SovietRxiv

Soviet-era science, translated into English

V. KOURZHIM, A. K. LAVRUKHINA, and S. S. RODIN

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.84449

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

CHEMISTRY

V. KOURZHIM, A. K. LAVRUKHINA, and S. S. RODIN

APPLICATION OF AMMONIUM PHOSPHOTUNGSTATE FOR THE ION-EXCHANGE SEPARATION OF RUBIDIUM AND CESIUM

(Presented by Academician A. P. Vinogradov on 6 IV 1961)

Recently, inorganic compounds, owing to their high radiation stability, have increasingly come to be used as ion-exchange materials. In a number of cases inorganic ion exchangers possess high selectivity and therefore make it possible to separate rapidly and effectively elements with similar chemical properties. For this purpose, in addition to the zeolites and clays used earlier, oxides of metals are now being applied (Al_2O_3, ZrO_2, TiO_2, SnO_2, ThO_2, and others) and certain salts (for example, zirconium tungstate, molybdate, and phosphate) ([1,2]).

The ion-exchange properties of ammonium salts of heteropoly acids have been studied: phosphomolybdic, phosphotungstic, silicomolybdic, silicotungstic, and arsenotungstic acids. A higher exchange capacity and selectivity with respect to individual alkali metals has been found in comparison with organic resins; for example, in $0.1\,N$ ammonium nitrate solutions, for ammonium phosphomolybdate $K_d(\mathrm{Cs}) = 5515$, $K_d(\mathrm{Rb}) = 193$; for ammonium phosphotungstate $K_d(\mathrm{Cs}) = 3950$, $K_d(\mathrm{Rb}) = 134$; and for the organic cation exchanger Dowex-50 $K_d(\mathrm{Cs}) = 62$ and $K_d(\mathrm{Rb}) = 52$ ([9]).

Earlier we attempted to separate the heavy alkali metals (Fr, Cs, and Rb) by coprecipitation with various heteropoly acids ([12–15]). However, the differences in the degrees of coprecipitation found for individual alkali metals were greatly diminished when the indicated metals were present in a mixture. For this reason, quantitative separation of the heavy alkali elements by coprecipitation with heteropoly acids, as well as with other precipitates, was not achieved.

Recently Smith and co-workers published a paper ([10]) on the separation of alkali metals on a column made of ammonium phosphomolybdate. Krtil and Kourzhim ([11]) showed that the chemical stability of ammonium phosphotungstate in neutral and strongly acid media is higher than that of ammonium phosphomolybdate, and that the sorption capacity of the former salt is twice as high as that of the latter. In light of the facts set forth, it was of interest to carry out the separation of the most difficult-to-separate heavy alkali elements on a column packed with ammonium phosphotungstate.

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Particular attention in our work was devoted to the preparation of the column. The preparation of a column from ammonium salts of heteropoly acids is greatly complicated by the very high resistance offered by the microcrystalline salt to the solution passing through it. To reduce the hydraulic resistance of the column it is necessary to use a loose packing material. As such a packing material we used finely fibrous tremolite asbestos, belonging to the group of amphibole asbestoses. This asbestos proved to be the best packing material among those we tested: silica gel, glass fabric, cellulose, and cork powder.

A glass column with an internal diameter of 5 mm and a height of about 30 mm was filled with a suspension of asbestos in a 1 M solution of NH_4NO_3. Through it was passed—

a 0.2 M solution of phosphotungstic acid was passed through, and then a 0.3 M solution of NH_4NO_3; the salt formed was firmly retained by the asbestos fibers. After this, 0.1 ml of a 1 M HNO_3 solution containing Rb^{86} and Cs^{134} was introduced, in the presence of 10^{-4} and 10^{-6} M rubidium and cesium, respectively. Experiments on the sorption of Cs^{134} by asbestos showed that under these conditions only 10% of the introduced activity is sorbed, and this is very easily washed out with water.

