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The Separation of the Bivalent from the Trivalent Kations in the Presence of Phosphate by a Modified Ammonia Method, and Comparison of Results thus Obtained with Results of Separation by the Urea Method

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The separation of Mg, Ca, Sr and Ba from Al and Cr in the presence of phosphate has been accomplished by adding dropwise the system in which the cations have to be separated to a solution of ammonium nitrate containing the quantity of freshly distilled ammonia necessary to give a *p*H-value of 6.9 to 7 in the solution after precipitation. The upper limits of phosphate content at which the separation is still feasible have been determined both for the above separations and for the separation of the bivalent ions from Fe in the presence of phosphate. The comparison of the results thus obtained with the results of separations of the same cations by the urea method shows that the upper limit of phosphate content at which the separation succeeds is higher for the urea method than for the ammonia method. In both methods this limit — for a given trivalent ion and a changing bivalent ion — changes in proportion to the solubility product of the secondary phosphate of the bivalent metal, and — for a given bivalent ion and a changing trivalent ion — in inverse proportion to the solubility product of the phosphate of the trivalent metal.

One of the fundamental conditions for the successful separation of the cations of the ammonium carbonate group from the cations of the ammonia group, specially in the presence of phosphates, is an appropriate *pH*-value in the neighbourhood of the neutral point on the acid side.[1] Moreover, the circumstances must be such as to avoid coprecipitation. If these conditions are obtained, the trivalent cations will be completely precipitated, and no bivalent ions will be lost by coprecipitation.

Since those conditions cannot be achieved by direct precipitation with ammonia, a great number of authors have tried to develop an appropriate method for the above mentioned separation.[2] All these methods can be grouped under two headings: methods employing ammonia as precipitating agent, and methods in which the precipitating ion is formed by hydrolysis. In the first group the inverted ammonia method is most important.[3] We have in a previous work applied this method in a modified form to the separation of the bivalent cations from iron in the presence of phosphates, without determining the upper limit of phosphate content at which the separation is still feasible. In the experimental part of the present paper we are giving the results of the application of this method to the separation of Mg, Ca, Sr and Ba from Al in the presence of phosphates, as well as to the separation of the same bivalent ions from Cr, again in the presence of phosphates. We have, in addition, determined the upper limits of phosphate content at which the separation of those bivalent ions not only from Al or Cr, but also from Fe is possible.

In the second group the urea method must be specially mentioned, in which the precipitating ion is formed by gradual hydrolysis of urea when the system is heated, local supersaturations being quite impossible. Presuming that this method should be suitable for the same separations, we carried out the separation of the individual bivalent ions in turn from Al, Fe and Cr, in the presence of phosphates, determining each time the upper limit of phosphate content at which the separation is still possible by the urea method.

Having thus carried out the separation of the bivalent ions in turn from the single trivalent ions in the presence of phosphates both by the modified ammonia method and the urea method, we are able to compare the results obtained by the two most important representatives of the above mentioned groups of methods. This comparison is given in the conclusions.

EXPERIMENTAL

(In collaboration with I. Zajc, A. Pašagić and K. Kojdić)

TABLE I

Separation of magnesium, calcium, strontium and barium from chromium in the presence of phosphate

Nr.	XO	Cr_2O_3	P_2O_5	Ratio of component oxides	*p*H	XO			X
	taken g.					found g.	difference		
							mg.	‰	
1.	0.1131	0.1131	0.0282	4:4:1	6.90	0.1132	+0.1	+ 0.9	Mg
2.	0.1131	0.1131	0.0353	4:4:1.25	6.90	0.1132	+0.1	+ 0.9	
3.	0.1131	0.1131	0.0423	4:4:1.50	6.90	0.1080	—5.1	—45.0	
4.	0.1236	0.1236	0.0154	4:4:0.50	6.90	0.1237	+0.1	+ 0.8	Ca
5.	0.1236	0.1236	0.0206	4:4:0.75	6.95	0.1234	—0.2	— 1.6	
6.	0.1236	0.1236	0.0309	4:4:1	7.0	0.1219	—1.7	—13.7	
7.	0.1287	0.1287	0.0080	4:4:0.25	7.1	0.1288	+0.1	+ 0.8	Sr
8.	0.1287	0.1287	0.0080	4:4:0.25	7.1	0.1289	+0.2	+ 1.6	
9.	0.1287	0.1287	0.0161	4:4:0.5	7.0	0.1269	—1.8	—14.0	
10.	0.1190	0.1190	0.0015	4:4:0.05	6.85	0.1187	—0.3	— 2.5	Ba
11.	0.1190	0.1190	0.0015	4:4:0.05	7.0	0.1192	+0.2	+ 1.7	
12.	0.1190	0.1190	0.0030	4:4:0.1	6.95	0.1166	—2.4	—20.1	

