SORPTION OF POLYVALENT ELEMENTS ON SILICA GEL. III.*
ISOLATION OF PROTACTINIUM BY SORPTION ON SILICA GEL FROM THE SOLUTIONS OF HCl AND H_2SO_4

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The sorption of trace amounts of protactinium on silica gel has been studied under dynamic conditions together with the desorption effectiveness of various aqueous and aqueous-organic solutions. The possibility to separate protactinium, zirconium, hafnium and niobium in the hydrochloric or sulphuric acid solutions has been proved experimentally. Protactinium has also been separated from the activated thorium salts and from the uranium ore. The mixture of 30% of 11·5M-HCl and 70% of 2-propanol or 10M-H_2SO_4 can be used for the elution of protactinium adsorbed on the column of silica gel.

The sorption on silica gel is often used for the separation of protactinium from thorium, uranium and from certain fission products as well as for the isolation of the nuclide ^{231}Pa from waste solutions in the uranium ore processing[1-6]. This procedure is very selective, it allows the isolation of protactinium even from very diluted solutions and it can be used also in strongly acid media. In studies published up to the present time a considerable attention has been paid to the sorption of protactinium from nitric acid solutions because this acid is commonly used in the processing of nuclear fuels in aqueous medium. This medium has, however, some disadvantages, firstly because the nitrate ions possess a low complexing ability and, secondly, because the handling with it is connected with complications. The sorption of protactinium from the hydrochloric acid and sulphuric acid solutions is somewhat lower than from the nitrate medium[7]. Nevertheless, the values of distribution coefficients are sufficiently high so that they allow a quantitative sorption of protactinium on a column of silica gel in a wide range of HCl and H_2SO_4 concentrations. An advantage of using these solutions consists mainly in the perfectly reproducible behaviour of protactinium in the course of several months which is undoubtedly connected with the formation of simple and stable complexes.

The aim of this study is to investigate in detail the possibility of protactinium isolation and separation from several other elements in the chloride and sulphate media, respectively.

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EXPERIMENTAL

Reagents and Procedure

The preparation of stock solutions of the radionuclides ^{95}Zr, ^{95}Nb, $^{175,181}Hf$, and ^{233}Pa in 11M-HCl and 10M-H_2SO_4, respectively, has been described elsewhere[7,8]. The solutions containing organic solvents were always prepared immediately before the experiment. Silica gel CH (Spolana, Neratovice) of the specific surface area of 375 m^2/g and of the average granularity of 0·13 mm was used in batch experiments. For reasons alrady discussed[8] silica gel Gw (Grace GmbH, Bad Homburg) of the specific surface area of 340 m^2/g and of the average granularity of 0·07 mm was used in dynamic conditions.

The rate of desorption was determined by shaking 0·1 g of silica gel (with the adsorbed protactinium) with 4 ml of the solution[7]. In certain time intervals 40 µl-samples of the solution were taken and used for the measurement of radioactivity. Columns with the inner diameter of 5 mm and length of 80 mm were used for experiments under dynamic conditions. The column was first poured through with the eluent, than 0·05 ml of the solution of separated elements in 11M-HCl (or 10M-H_2SO_4) was adsorbed on the column top and eluated by the necessary amount of the eluent. In the studies on the desorption effectiveness of eluents a certain amount of protactinium was adsorbed on the colum from 1 ml samples of the solution in 10M-HCl (or 1M-HCl, respectively). In all cases the flow rate was kept within 0·4 and 0·5 ml cm^{-2} min^{-1}. The solution radioactivity was measured with the counter NZQ 612 (Tesla) equipped with the scintillation detector NaJ(Tl). The purity of individual fractions after the separation was controlled by the spectrometer equipped with the semiconductor Ge(Li) and with the 1024-channel pulse height analyzer. The temperature in all experiments was held at 22 ± 2°C.

RESULTS AND DISCUSSION

Sorption from the Hydrochloric Acid Solutions

In preliminary experiments it has been found that protactinium is quantitatively adsorbed on the silica gel column at any concentration of the hydrochloric acid. Protactinium cannot be eluted even by amounts of the hydrochloric acid corresponding to ten bed volumes of the column. The presence of Th, U(VI), and Fe(III) at concentrations lower than 0·5 mol/l has no effect on the sorption. In contrast to zirconium, hafnium and niobium[8] the high sorption ability of protactinium inevitably requires an appropriate eluent. According to[9] protactinium can be eluted either by solutions of strong complexing agents as HF, H_2O_2, $H_2C_2O_4$ and some α-hydroxycarboxylic acids, or by the mixed aqueous–organic solutions (e.g., by a mixture of 9M-HNO_3 with C_2H_5OH (1 : 1) or by n-octyl alcohol saturated with nitric acid). It can be presumed that the use of mixed solutions for the elution of sorbed protactinium offers many advantages because in this case practically all troubles with the complexing agent removal from the eluate disappear. We have therefore decided to study in detail the desorption effectiveness of protactinium by the mixed solutions of hydrochloric acid and organic solvents.

