## 70. *An Improved Qualitative Separation of the Iron Group in the Presence of Phosphate.*

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The older forms of the phosphate separation table are defective in that several units % of certain metals are liable to escape detection: even when the losses are only partial, they are so large and variable as to give a distorted indication of the relative proportions

of the metals present. By the application of the following principles a method has now been devised which gives an approximate indication of quantities and permits, even in the more difficult cases, the detection of 0·5% of a metal in 1 g. of mixed phosphates: (i) as far as possible, separations are effected in acid solution, thus avoiding the necessity for removing the phosphate radical; (ii) precipitates which tend to be colloidal are formed from solutions more acid than usual, thus minimising adsorption errors; (iii) crystalline precipitates are formed from solutions of relatively low acidity, thus minimising solubility losses; (iv) the metals most liable to be lost by adsorption are precipitated at an early stage.

*Examination of Older Methods.*—The improved tin method of removing phosphate, in which the separation is effected in a highly acid solution (Gattermann and Schindhelm, *Ber.*, 1916, **49**, 2416), has much to recommend it. The adsorption losses are, nevertheless, considerable, and the need of an extra passage of hydrogen sulphide to remove the excess of tin is a practical disadvantage. The lead method of Balarew (*Z. anorg. Chem.*, 1922, **121**, 254) and the bismuth method of Keschan (*Z. anal. Chem.*, 1925, **65**, 346) were not examined in great detail because they did not offer prospects of further improvement.

The large losses of the acetate method are not due wholly to adsorption, as is generally supposed, but in part to the use of a buffer of $p_H$ 4—5, a value far too high to ensure that the desired metals remain in solution when the mixture is boiled. The phosphates of iron, aluminium, and chromium can be precipitated almost quantitatively at $p_H$ values of 1·5, 2·5, and 3 respectively, but for the method in question a higher value has to be used to enable excess of iron to be eliminated as basic acetate. The barium carbonate method involves a still higher $p_H$ value (*ca.* 5·8) but is not on this account worse than the acetate process, since the metals of the iron group are filtered off in the cold. The method is, however, inconvenient for qualitative analysis.

Some existing forms of the acetate separation (*e.g.*, Noyes, "Qualitative Chemical Analysis," 1922, 9th Edn.), by a preliminary boiling of the precipitate with sodium peroxide and sodium carbonate, avoid the necessity of precipitating all the phosphate. It is well known that the extraction of zinc may be far from quantitative. On analysing a test mixture containing the eleven metals of the phosphate group, it was found that a single extraction removed only about 50% of the aluminium, and a second extraction a further 25%. With chromium, one extraction removed only 25%, and a second extraction a further 25%. Although this procedure is inefficient for the metals in question, it has the great advantage of eliminating most of the phosphate radical. Nevertheless, the removal of the remainder by the basic acetate method leads to an appreciable loss of the barium-group metals. As a preliminary to the new method, an extraction with sodium peroxide might be useful if the substance to be examined consisted almost wholly of aluminium or chromium phosphate.

Remy (*Z. anal. Chem.*, 1919, **58**, 385) has described a process which utilises phosphate as a group reagent and avoids the necessity of eliminating excess of this radical. His use of concentrated aqueous ammonia to prevent the precipitation by phosphate of certain metals is excellent for nickel and reasonably good for cobalt, but leads to difficulty in the detection of 0·5% of zinc. The attempt to precipitate sulphates of barium and strontium from a phosphate solution before the removal of iron, etc., involves such a high acidity that the solubility of strontium sulphate is appreciable. It was at first hoped to incorporate in the new separation Remy's method for separating magnesium and manganese by precipitating the latter as manganese ammonium phosphate in the presence of an acetate buffer. As this precipitation is not sufficiently quantitative, an attempt was made to improve the method by standardising the concentrations of ammonia and phosphate and by using a phosphate buffer to enable higher $p_H$ values to be employed. It was found that at $p_H$ 6·8 manganese is almost quantitatively precipitated, and magnesium if present alone is left mainly in solution, but if both are present there is a considerable loss of the latter. The modified method could not be relied upon to detect less than 3% of magnesium and was therefore abandoned.

