.5–5.0 mg.
Amount of calcium in HCl.	4.9	5.0	4	0.0–0.5 mg.

$CaC_2O_4.H_2O$ was found to be practically insoluble in cold dilute acetic acid; therefore, these results show the amounts of calcium present as carbonate and oxalate respectively. The test with $(NH_4)_2C_2O_4$ enabled 0.05 mg. Ca to be detected.

Similar experiments were tried with 5 mg. Sr; 30 cc. 3 per cent. $Na_2C_2O_4$ were first added and then in separate experiments 1 cc. and 2 cc. 10 per cent. Na_2CO_3: in such case all the strontium dissolved in the acetic acid, showing that the strontium oxalate was converted into carbonate in this treatment. SrC_2O_4 was found to be nearly insoluble in acetic acid, and the test with $(NH_4)_2C_2O_4$ scarcely enabled 0.5 mg. Sr to be detected.

Effect of the Presence of Barium Chromate.—To 5 mg. Ba as nitrate were added in succession 20 mg. K_2CrO_4 dissolved in a little water, 30 cc. 3 per cent. $Na_2C_2O_4$ and 2 cc. 10 per cent. Na_2CO_3; the mixture was boiled for 5 minutes and filtered and the precipitate washed: the precipitate was yellow, showing the presence of some $BaCrO_4$. 5 cc. dilute acetic acid was poured through the filter, K_2CrO_4 was added and the mixture boiled: a precipitate corresponding to about 3 mg. Ba resulted.—The experiment was repeated with 50 and with 100 mg. K_2CrO_4: not more than 0.5 mg. Ba dissolved in the acetic acid, showing that in these experiments no $BaCrO_4$ was converted into carbonate, as in the preceding experiment with less K_2CrO_4.

P. 85, N. 3. *Delicacy of Test for Strontium.*—0.5 and 1.0 mg. Sr as nitrate were treated by P. 85: satisfactory tests were obtained in each case.—The experiments were repeated except that the strontium was first precipitated as chromate by P. 84: the results were the same.—In an experiment with no strontium a perfect blank test was obtained. The test with ammonium carbonate enables 0.3 mg. Sr in the acetic acid solution to be easily detected.

Effect of the Presence of Calcium and Magnesium.—5 mg. Ca as nitrate were treated by P. 85, the mixture being boiled for 5 minutes: a perfect blank was obtained.—The experiment was repeated with 10 mg., the mixture being boiled 5 minutes: the result was the same.—The experiment was repeated three times with 30 mg. and once with 50 mg. Ca: in two of these experiments good blank tests were obtained, but in the third and in the experiment with 50 mg. a small turbidity resulted, corresponding to about 0.3–0.4 mg. Ca.—No test was obtained with $(NH_4)_2CO_3$ when the acetic acid solution contained 0.2 mg. Ca. The results obtained above, when calcium was tested for in the acetic acid solution with $(NH_4)_2C_2O_4$, show that this solution always contained 0.05 to 0.2 mg. Ca.

Fifty mg. Mg as nitrate were treated by P. 85: a small gelatinous precipitate of $Mg(OH)_2$, corresponding to 5 to 10 mg. Mg, was obtained which dissolved in the acetic acid; no precipitate formed in the ammonium carbonate solution in several hours, but a small crystalline one separated out over night.

P. 86, N. 1. *Solubility of $CaC_2O_4.H_2O$ in Water.*—See A. F. Holleman,[1] Kohlrausch and Rose,[2] Richards, McCaffrey and Bisbee.[3] According to the last-named authors the solubility is 4.7×10^{-5}, 6.5×10^{-5}, and 9.6×10^{-5} mols per liter at 25°, 50° and 95° respectively.

Solubility of $MgC_2O_4.2H_2O$.—According to the conductivity measurements of Kohlrausch,[4] the solubility at 18° is 2.6×10^{-3} mols per liter.

Separation of Calcium from Magnesium by Ammonium Oxalate.—400 mg. Mg as chloride were dissolved in 10 cc. 30 per cent. acetic acid; the solution was neutralized with NH_4OH (0.90) and an excess of 3 cc. added; the mixture was diluted to 250 cc., 10 cc. 20 per cent. K_2CrO_4 solution and 50 cc. alcohol were added making the total volume 310 cc.; the mixture was heated to boiling and 20 cc. 4 per cent. $(NH_4)_2C_2O_4.H_2O$ solution added: a small precipitate corresponding to about 0.5 mg. Ca formed. This was filtered off, 15 cc. more oxalate solution were added and the mixture was boiled: no more precipitate separated.—The experiment was repeated except that 1.0 mg. Ca as nitrate was also added: a larger precipitate separated than in the former case. This was filtered off and treated by P. 87: a precipitate of $CaSO_4$ separated at once on adding alcohol.