The desorption kinetics of protactinium in batch conditions is given in Fig. 1. The choice of individual solvents and of the mixture compositions is based on the results obtained in our previous study[10]. The desorption kinetics by the solution of 0·05M-$H_2C_2O_4$ has been used for comparison. From these data it is evident that the desorption by the oxalic acid proceeds with a lower rate than that by aqueous–

organic alcoholic solutions. This difference is probably due to a different desorption mechanism. The desorption of protactinium by oxalic acid proceeds *via* the formation of anionic complexes whereas the desorption by the mixed solutions is based on the formation of nonsorbable solvates. The solvate formation rate is evidently greater than the rate of the formation of oxalato complexes.

The results obtained for the desorption under dynamic conditions correspond in principle to those obtained in batch conditions. The protactinium elution curves for various eluents are presented in Fig. 2. From these results it turns out that the mixture of 70% of 2-propanol and 30% of 11·5M-HCl is the most effective eluent. A very narrow elution peak that allows to prepare concentrated solutions of protactinium has been obtained with this eluent. Also the amount of the non-eluated protactinium is very low. A decrease of the alcohol content in the mixture causes a broadening of the elution peak and an increase of the amount of non-eluated protactinium on the column. The use of lower alcohols or acetone has a similar effect.

From Fig. 2 it also follows that protactinium desorption depends also on the medium from which it was adsorbed. This behaviour agrees with the formerly observed "memory-effect" of silica gel[7] and it is evidently caused by the sorption of a a great variety of protactinium complexes, the nature of which depends on the acidity of the solution. From these results it follows that it is better to adsorb protactinium from more concentrated solutions of the hydrochloric acid, *i.e.* from solutions in which its hydrolysis is suppressed.

The other part of this study has been devoted to the separation of protactinium from several other elements. From the practical point of view the possibility of the separation of protactinium from zirconium and niobium is the most interesting because all these elements have a very similar behaviour. From the comparison of sorption properties of the mentioned elements it follows that a good choice of the composition of the eluent allows their complete separation. Examples of the separation procedures are presented in Figs 3—5. The composition of individual solutions has been chosen using the already published results[8].
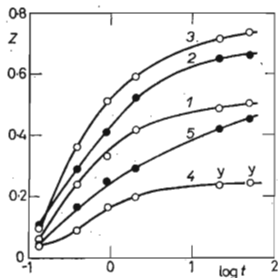
FIG. 1

Desorption Kinetics of Protactinium under Batch Conditions

The composition of desorption solutions: *1* 70% of 11M-HCl +30% of ethanol; *2* 30% of 1-propanol; *3* 30% of 2-propanol; *4* 30% of acetone; *5* 0·05M-$H_2C_2O_4$. Z the fraction of desorbed Pa, t the desorption time, h. Protactinium was adsorbed from 11M-HCl. Silica gel CH, granularity 0·13 mm. *y* yellow solution.

The separation of protactinium from elements that cannot be adsorbed on silica gel from an acid solution is substantially simpler. The isolation of the radionuclide ^{233}Pa from thorium activated by neutrons represents the most frequent example of this problem. It has been found that for this purpose it is sufficient to dissolve the irradiated oxide or thorium(IV) nitrate in the hydrochloric acid and to pour this solution through the column of silica gel. After washing the column with the hydrochloric acid solution (which removes completely this present thorium) protactinium can be eluted by an appropriate eluent. The hydrochloric acid concentration used in sorption solutions and for the washing out of the column can range from $1-12$M-HCl. From reasons mentioned above it is, however, more suitable to use more concentrated solutions of the acid. Similarly, the concentration of thorium has also a small effect on the separation and on the final yield. In the case when protactinium was adsorbed from the 5M-HCl solution and the mixture of 11·5M-HCl and 2-propanol (3 : 7) has been used as the eluent, the separation yield amounted to 92%.
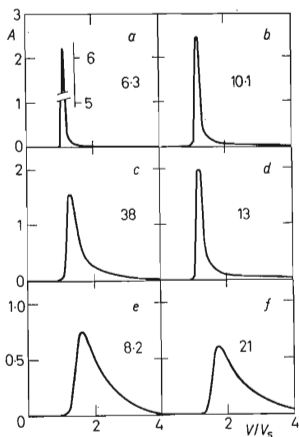
Fig. 2