For the separation of Al, Fe and Cr from Mg, Ca, Sr and Ba, the following procedure was used:

10 g. of NH_4NO_3 were weighed and dissolved in 80 ml. of water; the solution was heated to boiling and the amount of freshly distilled ammonia solution (1 : 9) was added, in order to achieve a *p*H-value of 6.9 to 7.0 in the final solution. This amount had been determined by a previous experiment. To the hot solution 50 ml. of the examined solution was then dropwise added. This solution contained the trivalent metal as chloride, the bivalent metal as chloride or nitrate, and the phosphoric acid as disodium phosphate. The solution with the precipitate was then covered with a watch glass and allowed to stand for 20 minutes at a temperature

of 60°C, during which time it was three times washed by decantation with 100 ml. (each time) of a 0.5% solution of NH_4NO_3. When the solution acquired room temperature, its *p*H-value was measured. The precipitate was then separated by filtration and the bivalent metal was determined in the filtrate.

TABLE II

Separation of magnesium, calcium, strontium and barium from aluminium in the presence of phosphate

Nr.	XO	Al_2O_3	P_2O_5	Ratio of component oxides	*p*H	XO found g.	difference		X
	taken g.						mg.	‰	
1.	0.1182	0.1194	0.0428	4:4:1.25	6.90	0.1182	±0.0	± 0.0	Mg
2.	0.1182	0.1194	0.0447	4:4:1.50	6.90	0.1179	—0.3	— 2.5	
3.	0.1182	0.1182	0.0515	4:4:1.75	6.90	0.1171	—1.1	— 9.3	
4.	0.1237	0.1237	0.0304	4:4:1	6.95	0.1238	+0.1	+ 0.8	Ca
5.	0.1237	0.1237	0.0381	4:4:1.25	6.95	0.1236	—0.1	— 0,8	
6.	0.1237	0.1237	0.0456	4:4:1.50	6.95	0.1225	—1.2	— 9.7	
7.	0.1298	0.1298	0.0261	4:4:1	6.90	0.1292	—0.6	— 4.6	Sr
8.	0.1298	0.1298	0.0261	4:4:1	6.90	0.1296	—0.2	— 1.5	
9.	0.1298	0.1298	0.0326	4:4:1.25	6.90	0.1290	—0.8	— 6.2	
10.	0.1309	0.1309	0.0081	4:4:0.25	6.90	0.1308	—0.1	— 0.7	Ba
11.	0.1309	0.1309	0.0081	4:4:0.25	6.90	0.1307	—0.2	— 1.5	
12.	0.1309	0.1309	0.0163	4:4:0.50	6.90	0.1275	—3.4	—25.9	

TABLE III

Determination of the upper limit of phosphate content for the separation of magnesium, calcium and barium from iron in the presence of phosphate

Nr.	XO	Cr_2O_3	P_2O_5	Ratio of component oxides	*p*H	XO			X
	taken g.					found g.	difference		
							mg.	‰	
1.	0.1131	0.1131	0.0353	4:4:1.25	7.00	0.1130	—0.1	— 0.9	Mg
2.	0.1131	0.1131	0.0423	4:4:1.50	7.05	0.1084	—4.7	—41.5	
3.	0.1237	0.1237	0.0309	4:4:1	6.95	0.1238	+0.1	+ 0.8	Ca
4.	0.1237	0.1237	0.0386	4:4:1.25	6.90	0.1211	—2,6	—21.0	
5.	0.1277	0.1277	0.0212	4:4:0.75	6.95	0.1278	+0.1	+ 0.8	Sr
6.	0.1277	0.1277	0.0319	4:4:1	6.95	0.1227	—5.0	—39.1	
7.	0.1309	0.1309	0.0048	4:4:0.15	6.60	0.1308	—0.1	— 0.7	Ba
8.	0.1309	0.1309	0.0081	4:4:0.25	6.95	0.1270	—3.9	—29,7	

CONCLUSIONS

The graph Fig. 1 shows the upper limit of phosphate content at which the separation of Mg, Ca, Sr and Ba from Al, Fe and Cr is feasible in the presence of phosphate, both by the modified ammonia method and the urea method, as a function of the solubility product of the secondary phosphate of the bivalent metals.