The experiment with 400 mg. Mg was repeated, except that the total volume of the solution was 210 instead of 310 cc.: a large precipitate separated on cooling.—This experiment was repeated with 300 mg. Mg, the total volume being 210 cc.: the hot solution was clear after adding the ammonium oxalate, but a small precipitate separated

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[1] *Z. physik. Chem.*, **12**, 129 (1893).

[2] *Ibid.*, **12**, 241 (1893).

[3] *Z. anorg. Chem.*, **28**, 85 (1901).

[4] *Z. physik. Chem.*, **50**, 356 (1905).

on cooling; this precipitate dissolved when the mixture was heated to about 70°, but separated again on cooling, thus showing that the solubility of the magnesium precipitate increases rapidly with the temperature.—The experiment was repeated with 200 mg. Mg, the volume being 200 cc.; no precipitate separated even on long standing at room temperature.—These experiments show that the volume should not be less than 300 cc. when much magnesium is present, but that the volume may be much smaller if the amount of magnesium is small.

P. 87, N. 1. *Solubility of $CaSO_4.2H_2O$.*—For the solubility in water at temperatures between 0° and 100° see Hulett and Allen.[1] For the solubility in H_2SO_4 solutions see Cameron and Breazeale.[2] The solubility in water in mols per liter at 25° is 0.0153, and there is a maximum solubility of 0.0208 mol per liter in an acid containing 75 g. H_2SO_4 per liter. With rising temperature the solubility in H_2SO_4 increases and the maximum solubility is in more concentrated solutions. The laboratory acid of spec. grav. 1.2 contains 328 g. H_2SO_4 per liter, and the solubility of $CaSO_4$ in it is over half the maximum solubility.

P. 87, N. 2. *Behavior of Strontium or Magnesium in the Confirmatory Test for Calcium.*—Ten mg. Sr as nitrate were precipitated as oxalate by adding NH_4OH, $(NH_4)_2C_2O_4$ and heating; the mixture was filtered and the precipitate washed twice with water. A 5 cc. portion of H_2SO_4 (1.20) was poured repeatedly through the filter, and finally 15 cc. 95 per cent. alcohol were added to the solution: the mixtures became turbid at once; after settling, the precipitates corresponded in amount to that obtained with 0.2–0.3 mg. Ca.—The experiment was repeated with 2 mg. Sr as nitrate, which was added directly to 5 cc. H_2SO_4, various concentrations of H_2SO_4 being used; from 1 vol. H_2SO_4 (1.20) in 10 cc. to H_2SO_4 (1.20) in each case the result was nearly the same as before.

50 mg. Mg as $MgCl_2$ were dissolved in 5 cc. H_2SO_4 (1.05) and 15 cc. alcohol were added: no precipitate separated, even on long standing.

P. 88, N. 1. *The Precipitation of Magnesium by Phosphate.*—In each of a series of experiments 0.5 mg. Mg as $Mg(NO_3)_2$ was dissolved in 10 cc. 30 per cent. acetic acid, 10 cc. 20 per cent. K_2CrO_4 solution were added, the solution was neutralized with NH_4OH and diluted to 250 cc. 50 cc. alcohol and varying amounts of NH_4OH (0.90) and of 7 per cent. $Na_2HPO_4.12H_2O$ solution were added and the mixture shaken. The following table shows the time in which the solution became turbid.

	No. cc. 7 per cent. $Na_2HPO_4.12H_2O$ added.		
Excess NH_4OH (0.90).	10.	20.	30.
3 cc.	15 min.	15 min.	15 min.
13 cc.	7 min.	3 min.	3 min.
30 cc.	. .	2 min.	2 min.

In each case the turbidity became more distinct in a few minutes and a crystalline precipitate settled out in 1 to 1½ hours. These experiments show that the presence of a considerable excess of NH_4OH makes the precipitation more rapid.

