

SORPTION OF POLYVALENT ELEMENTS ON SILICA GEL. IV.*

SEPARATION OF THE TETRAVALENT AND PENTAVALENT PROTACTINIUM

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The possibility of the tetravalent and pentavalent protactinium separation on silica gel has been studied and it has been found that in the presence of hydrochloric and sulphuric acids the protactinium adsorbed on the silica gel column is reduced and washed out by chromium(II) solutions whereas the non-reduced fraction of protactinium remains adsorbed on the column. The method has been tested with trace amounts of the ^{233}Pa nuclide. It has been found that under similar conditions the elution of niobium from silica gel proceeds only partly.

Haissinsky and Boussieres^{1,2} prepared tetravalent protactinium in aqueous solutions by the reduction of acid solutions of Pa(V) by the zinc amalgam. Pa(IV) was separated from Pa(V) by the coprecipitation with lanthanum fluoride. Although very effective⁴, this procedure is rather complicated and the product might be contaminated by other elements, namely by the fluoride ions. In the preceding papers the protactinium sorption on silica gel from the hydrochloric and sulphuric acid solutions has been studied in detail^{5,6}. It has been found that Pa(V) is quantitatively sorbed on the column of silica gel from the 1-12M-HCl or 1-8M-H₂SO₄ solutions. However, the comparison of these results with the analogous data for other tetravalent elements (Zr, Hf) shows substantial differences in their behaviour that allows their separation. Because Pa(IV) is a typical analogue of these elements as regards the formation of chloro and sulphato complexes as well as their hydrolytic reactions, an easy separation of the tetra- and pentavalent forms of protactinium on the silica gel column can be presumed.

The aim of this work is to study the possibility of the separation of Pa(V) and Pa(IV) using the sorption on silica gel and to work out a simple method for the preparation of the tetravalent protactinium solutions that could be used for further studies without any other processing.

EXPERIMENTAL

All the reagents used were of the analytical grade purity. The preparation of stock solutions of ^{233}Pa and ^{95}Nb was described elsewhere^{5,6}, together with the experimental procedures used. The liquid amalgam was prepared by heating 3 g of the granulated zinc with 100 g of mercury in the presence of sulphuric acid, diluted in the ratio 1 : 10. The amalgamated zinc was prepared by addition of few drops of mercury to the granulated zinc also in the presence of sulphuric acid.

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The chromatographic columns of the inner diameter of 5 mm were filled with silica gel with wide pores (Grace GmbH, Bad Homburg), of the specific surface area of $340 \text{ m}^2/\text{g}$ and of the granularity of 0.07 mm. The silica gel column height was 8 cm, the flow rate was $0.4 \text{ ml cm}^{-2} \text{ min}^{-1}$.

RESULTS

The solutions of trace amounts of ^{233}Pa in 6M-HCl, containing 10^{-2} mol of Cr(III), was first reduced in the nitrogen atmosphere by the amalgamated zinc for about 1 hour. The reduction vessel was connected by a stop-cock with the chromatographic column. The completion of reduction was signaled by the change of the solution colour from green to light blue. The solution was then poured through the column that was previously washed by the reduced solution of the same composition which, however, did not contain any protactinium. At the end of the procedure the column was again washed with the 10^{-2}M solution of Cr(II) in 6M-HCl. It has been found that under these conditions about 85–90% of protactinium passes through the column. The sorption of protactinium from the non-reduced solution is, however, quantitative. In an other series of experiments protactinium was first adsorbed from the 6M-HCl solution on the silica gel column and then it was eluted by the 10^{-2}M solution of Cr(II) in 6M-HCl. The elution solution was prepared separately by reduction with the liquid amalgam and the column was filled by a special pipette for handling the solutions in an inert atmosphere.

Results of these experiments are presented in Table I. It is evident that even in this case protactinium is reduced and eluted from the column. The shape of the curve in Fig. 1 indicates a considerable velocity of the reduction process. An overwhelming part of the formerly sorbed radioactivity is eluted immediately after the free volume of the column. The somewhat extended tail of the elution curve is most probably caused by the diffusion of protactinium from the less accessible pores of silica gel. Analogous results have also been obtained for the elution of presorbed protactinium using as the eluent the solution of the same composition but prepared in the Jones reductor. In all three experiments the Cr(II) ions act not only as the reducing agent but also as a stabilizer of Pa(IV) (ref.⁴).

Because the separation using the reduction of the adsorbed protactinium is substantially simpler, only this method has been used in all subsequent experiments. The results of experiments, in which the elution effectiveness of reducing solutions of vari-

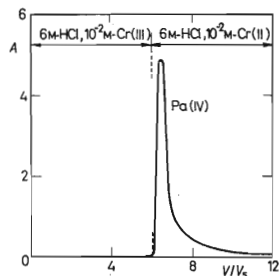


FIG. 1

Elution of Protactinium by Cr(II) Solution in 6M-HCl

A the radioactivity of the eluate (in 10^3 cpm), V the volume of the solution that passes through the column, V_s the free volume of the column. Pa(V) was presorbed on the column from 1 ml of 6M-HCl.

ous compositions was studied, are presented in Table I. The shapes of the elution curves are in all these cases analogous to those of Fig. 1. It is evident from the table that the elution of protactinium by solutions of Cr(II)-salts is satisfactory whereas the V(II)-salts do not eluate protactinium. What remains so far unsolved is the problem of the applicability of the proposed procedure for the separation of macro-amounts of protactinium in different valence states. For this purpose rather high, for us unattainable, amounts of the nuclide²³¹Pa should have been used.

Several experiments with the reduction of presorbed niobium were done for comparison. This element exists also in several valence states⁷ and in its pentavalent state it is practically quantitatively sorbed on silica gel from the solutions⁸ of 1–8M-HCl. From Table I it follows that in this case it is evidently reduced by both Cr²⁺ and V²⁺ ions but, on the other hand, the desorption does not proceed quantitatively. This behaviour can be conceivably explained by the assumption that under the given conditions niobium is present in several different chemical forms and that only a certain part of it can react with the reducing agent and can be eluated. Because the desorption effectiveness increases with the increasing concentration of the hydrochloric acid, we assume that the reduction of niobium is affected by its partial hydrolysis.

TABLE I
Reduction of Pa and Nb under Dynamic Conditions
6M-HCl was used as medium in most experiments.

Pa		Nb	
Reducing agent 10 ⁻² M	Reduced form ^a in the eluate, %	Reducing agent 10 ⁻² M	Reduced form ^a in the eluate, %
Cr(II)	95 ^b	Cr(II)	28
Cr(II) ^c	96	V(II)	13
V(II)	1	Cr(II) ^e	75
Cr(II) ^d	92	V(II) ^e	20

^a After passing five free volumes of the column; ^b the average value of three experiments; ^c 11.5M-HCl; ^d 3M-H₂SO₄. ^e 8M-HCl.

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