Desorption of Protactinium under Dynamic Conditions

The composition of eluents: 30% of 11·5M-HCl + 70% of 2-propanol (a,b); 70% of acetone (c); 70% of ethanol (d); 70% of 11·5M-HCl + 30% of 2-propanol (e); 0·05M-$H_2C_2O_4$ (f). Protactinium was adsorbed from 10M-HCl (a,c—f); from 1M-HCl (b). Numbers at curves indicate the amount of Pa (in %) adsorbed on the column after washing-out of 5 free volumes of the column. Silica gel Gw, granularity 0·07 mm. A the eluate activity (10^3 cpm), V the volume of the solution poured through the column, V_s the free volume of the column.
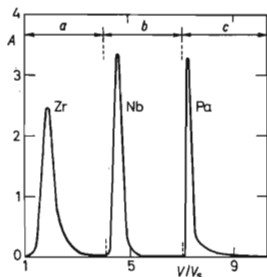
FIG. 3

Separation of Zr, Nb, and Pa on the Silica Gel Column

The composition of eluents: *a* 7·1M-HCl; *b* 11·5M-HCl; *c* 30% of 11·5M-HCl + 70% of 2-propanol. Silica gel Gw, granularity 0·07 mm, protactinium was adsorbed from 11M-HCl. For the ordinate- and abscissa notation *cf.* Fig. 2.
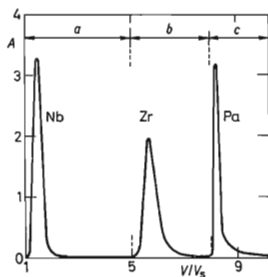

FIG. 4

Separation of Nb, Zr, and Pa on the Silica Gel Column

The composition of eluents: *a* 90% of 1M-HCl + 10% of dioxane; *b* 11·5M-HCl; *c* 30% of 11·5M-HCl + 70% of 2-propanol. Silica gel Gw, granularity 0·07 mm, protactinium was adsorbed from 11M-HCl. For the ordinate- and abscissa notation *cf.* Fig. 2.
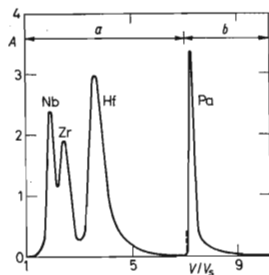

FIG. 5

Separation of Nb, Zr, Hf, and Pa on the Silica Gel Column

The composition of eluents: *a* 90% of 11·5M-HCl + 10% of methanol; *b* 30% of 11·5M-HCl + 70% of 2-propanol. Silica gel Gw, granularity 0·07 mm, protactinium was adsorbed from 11M-HCl. For the ordinate- and abscissa notation *cf.* Fig. 2.
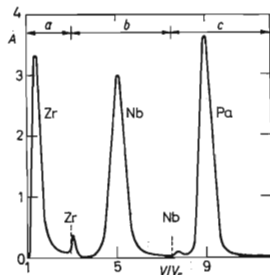

FIG. 6

Separation of Zr, Nb, and Pa on the Silica Gel Column

The composition of eluents: *a* 1M-H_2SO_4; *b* 5M-H_2SO_4; *c* 10M-H_2SO_4. Silica gel Gw, granularity 0·07 mm, protactinium was adsorbed from 11M-HCl. For the ordinate- and abscissa notation *cf.* Fig. 2.

Protactinium and uranium can be separated by an analogous procedure. This method can be employed *e.g.* for the isolation of the natural isotope ^{231}Pa. In order to test this method a known amount of the radionuclide ^{233}Pa was added to 1 g of the uranium concentrate (with 10% of uranium) and the ore was dissolved in the mixture of concentrated HNO_3 and HCl (1 : 3). The precipitate of the silicic acid was dissolved in 40% HF and, after the removal of the insoluble residue, the solution was several times evaporated with the concentrated hydrochloric acid on a teflon dish. The combined filtrates of the total volume of 15 ml were poured through the column of silica gel. The column was then washed out by the 11·5м-HCl and protactinium eluated by the mixture of the hydrochloric acid and 2-propanol. The yield amounted to 83%.

The Sorption from Sulphuric Acid Solutions

The sorption of protactinium on silica gel from the sulphuric acid solutions gradually decreases with the increasing concentration of the acid so that from 10м-H_2SO_4 it is not adsorbed on the column[7]. This fact allows not only an effective separation of protactinium from several other elements but also the desorption of protactinium directly by the sulphuric acid solutions. An example of the separation of protactinium, zirconium and niobium is presented in Fig. 6. The sulphuric acid concentration in the solutions used for the elution of zirconium and niobium is based on the results of our preceding studies[7,11]. An analogous procedure can be used also for the protactinium separation from thorium and uranium that are not sorbed on silica gel from the sulphuric acid solutions.

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