The experiment with 13 cc. excess NH_4OH (0.90) and 20 cc. 7 per cent. $Na_2HPO_4.12H_2O$ was repeated with 0.3, 0.2, 0.1 and 0.0 mg. Mg respectively: in the experiment with 0.3 mg. the solution became turbid in 10 minutes, the test was very distinct in 15 minutes and a crystalline precipitate collected within 1½ hours; with 0.2 mg. a slight turbidity appeared in 15 minutes, the test was fairly distinct in 30 minutes and a small precipitate had collected within 1½ hours; with 0.1 mg. no turbidity could be seen but a minute precipitate separated in 2 hours; in the blank experiment there was no turbidity and no precipitate separated in several hours.

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[1] THIS JOURNAL, 24, 674 (1902).

[2] *J. Physic. Chem.*, **7**, 574 (1903).

Precipitation of Calcium as Phosphate.—The last experiment was repeated with 2 and with 5 mg Ca as nitrate: the solution became turbid almost at once in the experiment with 5 mg., and slightly turbid after about one hour in the experiment with 2 mg.

***P. 91*a*, N. 2.** *Precipitation of Lithium as Phosphate.*—To determine the delicacy of the test, 0.3 and 0.5 mg. Li as LiCl were dissolved separately in 3 cc. water; 0.5 cc. 10 per cent. NaOH solution and 1 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution were added; the mixture was heated to boiling in a large test-tube, 1 cc. alcohol was added, and the mixture boiled: a white precipitate formed almost at once.—The experiment was repeated with 0.2 mg. Li: even after boiling off a large part of the alcohol the solution was almost clear, but on adding a second portion of alcohol and again boiling a very distinct precipitate was obtained.—A blank experiment was made without adding any lithium: a clear solution was obtained even after adding alcohol and boiling it off four times.—The precipitates obtained in these experiments were filtered off, washed thoroughly with cold NH_4OH (0.96), and dissolved in dilute HCl; the solutions were evaporated to about 1 cc., and the color imparted to the flame was tried: the red color was easily seen in the experiment with 0.5 mg. Li, but was not very distinct in that with 0.3 mg. Li, owing to the yellow sodium flame. By means of a spectroscope, however, lithium was easily detected in both cases.

To determine the effect of the presence of alcohol, the experiment was repeated with 1 and with 2 mg. Li, except that no alcohol was added; the test-tube was heated to boiling and then placed in a steam bath near 100°: with 2 mg. a precipitate appeared on heating, but with 1 mg. none appeared in 10 minutes.

Experiments with varying amounts of NaOH and Na_2HPO_4 indicated that the test was most delicate when an excess of 0.3 to 0.5 cc. of the 10 per cent. NaOH solution and from 1 to 2 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution were used.

P. 92, N. 1–2. *Test for Potassium with Sodium Cobaltinitrite.*—For the composition of the precipitate $K_2NaCo(NO_2)_6H_2O$ see Adie and Wood,[1] and Drushel.[2]

0.3 and 0.5 mg. K as KCl were dissolved separately in 5 cc. water and 5 cc. of $Na_3Co(NO_2)_6$ reagent (two days old) added: the solution became turbid within 1 to 4 minutes, and precipitates settled out quickly.—These were filtered off and washed with water: the yellow precipitates were easily seen on the white filter.—The experiment was repeated with 0.2 mg. K: in 20–30 minutes the solution was slightly turbid, and the precipitate began to settle out in about two hours.—The experiment was repeated with 0.1 mg. K: after two hours the solution was clear, but a small precipitate settled out in 6 to 10 hours.—A blank experiment was made, without adding any potassium: the solution remained clear for two days.

To determine the effect of the age of the reagent, the experiments with 0.3 and 0.5 mg. K were repeated, except that an old reagent was used, which had been kept in a stoppered bottle for four months: the results were the same.

To determine the effect of the presence of acetic acid, separate 0.5 mg. portions of K as KCl were dissolved in 5 cc. of solution containing respectively 0, 0.5, 1.0, and 2.5 cc. 30 per cent. acetic acid, and 5 cc. of the reagent added: in each case the solution became distinctly turbid within 1 minute.—The experiments were repeated with 0.3 mg. K: each solution became turbid in less than 5 minutes.—Therefore the presence of acetic acid does not decrease the delicacy of the test.

Behavior of $Na_3Co(NO_2)_6$ towards Various Substances.—2 mg. NH_4 as NH_4NO_3 were dissolved in 5 cc. water and 5 cc. reagent added: a precipitate formed almost at once.—The experiment was repeated with 0.5 and 1 mg. NH_4: with 1 mg. a precipitate formed in about 10 minutes; with 0.5 mg. on standing several hours. On filtering

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[1] *J. Chem. Soc.*, **77**, 1076 (1900).