## Experimental.

*Outline of the New Method.*—After the removal of Group II, an excess of $(NH_4)_2HPO_4$ is added in addition to $NH_4Cl$ aq. and $NH_3$ aq., in order that all the common bases except Na, K, and $NH_4$ shall be pptd. in the phosphate group. After a portion of the ppt. has been tested for Mn with $NaBiO_3$, the main portion is dissolved and the phosphates of Fe, Al, and Cr are pptd. by a formate buffer of $p_H$ 3. Without filtration, $BaSO_4$ and $SrSO_4$ are pptd. by $(NH_4)_2SO_4$. This procedure avoids both the adsorption losses, which would occur if the phosphate ppt. were first filtered off, and the high solubility loss that would result if $SrSO_4$ were removed from a highly acid solution before pptn. of the phosphates. Zn is pptd. as ZnS from the filtrate under conditions which approximate to those recommended for its quant. separation by Fales and Ware (*J. Amer. Chem. Soc.*, 1919, **41**, 487). After concn. of the filtrate, Ca is pptd. as $CaC_2O_4$. In separate portions of the remaining solution, Co is tested for by α-nitroso-β-naphthol, Ni by dimethylglyoxime, and Mg by Titan-yellow. Interference with the latter test by Co, Ni, and traces of Mn can be prevented by adding KCN. If Mn is present in quantity, a preliminary separation of the Mg with KCN and NaOH is desirable.

The following table shows the quant. results (as yields %) obtained for those metals most liable to be lost during the phosphate separation; it relates to 1·1 g. portions of a mixture of equal weights of the phosphates of Fe, Al, Cr, Ni, Co, Mn, Zn, Ba, Sr, Ca, and Mg. In carrying out the analyses no attempt was made to avoid usual losses incidental to qual. work such as those due to incomplete washing of ppts., evaporation in open vessels, and the removal of small portions for subsidiary tests. The basic acetate method used for comparative purposes was of an improved type, in which all the phosphate radical is removed by $FeCl_3$ at $p_H$ 5. Adsorption losses were minimised by precipitating the phosphate from 150 c.c. of liquid, the filtrate being concentrated to 20 c.c. for the subsequent analysis.

| | Ba. | Sr. | Ca. | Zn. | Mg. |
|---|---|---|---|---|---|
| Basic acetate method ..... | 3 | 14 | 40 | 20 | 38 |
| New method ..... | 87 | 80 | 87 | 77 | 84 |

The yields obtained show, not only the marked improvement effected by the new method, but also that it gives trustworthy indications as to relative quantities. The analysis for the 11 metals specified can normally be carried out in less than 3 hr. The min. sensitivity limit of 5 mg. of a metal in 1 g. of mixture compares favourably with many of the qual. separations commonly used when phosphate is absent. For instance, Curtman and Frankel (*J. Amer. Chem. Soc.*, 1911, **33**, 724; 1912, **34**, 1493), in attempting to improve the detection of Ba, showed that 25—50 mg. of this metal may escape detection in the usual separation process. Tests of the new separation, made in this laboratory by persons previously unacquainted with the method, have shown that much greater certainty can be obtained in the analysis of substances containing 6—11 metals in the phosphate group than was formerly the case with mixtures of 3 or 4 phosphates.

### *Separation of the Iron Group in Presence of Phosphate.*

Dissolve small portion of ppt. in $HNO_3$ and test for **Mn** with $NaBiO_3$ (S 1).*
Dissolve remainder in dil. HCl, dil. to 60—70 c.c., add $NH_4OH$ till $p_H$ is approx. 3, and add 10—20 c.c. of formate buffer of $p_H$ 3; boil, and slowly add 10 c.c. 8*N*-$(NH_4)_2SO_4$. Filter (S 2).

*Ppt.* Add $H_2O$, $Na_2SO_4$, and $Na_2O_2$; boil, cool, and filter (S 3).

*Filtrate.* Examine for **Al** and **Cr** (S 4).

*Residue.* Boil with dil. $H_2SO_4$ and filter (S 5).

*Filtrate.* Examine for **Fe**.