It is apparent that the upper limit of phosphate content at which the separation of the trivalent ions from the bivalent ions is still successful, is higher for the urea method than for the ammonia method. This is due to the gradual formation of the precipitating ion by the hydrolysis of the urea, which method of precipitation precludes supersaturation of ammonia and alcaline reaction. This is not the case to the same extent in the modified ammonia method. Another cause of the different action of the phosphate ion in the two methods is in the different size of the primary particles formed and the different manner of ageing of the precipitate, which causes differences in the coprecipitation effects. The graph reveals, moreover, that the upper limits of phosphate content for both methods and for all three trivalent cations fall off from Mg to Ba, this being due to the fact that the solubility product of the secondary phosphates of the bivalent metals falls off in the same order. This solubility product is higher for the bivalent metals than for the trivalent ones (the difference is about 10^{10}); still greater are the differences between the solubility products of the hydroxydes of those two groups of metals. Thus the pk_t of the most soluble hydroxyde of a trivalent metal is 31, while for the least soluble hydroxyde of a bivalent metal it amounts to 10.8. This fully explains the fact that the trivalent cations were precipitated, while the bivalent ions remained in solution. The completeness of the separation depends, of course, on the pH-value of the system in which the separation is accomplished. The highest limit of phosphate content for both methods and for a

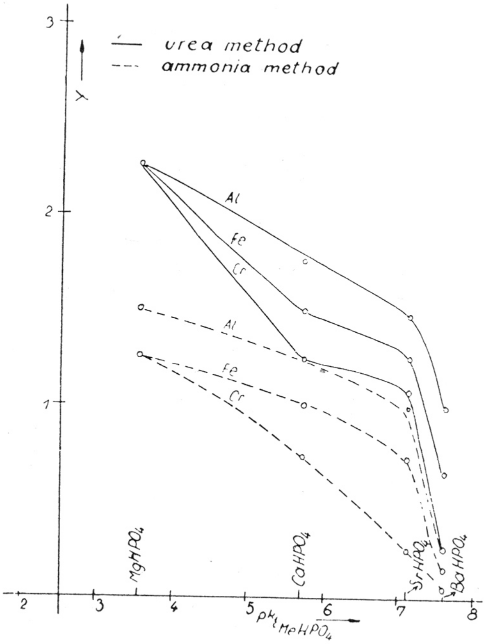

Fig. 1. Graphical representation of the depedence of the upper limit of the phosphate content (Y) at which the separation of Mg, Ca, Sr and Ba from Al, Fe and Cr is feasible in the presence of phosphate, of the way of precipitation and of the solubility product of $MeHPO_4$ against the proportion $Me_2O_3 : MeO : P_2O_5 = 4 : 4 : Y$ of the components.

given bivalent ion is highest when the trivalent ion is aluminium, the next highest when it is iron; the lowest value is obtained for chromium. This is due to the fact that the solubility product is lowest for aluminium phosphate and highest for chromium phosphate.