[2] *Am. J. Sci.* [4], **24**, 433 (1907); **26**, 329 (1908).

and washing, the precipitate was found to be more orange-colored than the potassium salt.

50 mg. Li as LiCl were dissolved in 5 cc. water and 5 cc. reagent added: in two days only a minute precipitate settled out, corresponding to about 0.2 mg. K.—The experiment was repeated with 100 mg. Li: only a very small precipitate settled out on standing, which was not greater than that expected from the potassium impurity.

50 mg. of Ca, Sr, Ba, and Mg as nitrate were dissolved in separate experiments in 5 cc. water and 5 cc. reagent added: no precipitate formed in 2 hours in any case.

To 5 cc. of solution containing 1 cc. 10 per cent. NaOH were added 5 cc. of the reagent: the solution slowly darkened, and was almost black in two minutes, and when filtered yielded a black very finely divided precipitate.

To 2 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution were added 3 cc. water and 5 cc. $Na_3Co(NO_2)_6$ reagent: no precipitate formed.

To 1 cc. alcohol and 4 cc. water were added 5 cc. reagent: no précipitate formed in 18 hours.

Two cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution, 1 cc. alcohol, and 2 cc. water were mixed and treated with 5 cc. $Na_3Co(NO_2)_6$ reagent and the mixture allowed to stand over night: a film covered the glass and some crystals adhered to it. On filtering and washing, the film was found to be light violet and the crystals somewhat darker; on dissolving in HCl both were found to contain cobalt.—The experiment was repeated except that the mixture was evaporated almost to dryness, to expel the alcohol, and then dissolved in 5 cc. water before adding the $Na_3Co(NO_2)_6$ reagent: there was practically no precipitate, even on long standing.

P. 93, N. 1. *Effect of the Presence of Potassium Salts on the Test for Sodium.*—Neutral solutions of various mixtures of potassium and sodium, both as chlorides and nitrates, were evaporated in small flasks to about 1 cc., and cooled. In each case 2 cc. of the $K_2H_2Sb_2O_7$ reagent (P. 94, N. 1) were added; the mixture was shaken to dissolve any KCl or KNO_3 that had separated on cooling, and allowed to stand for several hours. The following table shows the number of milligrams of sodium present in each experiment.

	Chlorides.			Nitrates.		
Test for Na.	In 10 min.	Over night.	Failed.	In 10 min.	Over night.	Failed.
300 mg. K.....	10	7	6	.	6	4
200 mg. K.....	5	4	3	.	3	.
100 mg. K.....	3	2	1	.	2	1
50 mg. K.....	2	2	1	1	.	.
0 mg. K.....	1	.	.	1	.	.

It is evident that the presence of KCl and of KNO_3 greatly decreases the delicacy of the test for sodium.

The experiments with 300 mg. K were repeated except that a large part of the K was separated as K_2SO_4 by the process described in P. 93: with 3 mg. Na a very satisfactory test was obtained in 15 minutes; with 2 mg. Na a few small crystals separated on standing over night, but the test was practically a failure. In another experiment with 200 mg. K and 2 mg. Na, a distinct test for sodium was obtained in about 2 hours.

P. 93, N. 2. *Action of Potassium Pyroantimonate on Lithium.*—In separate experiments 2, 5 and 10 mg. Li as LiCl were treated by P. 94: in each experiment a crystalline precipitate very similar in appearance to $Na_2H_2Sb_2O_7.6H_2O$ separated—with 10 mg. in a few minutes, with 5 mg. in about 1 hour and with 2 mg. in 10 hours. The experiment was repeated with 1 mg. Li: no precipitate separated in 24 hours, and only a very small one in three days.—The experiments were repeated with freshly prepared $K_2H_2Sb_2O_7$ reagent, to which no KOH had been added: the results were the same.

P. 93, N. 2–3. *Precipitation of Lithium and Sodium as Fluorides.*—1.0 mg. Li and LiCl was dissolved in 2 cc. water, 1 cc. NH_4OH (0.90), and 2 cc. 20 per cent. NH_4F solution were added; a small precipitate separated in a minute or two, and was proved to be lithium by the flame test and by converting it into Li_3PO_4 by *P. 91*a*.—The experiment was repeated with 1 and with 2 mg. Li except that the initial volume was 5 cc. instead of 2 cc.: a very distinct precipitate of LiF separated at once with 2 mg., but the precipitate with 1 mg. after an hour was so small that the test with Na_2HPO_4 failed.