*Residue.* Boil with conc. $Na_2CO_3$ soln. Wash remaining residue, and examine it for **Ba** and **Sr** (S 6).

*Filtrate.* Heat; pass $H_2S$; filter (S 7).

*Ppt.* **ZnS.**

*Filtrate.* Concentrate; add $(NH_4)_2C_2O_4$ and let stand; filter (S 8).

*Ppt.* Ignite; dissolve residue in 2*N*-HOAc, add equal bulk of 0·25*N*-NaF, and boil. Turbidity or ppt. = presence of **Ca** (S 9).

*Filtrate.* Test separate portions for:
(1) **Co** with α-nitroso-β-naphthol (S 10).
(2) **Ni** with dimethylglyoxime (S 11).
(3) **Mg.** (i) *In absence of* Mn *in quantity.* Add Titan-yellow; if Co, Ni, or trace Mn is present, add KCN and acidify with HCl; make alk. with NaOH. Red ppt. = presence of Mg.
(ii) *If* **Mn** *is present in quantity,* Mg must be separated by KCN + NaOH before carrying out the Titan-yellow test (S 12).

* S 1 = Stage 1, etc.

### *Procedure.*

The following procedure is based on the assumption that the first two groups have been removed from 1 g. of mixture, that $H_2S$ has been boiled off, $Fe^{\cdot\cdot}$ oxidised to $Fe^{\cdot\cdot\cdot}$, and that the main phosphate group has been pptd. by $NH_4Cl$, slight excess of $NH_4OH$, and $(NH_4)_2HPO_4$.

*Stage* 1.—To a cold solution of 1/10—1/20 of the group ppt. in 4*N*-$HNO_3$, add about 1 g. of $NaBiO_3$; a purple colour indicates presence of Mn.

*Note* 1. The colours of Ni and Co do not appreciably interfere, but the detection of traces of Mn could be facilitated by observation of absorption spectrum.

*Note* 2. Cr in moderate amount does not interfere. In its presence the bismuthate test is preferable to the use of the otherwise permissible $PbO_2$ + conc. $HNO_3$ test, because the $CrO_4''$ formed in the latter interferes to a greater extent than $Cr'''$. If the original substance consists largely of $CrPO_4$, the sensitivity of the $NaBiO_3$ test is reduced to about 20 mg. per g. of original substance and it would then be desirable to test for Mn in the filtrate from Stage 2. Since this solution contains reducing agents, the test portion must be pptd. with $NH_4OH$, and the ppt. used for the Mn test.

*Stage* 2.—Dissolve the group ppt. in HCl, dilute the solution to 60—70 c.c., and adjust the $p_H$ value to approx. 3 by one of the following methods: (i) Add $NH_4OH$ till a slight turbidity forms; add 20 c.c. of formate buffer [57 g. $H{\cdot}CO_2Na$ and 85 c.c. 23·5*N*-$H{\cdot}CO_2H$ (*d* 1·200) per l.]: this should give a $p_H$ within the permissible limits of 2·7—3·2. (ii) Alternatively, if an indicator is available the alk. colour of which would not interfere with the Titan-yellow test for Mg, it may be added to the main solution as a guide to the addition of $NH_4OH$. Benzylanilineazobenzenesulphonic acid is suitable if used sparingly, $p_H$3 being indicated by an orange-yellow. Method (ii) has the advantage that 10 c.c. of formate buffer suffice, thus minimising the danger of loss through spurting when the solution is concentrated (Stage 8). After addition of the buffer, boil the solution, add 10 c.c. of 8*N*-$(NH_4)_2SO_4$, and filter; the $(NH_4)_2SO_4$ should be added slowly to ensure that $BaSO_4$ comes down in an easily filterable form.

*Stage* 3.—Suspend the ppt. in cold $H_2O$ containing $Na_2SO_4$ (1—2 g.) to reduce the solubility of $SrSO_4$. Slowly add 1—3 g. of $Na_2O_2$, and boil till excess of the latter has been decomposed Cool somewhat and filter.