REFERENCES

1. K. K. Järvinen, *Z. anal. Chem.* **66** (1925) 81.
2. B. Šolaja, *Z. nal. Chem.* **80** (1930) 334; B. Šolaja, M. Kranjčević and M. Kockar, *Arhiv hem. i farm.* **4** (1930) 136; R. Ripan, *Bull. soc. stiinte Cluj* **6** (1931) 208; B. Smith, *J. chem. Soc.* **1933** 253; P. E. Williams and H. T. Briscoe, *Chem. News* **145** (1932) 177; H. Terlet and A. Brian, *Ann. fals. et fraudes* **28** (1935) 605; E. A. Ostroumov, *Redkie Metal.* **2**, No. 5, (1933) 25; W. M. Svenigordskaya and T. N. Smirnova, *Redkie Metal.* **2**, No. 5, (1933) 32; G. Charlot, *Bull. soc. chim. France* [5] **4** (1937) 1235; G. Charlot, *Bul. soc. chim. France* [5] **4** (1937) 1244; E. A. Ostroumov, *Zavodskaja Lab.* **6** (1937) 16; V. K. Solutukhin, *Zhur. Priklad. Khim.*, **10** (1937) 1291; C. Gh. Macarovici, *Bull. soc. stiinte, Cluj* **9** (1939) 207; C. Bordoni, *Ann. chim. appl.* **33** (1943) 10; R. Gilchrist, *J. Research Natl. Bur. Standards* **30** (1943) 89; Kallmann, *Anal. Chem.* **20** (1948) 449; H. H. Willard, *Anal. Chem.* **22** (1950) 1372; H. H. Willard and J. L. Sheldon, *Anal. Chem.* **22** (1950) 1162; L. Gordon, *Anal. Chem.* **24** (1952) 459; T. Tanaka, and K. Hayashi, *J. Chem Soc. Japan, Pure Chem. Sect.* **73** (1952) 44; Ph. J. Elving and R. E. Van-Atta, *Anal. Chem.* **22** (1950) 1075; S. K. Sušić and N. V. Njegovan, *Anal. Chim. Acta* **7** (1952) 304; G. M. Limaye, *Bombay Technologist* **4** (1953—54) 69; A. P. Teren'ev, E. G. Ruhadze and K. I. Litvin, *Zhur. Anal. Khim.* **11** (1956) 55; P. Blanc and J. Racine, *Chim. anal.* **37** (1955) 265.
3. M. Ferrich, *Glasnik Khem. Druschtva Kraljevine Jugoslav.* **6** (1935)
4. F. Krleža, *Thesis,* Zagreb 1942, F. Krleža, *Arhiv kem.* **25** (1953) 97.
5. H. H. Willard and Ning Kang Tang, *J. Am. Chem. Soc.* **59** (1937) 1190; H. H. Willard and L. Sheldon, *Anal. Chem.* **22** (1950) 1163.
6. F. Krleža, M. Savić and J. Kićanović, *Glasnik društva hemičara narodne rep. Bosne i Hercegovine* **5** (1956) 55; F. Krleža, *Glasnik društva hemičara narodne rep. Bosne i Hercegovine* **6** (1957) 34; F. Krleža, J. Kićanović and V. Marković, *Glasnik društva hemičara narodne rep. Bosne i Hercegovine* **6** (1957) 41.

IZVOD

Odjeljivanje monoksida od seskvioksida u nazočnosti fosfata modificiranom amonijak metodom i komparacija dobivenih rezultata s rezultatima odvajanja metodom ureje

F. Krleža

Izvršeno je odjeljivanje Mg, Ca, Sr i Ba od Al, a zatim odjeljivanje istih dvovalentnih kationa od Cr, u oba slučaja u nazočnosti fosfata. Odjeljivanje se vršilo tako, da se sistem, u kojemu treba odvojiti Mg, Ca, Sr ili Ba od Al, odnosno od Cr, dodaje, kap po kap, uz miješanje, u otopinu amonijeva nitrata, koja sadrži potrebnu količinu svježe destiliranog amonijaka, tako da *p*H vrijednost nakon taloženja iznosi 6.9 do 7. Kod toga su određene gornje granice količine fosfata, do kojih su izvedena odjeljivanja moguća, a zatim su istom metodom utvrđene i gornje granice fosfata kod odjeljivanja Ca, Sr, Ba i Mg od Fe. Komparacija dobivenih rezultata s rezultatima odjeljivanja tih kationa, koja smo prije izvršili metodom ureje, pokazuje, da je gornja granica količine fosfata, do koje je odjeljivanje moguće kod metode ureje, viša i da se ona kod obiju metoda za sva tri trovalentna kationa mijenja proporcionalno s k_t (k_t = produkt topljivosti) sekundarnoga fosfata dvovalentne kovine, odnosno obrnuto proporcionalno s k_t fosfata trovalentne kovine za pojedinu dvovalentnu kovinu.

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