The above experiments were repeated with 100 mg. Na as NaCl: in the smaller volume a precipitate of NaF formed at once: in the larger volume no precipitate separated.

Experiments with 0.5 mg. Li showed that this amount could be detected by evaporating the solution to 0.5 cc., adding 0.5 cc. NH_4OH (0.90) and 1 cc. 20 per cent. NH_4F solution, but that 0.5 cc. was then about the limit of detectability. Under these conditions a precipitate of NaF was obtained at once with 30 mg. Na as NaCl, but not with 20 mg.

For the precipitation of lithium as fluoride and the detection of sodium in the filtrate see T. A. 219–221.

P. 93, N. 4. *Separation of Sodium and Lithium by Alcohol Ether.*—Mixtures of chlorides of sodium and lithium were treated by the process described in the note. The lithium was confirmed by *P. 91*a*; the sodium by P. 94, including the flame test. The results are recorded as in the Test Analyses.

No.	1.	2.	3.	4.	5.	6.
Na...............	200 S	200	200	0 S	2 S	1 S–
Li...............	0 S	1 S	0.5 S–	100	100	100

In making the flame test for sodium in No. 6 the yellow flame had a reddish tinge and the spectroscope showed the presence of lithium. On standing about 24 hours a few small crystals separated in the test for sodium in No. 4, but the flame was red, not yellow. In these analyses the lithium had not been carefully washed out of the filter paper.

P. 94, N. 1–2. *Composition of Alkali Antimonates.*—Several different solid compounds of each element are known and formulae have been assigned chiefly from their behavior when heated. Thus the ordinary compound of sodium which has the composition $NaSbO_3.3\frac{1}{2}H_2O$, loses water when heated, but the last half molecule remains even at 350°, Knorre and Olschewsky.[1] The three molecules that are given off readily are considered to be water of crystallization, and the remainder to be chemically combined; the formula is therefore written $Na_2H_2Sb_2O_7.6H_2O$. The question of the composition of the solutions is still an open one.

Test for Sodium with Potassium Antimonate.—1 mg. Na as NaCl was dissolved in 1 cc. water and 2 cc. of the freshly prepared alkaline potassium antimonate reagent (see N. 1) were added: after 5 minutes a small nearly colorless precipitate adhering to the glass could be seen, which in 15 minutes has become much more distinct and in 30 minutes had become white and opaque. As it adhered very firmly to the glass, the solution was poured out; the precipitate was washed with water several times, and finally the test-tube was filled with water: after several hours the precipitate still remained on the glass. The water was poured out and HCl added: the precipitate dissolved, more rapidly on warming.—The experiment was repeated several times with 0.5 mg. Na: in 30–60 minutes small colorless crystals were seen adhering to the glass, which became more distinct on standing 30 to 60 min. longer, though the precipitate remained nearly colorless.

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[1] *Ber.*, **18**, 2360 (1885).

To determine the effect of the amount of antimonate used the foregoing experiments were repeated using different reagents, in which 1, 2, 3, 5 and 8 g. pyroantimonate were added to 100 cc. boiling water, after which the solutions were boiled for a minute or two until almost all the salt disappeared. The results are given in the following table. In each case the sodium chloride was dissolved in 1 cc. water, and 2 cc. of a reagent were added.

Pyroantimonate in 100 cc.		1 gm.	2 gms.	3 gms.	5 gms.	8 gms.
2 mg. Na	slight test in........	5	2–5	3	10	10 min.
	distinct test in.......	5–30	5–30	5	15	30
1 mg. Na	slight test in........	7–10	5	5	20	10–60 min.
	distinct test in.......	30–60	10–30	10–30	60	(over night)
0.5 mg. Na	slight test in........	...	30–60	30–60	(no test in	......
	distinct test in.......	90 min.	60–90	60–90	1 hr.)	......

It is evident that the second and third reagents give the most satisfactory results. The former is the one recommended in the process.

Effect of the Alkalinity of the Potassium Pyroantimonate Reagent.—A solution was prepared from 2 g. of the commercial salt and 100 cc. water as described in N. 1, but no KOH was added: it was clear and reacted neutral to litmus paper.—To a portion a few drops of HCl were added: a white flocculent precipitate separated quickly.—The neutral (2 per cent.) solution was placed in a corked test-tube and allowed to stand: it remained clear over night, but after a few days a white flocculent precipitate separated out. The clear solution was poured off and again allowed to stand: a precipitate again formed, which ran through the filter. After six weeks 2 cc. of the solution were added to 1 cc. of a NaCl solution containing 2 mg. Na: no crystalline precipitate formed, even on standing several hours. The solution now reacted alkaline to litmus paper.—Various other strengths of the reagent were tested in the same way, portions of the solutions being set aside before KOH was added: the 1 per cent. solution was neutral and decomposed very slowly; the 3 per cent. solution showed a very slight alkaline reaction and decomposed more rapidly than the 2 per cent. solution; the 5 and 8 per cent. solutions were distinctly alkaline, became very turbid over night, and large precipitates separated on standing.

