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An Anion-Exchange Method for the Separation of P-32 Activity in Neutron-Irradiated Biological Material

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Summary:

Strong hydrochloric-acid solutions containing small amounts of orthophosphoric and citric acid and radioactive tracers of the elements Na, P, K, Ca, Sc, Cr, Mn, Ni, Rb, Sr, Cs, Ba, La, and Ce were titrated with a water suspension of strongly basic anion-exchange resin in the hydroxide form. The titration was carried out to pH = 3.0. It was followed by filtration of the mixture on the top of a small anion-exchange column in the chloride form and a final washing with water.

Phosphorus was quantitatively adsorbed by the resin and the scandium retention was better than 96 per cent. The remaining elements passed quantitatively into the effluent, with the exception of nickel, which was adsorbed to a very small extent.

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1. Introduction

In the activation analysis of trace elements present in biological material the masking effect of P-32 Bremsstrahlung often presents a serious problem which can be solved only with the help of chemical separation techniques.

Different analytical methods for the separation of phosphate from trace metals have been described in the literature.

One of these methods, based on precipitation of the phosphate from strongly acid solution as zirconium phosphate, will in combination with a chemical group separation scheme allow of the separation of P-32 activity from all other radioactive elements present in neutron-irradiated biological material (1, 2). However, on account of the very extensive P-32 activity present in this kind of sample, the precipitation has to be carried out twice. Another disadvantage is that the precipitate is difficult to filter and to wash.

A cation-exchange procedure developed by Samuelson (3, 4, 5, 6) is widely used in different analyses of biological materials (7, 8, 9, 10, 11, 12, 13). Another ion-exchange method, recommending the separation of phosphate on a strongly basic anion-exchange resin, was first suggested by Gabrielson and Samuelson (14). Resin prepared in chloride or acetate form has been frequently used for the separation of mainly monovalent and divalent cations from phosphate in biological material (13, 14, 15, 16, 17, 18). However, little information is given in the literature about the application of these ion-exchange methods to phosphate solutions containing traces of trivalent cations of scandium, chromium, lanthanum and the rare earth elements. Experiments with solutions containing chromium phosphate have shown that the cation-exchange method fails under normal working conditions owing to complex formation (19).

In the present work a method initially worked out in order to separate Sc, Zr, Nb, Hf and Ta as citrate complexes on a Dowex 2, chloride column (1) has been modified to include also the separation of phosphorus. Here, however, anion-exchange resin in the hydroxide form has been used for the titration step instead of NaOH.

2. Experimental

Strong activities of the irradiated 14 compounds of elements shown in Table 1, column 1, were individually dissolved in boiling 6n HCl with the dropwise addition of a small amount of 30 per cent H_2O_2. Activities of the isotopes given in column 2 of the Table may, together with additional rare-earth activities, be present in biological samples after a previous distillation procedure and a subsequent sequential separation of chloride complexes on small anion-exchange columns (1, 2).

In a typical run a suitable strength of gamma activity was pipetted out of one of the solutions and added without carrier to a 50 ml tall beaker together with 10 ml of a 6n HCl solution of $NaH_2PO_4 \cdot 1\ H_2O$ containing 0.4 mg P/ml. This mixture was carefully boiled down to 1.5-2 ml on a hot plate and then cooled. One ml of a 0.1 m citric-acid solution was added and the solution diluted to 20-25 ml with H_2O. The solution was then stirred with a magnetic stirrer and titrated with a water suspension of Dowex 2 x 10, 200-400 mesh resin in the hydroxide form to pH = = 3.0. The pH of the solution was continuously controlled with a pH-meter during the titration. The mixture of resin and water was added dropwise as a thick slurry until the pH of the solution rose to about 2. During the further titration to the final pH value of 3.0 the resin slurry was successively diluted with small amounts of water to avoid the risk of overtitration. In these experiments the total amount of wet resin needed for a titration

varied between 8 and 10 ml. The simultaneously added amount of water was about 15 ml.

After the titration step the mixture was suction-filtered at a rate of about 4 ml/min. The filtration was done on a layer of 10 ml wet Dowex 2 x 10, 200-400 mesh resin in the chloride form. This layer had been prepared in a sintered glass filter crucible, 2 cm in diameter and 10 cm in height. It was washed with water and suction-dried before the filtration. The mixture of the Dowex 2, hydroxide resin and the hydrochloric-acid solution was swirled before its careful addition to the top of the chloride column. The column resulting after the filtration step (18-20 ml wet resin) was washed with 9 x 3 ml H_2O at a rate of about 4 ml/min.

The resin was mixed with water, stirred and allowed to settle to ensure an even distribution of activity throughout the mass. The combined filtrate and washings from the column were evaporated to a small volume and diluted with water to the same volume as the homogenized resin. Finally, the activities of these two samples were compared under identical geometrical conditions with a multi-channel gamma spectrometer.

In the case of the P-32 sample the effluent from the column was controlled for activity also after evaporation to dryness.

3. Results

In Table 1, column 3, are given the percentages of adsorption on the ion-exchange resin of the different elements studied in the present work. The results are the means of double-determinations.