*Stage* 4.—Examine separate portions of the filtrate for Al and Cr by any convenient method Since the solution is liable to contain much $PO_4'''$, oxidation to perchromic acid by $H_2O_2$ in acid solution is preferable to the $Pb(OAc)_2$ test for Cr.

*Stage* 5.—Boil the residue with sufficient dil. $H_2SO_4$ to dissolve $Fe(OH)_3$. Owing to the relatively high solubility of $SrSO_4$, a large vol. should be avoided. Filter the solution and test the filtrate for Fe.

*Stage* 6.—Boil the residue for 3—4 min. with 10—12 g. of anhyd. $Na_2CO_3$ in about 50 c.c. of $H_2O$, filter off the ppt., and reject the filtrate. This converts the greater part of the alkaline-earth sulphates into carbonates, which are washed, dissolved in a suitable acid, and examined by any of the usual methods for Ba and Sr. Unless $Ca_3(PO_4)_2$ is present in the original substance to a greater extent than 0·4 g. (≡ 0·15 g. Ca), very little will be present at this stage. Since a tolerably correct judgment as to the proportion of Ca may be based on Stage 9, examination for Ca is not essential here, but the tests employed for Ba and Sr must be such as would not be interfered with by Ca.

*Note.* If a considerable quantity of residue insol. in acid remains, it may be taken as indicating that Ba is present in amount exceeding 10—20% in the original substance.

*Stage* 7.—Heat the solution to its b. p. and pass $H_2S$ for several min., the solution being allowed to cool. Filter off any ZnS; if this ppt. is white and present in quantity, Zn scarcely needs further confirmation.

*Note.* If the Zn ppt. is dark, it is unnecessary to examine it for Ni and Co since practically all of these will remain in solution, but the usual separation for isolating Zn would be essential. To avoid this, it is advisable before passage of $H_2S$ to reduce the $p_H$ to 2·7 ± 0·2 by adding dil. $H{\cdot}CO_2H$ if necessary.

*Stage* 8.—Evaporate the filtrate to 15—20 c.c., add 15 c.c. of 0·5*N*-$(NH_4)_2C_2O_4$, and filter the solution after standing (see Note 3).

*Note* 1. The $p_H$ is not critical, but the rise due to loss of $H{\cdot}CO_2H$ on concn. is advantageous.

*Note* 2. On account of the $(NH_4)_2SO_4$ present, concn. of a solution satd. with $CaSO_4$ will ppt. only 1/5 of it. Examination of such a ppt. is not therefore necessary. The microscopic appearance (clusters of small needles) is, however, very characteristic.

*Note* 3. 5 Mins.' standing is sufficient if by that time a considerable ppt. has formed. Before it is concluded that Ca is absent, the solution should be kept for at least 20 min., by which time 1% of Ca in the original substance would cause a ppt. If traces are to be sought, it is advisable to prolong the standing to 1—2 hr., especially if at the end of 20 min. a faint turbidity is observable.

*Stage* 9.—Ash the filter-paper containing the $CaC_2O_4$ ppt. over a full Bunsen flame and heat the residue for a few min. longer, thus converting it into CaO or $CaCO_3$. Boil this with 2—5 c.c. of 2*N*-HOAc, filter off any insol. residue, add an equal bulk of 0·25*N*-NaF, and boil. A turbidity or ppt. of $CaF_2$ indicates presence of Ca.

*Note* 1. If the original substance contains a large proportion of Co or very large proportions of Ni, Mn, or Mg, their oxalates may be partially pptd. with the $CaC_2O_4$. The fluoride test under the conditions specified is not interfered with by these metals. Although this test for Ca is reasonably sensitive, the amount of ppt. is apt to be under-estimated, since owing to its colloidal character it is relatively transparent and does not flocculate rapidly. Long standing is not permissible, since the acid solution will slowly attack glass.

*Note* 2. Ca can if desired be confirmed spectroscopically in the oxalate ppt. Care must be taken in interpreting a simple flame-test since a minute amount of Sr may be present, and this with the ever-present trace of Na may give a flame likely to be mistaken for that due to Ca.