To try the effect of the presence of KOH, a solution of the antimonate reagent was prepared by dissolving 2 to 3 g. of the salt in 100 cc. boiling water and cooling; and to three 20 cc. portions of the neutral solution were added respectively 0.5, 1.0, and 2.0 cc. 10 per cent. KOH solution. These solutions were placed in corked test-tubes and set aside: a flocculent precipitate separated slowly in each solution, but it was much smaller than that obtained in a corresponding solution to which no KOH had been added. After 6 weeks 2 cc. of each solution were added to 1 cc. portions NaCl solution containing 1 and 2 mg. Na: A small but distinct crystalline precipitate separated in each case; within 10 minutes with 1 mg. Na, and within 3 to 5 minutes with 2 mg. The tests became more distinct on standing. The clear reagents were allowed to stand three months longer: a very small flocculent precipitate separated in each case. The tests with 1 and 2 mg. Na were then repeated: the results were exactly the same. A comparison of these results with those obtained above with freshly prepared solutions, shows that an alkaline reagent unlike a neutral reagent does not deteriorate appreciably in over four months.

The tests with 1 and 2 mg. Na were repeated with a freshly prepared reagent to which no KOH had been added: the results were almost exactly the same, showing that the delicacy of the test is not affected by the presence of alkali, nor by its amount.

About 3 grams of antimonate were added to 100 cc. 0.3–0.5 per cent. solution of

KOH, the mixture was heated to boiling, shaken well while hot, cooled, and filtered. Two cc. of this reagent were added to 1 cc. NaCl solution containing 3 mg. Na: no precipitate separated in a day, showing that the KOH must not be added to the solution until after it is cooled.

Behavior of Potassium Antimonate Reagent towards Various Substances.—In the following experiments the substance was dissolved in 1 cc. water and 1 to 2 cc. of the antimonate reagent added.

With 1 mg. NH_4 as NH_4NO_3, no precipitate over night. With 2 mg. NH_4, a turbidity in 1½ hours. With 5 mg. NH_4, turbidity in a few minutes. With 10 mg. NH_4, turbidity at once.

With 1.0 mg. Ca as nitrate, a large white gelatinous precipitate at once. With 0.2 mg. Ca, marked turbidity at once. With 0.1 mg. Ca: slight turbidity at once.

With 0.2 mg. Ba as nitrate, a slight turbidity at once.

With 0.1 mg. Mg as nitrate, a slight turbidity at once. With 0.3 mg. Mg, a marked turbidity.

In a number of experiments 400 mg. Mg as nitrate were precipitated as magnesium ammonium carbonate by P. 81, and the (neutral) filtrate tested for Na by P. 93: in one or two cases a perfect blank was obtained, but in others a small flocculent precipitate separated corresponding to 0.1 to 0.3 mg. Mg. But this turbidity was probably not due to magnesium since in another experiment no precipitate separated when KOH was added before testing for Na, and yet a small flocculent precipitate was obtained on adding the antimonate.

A few drops of alcohol were added to 1 cc. of reagent: a large white precipitate separated at once.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA.]

THE REDUCTION OF COPPER SULPHATE WITH HYDROXYLAMINE.

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In the test for free hydroxylamine with Fehling's solution, varying results, depending upon the concentration and temperature of the reagents, are obtained. If a few drops of Fehling's solution are added, to a cold dilute solution of hydroxylamine, a bright green precipitate, which soon changes brown, is formed. If the solutions are warm, the precipitate is yellow, and if they are warm, and also somewhat concentrated, the precipitate is red.

These observations induced the authors to undertake a study of the different stages which take place in the reduction of copper sulphate. This work led to the separation and identification of the following compounds:

$CuSO_4.NH_2OH$.—By adding an alcoholic solution of hydroxylamine to a solution of cupric chloride, Feldt[1] obtained violet-colored crystals, which, when removed from the solution, turned brown and decomposed before he was able to determine their composition. His experiments

[1] *Ber.*, **27**, 401.