For identification of the activities, the method of absorption of β-radiation in an aluminum filter was used. Owing to the large difference in the energies of the β-particles of Rb^{86} (1.79 MeV) and Cs^{134} (0.65 MeV) [16], it was possible to select a filter in which the degree of absorption of the β-radiation of the indicated isotopes differed greatly. The most suitable proved to be a filter of thickness 204 mg/cm^2. The radioactivity of the fractions obtained after separation on the column was measured on an MST-17 end-window counter both with an aluminum filter and without it. With the aid of this counting method it was very simple to identify the rubidium and cesium peaks obtained on the chromatogram and, in cases of their joint elution, to determine rather accurately the relative amounts of each isotope in each fraction from the formulas:

Fig. 1

$$A_{\mathrm{Rb}} = 6.82 \cdot A_{\mathrm{Al}} - 0.31 \cdot A_{\mathrm{tot}}$$

$$A_{\mathrm{Cs}} = 1.31 \cdot A_{\mathrm{tot}} - 6.82 \cdot A_{\mathrm{Al}},$$

where A_{Rb}, A_{Cs} are the activities of Rb^{86} and Cs^{134}, respectively; A_{Al} is the total activity measured with the filter, and A_{tot} is the total activity without the filter.

SovietRxiv

Elution of Rb^{86} and Cs^{134} from the column was carried out with ammonium nitrate solutions of various concentrations in the range from 0.3 M to 10 M. The experiments showed that rubidium is washed out with a 1 M solution of NH_4NO_3, and cesium with a 6 M solution of NH_4NO_3. Effective separation was achieved in 40–45 min. The chromatogram obtained in this case is shown in Fig. 1. For the purpose of separating rubidium and cesium we also tested ammonium salts of other heteropoly acids: silicomolybdic, phosphomolybdic, and silicotungstic. It turned out that rubidium and cesium can also be separated with the aid of ammonium silicomolybdate; however, this salt is more soluble in NH_4NO_3 solutions than ammonium phosphotungstate and therefore is slowly washed from the column during elution. For ammonium phosphomolybdate, chromatograms analogous to those in [10] were obtained. Owing to its high solubility, silicotungstate···

capacity in ammonium nitrate solutions cannot be used for chromatographic separations.

The described method of chromatographic separation on ammonium phosphorotungstate may prove to be very effective for the separation of highly radioactive rubidium and cesium isotopes, owing to the high radiation stability of these salts.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky
Academy of Sciences of the USSR

Received
4 III 1961

REFERENCES

1. K. A. Kraus, H. O. Phillips et al., Second United Nations International Conference on the Peaceful Uses of Atomic Energy 14 (p) 1832, June, 1958.

2. C. B. Amphlett, L. A. McDonald, M. T. Redman, J. Inorg. and Nucl. Chem., 6, 220 (1958).

3. N. Terlet, A. Brian, Aun. Falsific., 28, 546 (1935).

4. L. Gisiger, Zs. anal. Chem., 115, 15 (1938).

5. D. Meier, W. Treadwell, Helv. chim. acta, 34, 155 (1951).

6. H. Buchwald, W. Thistlethwaite, J. Inorg. and Nucl. Chem., 5, 341 (1958).

7. J. van R. Smith, Nature, 181, 1530 (1958).

SovietRxiv

8. J. van R. Smith, W. Robb, I. I. Jucobs, Nucleonics, 17, 116 (1959).

9. J. van R. Smith, I. I. Jucobs, W. Robb, J. Inorg. and Nucl. Chem., 12, 96 (1960).

10. J. van R. Smith, W. Robb, I. I. Jucobs, J. Inorg. and Nucl. Chem., 12, 104 (1960).

11. J. Krtil, V. Kouřim, J. Inorg. and Nucl. Chem., 12, 367 (1960).

12. A. K. Lavrukhina, S. S. Rodin, *Transactions of the Commission on Analytical Chemistry*, 9 (12), 284 (1958).

13. V. Kouřim, A. K. Lavrukhina, *ZhAKh*, 15, no. 3, 272 (1960).

14. A. K. Lavrukhina, A. A. Pozdnjakov, S. S. Rodin, Intern. J. of Appl. Rad. and Isotopes, 9, nos. 1-4, 34 (1960).

15. V. Kouřim, J. Inorg. and Nucl. Chem., 12, 370 (1960).

16. G. Siborg, I. Perlman, D. Hollender, *Table of Isotopes*, IL, 1956.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.