Citric acid was used in the present experimental runs to separate Sc-46 from the activities of the rare-earth elements and lanthanum (1, 2). These elements are instead adsorbed together with nickel on an anion-exchange column in the citrate form in the next group of the chemical separation scheme. Activities of Co-60 and Cu-64 were earlier also separated on this column (2). However, to counteract the serious masking effects observed, the activities of these isotopes are in an improved procedure isolated as a single group in an earlier stage of the group separation scheme. This is done by adsorption on a small anion-exchange column in the chloride form of the chloride complexes formed in 8n HCl solution. This separation step ends the series of fast sequential anion-exchange separations of chloride complexes outlined earlier (2) and will be described in detail elsewhere (20).

4.2. Comparison with the zirconium phosphate method

The main advantage of the present method as compared to the method based on zirconium phosphate precipitation is that it is much faster. The procedure does not include tedious elution steps and the filtrate obtained after the titration step can without pretreatment be continuously fed to an anion-exchange column in the citrate form for further group separations. However, from an analytical point of view the present method can not quite compete with the zirconium phosphate method. The reason for this is that the Sc-46 activity separated together with the phosphorus (Table 1) can probably be determined only after several months' decay of the strong P-32 activity present in biological material.

References

1. SAMSAHL K
Some chemical group separations of radioactive trace elements.
1962 (AE-82).

2. SAMSAHL K, BRUNE D, and WESTER P O
Simultaneous determination of 30 trace elements in cancerous and noncancerous human tissue samples with gamma-ray spectrometry.
1963 (AE-124).

3. SAMUELSON O
The use of base-replacing substances in analytical chemistry. I.
Z. Anal. Chem., 116 (1939) p. 328.

4. SAMUELSON O
The use of base-replacing substances in analytical chemistry. IV.
Svensk Kem. Tidskr., 52 (1940) p. 241.

5. SAMUELSON O
The use of base-replacing substances in analytical chemistry. V.
Svensk Kem. Tidskr., 54 (1942) p. 124.

6. SAMUELSON O
Studier rörande jonbytande fasta ämnen, Stockholm 1944.
Ingeniörsvetenskapsakademiens handl. 179.

7. KAHLE G, and REIF E
Determination of copper, lead, and zinc in blood plasma with the aid of the polarograph and cation exchangers.
Biochem. Z., 325 (1954) p. 380.

8. NIWAGUCHI T
Flame photometric determination of phosphorus.
Kagaku to Sôsa, 11 (1958) p. 16.

9. SCHNEYDER J
Determination of phosphoric acid in wine ash.
Mitt. Klosterneuburg, Ser. A, Rebe u. Wein, 6 (1956) p. 309.

10. SCHNEYDER J
Rapid procedure for analysis of tobacco ash.
Fachliche Mitt. Österr. Tabakregie, 1957, p. 25.

11. TORIBARA T Y, and SHERMAN R E
Analytical chemistry of micro quantities of beryllium.
Anal. Chem., 25 (1953) p. 1594.

12. YAMAMOTO K
Method of chemical analysis of trace elements in a living body. VIII:3.
Japan Analyst Bunseki Kagaku, 5 (1956) p. 340.

Determination of zinc, manganese, and copper in plant ashes . . . .
Utilization of coprecipitation phenomenon in the analysis of plant ashes by polarographic method.
Sci. Repts. Tohoku Univ., Ser. 1, 42 (1958) p. 98; p. 113.

13. SAMSAHL K, and SÖREMARK R
ICAA/29, 1961. International Conference on Modern Trends in Activation Analysis, College Station, Texas, U. S. A., December 15-16, 1961, College Station, 1962.

14. GABRIELSON G, and SAMUELSON O
Determination of potassium in the presence of sulfate and phosphate.
Svensk Kem. Tidskr., 62 (1950) p. 221.

15. GEHRKE C W, AFFSPRUNG H E, and LEE Y C
Direct ethylenediamine tetraacetate titration procedure for calcium in biological substances . . . .
Univ. Missouri Coll. Agr., Agr. Expt. Sta., Research Bull., No. 570 (1954).

16. GEHRKE C W, AFFSPRUNG H E, and LEE Y C
Direct ethylenediamine tetraacetate titration methods for magnesium and calcium.
Anal. Chem., 26 (1954) p. 1944.

17. JENNES R
Titration of calcium and magnesium in milk and milk fractions with ethylenediamine tetraacetate.
Anal. Chem., 25 (1953) p. 966.

18. LAPIDUS M, and MELLON E F
Determination of calcium in meat and bone meal.
J. Assoc. Offic. Agr. Chemists, 41 (1958) p. 411.

19. SAMUELSON O
Experiments with solutions containing nitrates and perchlorates.
Svensk Kem. Tidskr., 57 (1945) p. 158.

20. SAMSAHL K
To be published.

Table 1

1 Irradiated material	2 Isotope measured	3 % activity adsorbed
NaCl	Na-24	0
$NH_4H_2PO_4$	P-32	100
KCl	K-42	0
$CaCl_2$	Ca-47	0
Sc_2O_3	Sc-46	96.5
$CrCl_3$	Cr-51	0.8
$MnSO_4$	Mn-56	0
$NiSO_4$	Ni-65	2.7
RbCl	Rb-86	0
$SrCl_2$	Sr-87	0
CsCl	Cs-134	0
$BaCl_2$	Ba-131	0
$La(NO_3)_3$	La-140	0.4
$Ce_2(SO_4)_3$	Ce-141	0.3

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