*Stage* 10.—To a definite fraction (say 1/5) of filtrate from Stage 8, add excess of α-nitroso-β-naphthol (0·1% aq. solution of Na salt), and boil; a reddish-brown ppt. after a few mins.' standing indicates presence of Co.

*Note.* Other metals liable to be present should not normally interfere with this test, but if for any reason the ppt. is unduly dark, the test should be repeated after addition of a few c.c. of 2*N*-$H{\cdot}CO_2H$. In presence of much of this acid the test is still reasonably sensitive, but a trace of Co may require 5—10 mins.' standing before a ppt. forms; subsequent boiling facilitates pptn.

*Stage* 11.—Test another portion of filtrate from Stage 8 for Ni with a 1% alc. solution of dimethylglyoxime. Pptn. may be hastened by making alk. with $NH_3$ and warming. Since this treatment is liable to ppt. heavy-metal phosphates, the solution should finally be acidified with HOAc, whereupon only the Ni ppt. will remain undissolved.

*Note.* If Co is present in quantity, only a small portion of solution should be tested, and a relatively large volume of reagent employed. If traces of Ni are to be sought in the presence of a large quantity of Co, special precautions must be taken (see *e.g.*, Treadwell and Hall, " Analytical Chemistry," Vol. 1, p. 186, 6th edn.). If the method for separating Ni from Co by pptn. with NaOBr after treatment with KCN is preferred, it should be remembered that Mn and Mg may also be pptd.

*Stage* 12.—(a) *In the absence of* Co, Ni, *and* Mn. To 1/10th of the filtrate from Stage 8, add 1 c.c. of 0·02% aq. solution of Titan-yellow and 5 c.c. of 10*N*-NaOH; a red coloration or ppt. indicates presence of Mg.

(b) *In the presence of* Co, Ni, *or trace of* Mn. Proceed as in (a), but before adding the alkali dissolve about 1 g. of KCN in the cold solution (add a few c.c. of $H_2O$ if necessary) and add 2 c.c. of conc. HCl.

(c) *In the presence of* Mn *in quantity.* Add a mixture of 1/10th of the filtrate from Stage 8 with 1 c.c. of Titan-yellow to a cold solution of 2—3 g. of KCN in 10 c.c. of $H_2O$. Add 5 c.c. of 10*N*-NaOH and set aside for 3 min. (A trace of Mn may not be indicated at this stage.) Filter the liquid through coarse filter-paper and wash the ppt. with a little $H_2O$. Pour 10 c.c. of 2*N*-HCl several times through the filter, dissolve 1 g. of KCN in the resulting solution, and add 1 c.c. of Titan-yellow and 5 c.c. of 10*N*-NaOH. On prolonged standing, such a solution may give a slight brown ppt. due to Mn, but if Mg is present to the extent of 0·5% or more in the original substance, a red colour or ppt. will be evident in the course of a few min.

*Note* 1. On filtering an alk. solution of Titan-yellow in Stage 12 (c), adsorption by the filter-paper will give rise to a red colour. In the absence of Mg and cellulose fibres, Titan-yellow shows a yellow-orange colour in solutions of $p_H > 12$.

*Note* 2. As originally described by Kolthoff (*Chem. Weekblad*, 1927, **24**, 254; *Mikrochem.*, Emich Festschrift, 1930, 180; see also " B.D.H. Reagents for Spot Tests," 1932) for salts which could only yield $Mg(OH)_2$ on treatment with NaOH, the Titan-yellow test will give a red coloration with a solution containing 2 parts of Mg per 100,000. The sensitivity is considerably reduced by Stage 12 (c) and to a less extent by 12 (b). In any case, however, Mg must not be returned as present in quantity unless a large gelatinous ppt. is obtained. If in Stage 12 (c) a green gelatinous ppt. is obtained, it indicates that the proportion of KCN employed was too small. A finely divided pink ppt. which does not flocculate in a few min. implies some departure from the recommended conditions.

*Note* 3. The usual methods of testing for Mg in the presence of Mn by means of 8-hydroxyquinoline are less satisfactory than the recommended procedure, but a method involving the use of this reagent is being developed which, though less convenient than the cyanide method, is more suitable when it is necessary to examine for very small traces of Mg.

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