

SORPTION OF THE POLYVALENT ELEMENTS ON SILICA GEL. I.  
SORPTION OF PROTACTINIUM ON SILICA GEL  
FROM SOLUTIONS OF HCl AND H<sub>2</sub>SO<sub>4</sub>

R. CALETKA

*Nuclear Research Institute,  
Czechoslovak Academy of Sciences, Prague-Řež*

Received November 10th, 1970

The sorption of protactinium on silica gel from hydrochloric and sulphuric acid solutions has been investigated in order to establish the effect of the silica gel structure and of the composition of the aqueous phase on the sorption of protactinium and the kinetics of sorption and desorption of protactinium. The uptake of protactinium from hydrochloric acid solutions can be attributed to the sorption of neutral complexes of the type  $\text{Pa}(\text{OH})_n\text{Cl}_{5-n}$  (1–10M-HCl) and  $\text{H}_{x-5}\text{PaCl}_5$  (>10M-HCl,  $x = 6-8$ ). In dilute sulphuric acid solutions the adsorption of sulphato hydroxo complexes is to be expected while in the concentration range from 3 to 7M-H<sub>2</sub>SO<sub>4</sub> the adsorption of neutral bisulphato complexes of protactinium is assumed.

The silica gel has often been used as an adsorbent for the recovery of protactinium from acid solutions and for its separation from thorium, uranium and several fission products<sup>1-6</sup>. However, the sorption of protactinium on silica gel has not yet been studied in more detail except of the recent studies of the dependence of sorption on the concentration of several mineral acids<sup>7,8</sup>, the effect of other elements<sup>9</sup> and the sorption in the presence of various complexing agents<sup>10,11</sup>. The review of papers dealing with these problems is listed also in the monograph of Palshin and coworkers<sup>12</sup>.

Until now the sorption of protactinium from the solutions of nitric acid has been studied predominantly. Substantially lower attention has been devoted to the sorption from the solutions of other mineral acids. The main reason for this state of affairs can be seen in the fact that the nitric acid is the most common electrolyte in the processing of nuclear fuels in aqueous solutions in which protactinium is isolated. The behaviour of protactinium in nitric acid solutions is considerably influenced by the hydrolytic reactions that complicate the separation processes. For this reason we have decided to study in detail the sorption of protactinium from solutions of hydrochloric and sulphuric acids that have a higher complexing ability and are better known at the present time<sup>13</sup>.

## EXPERIMENTAL

## Reagents

The carrier-free amount of the nuclide  $^{233}\text{Pa}$  was prepared by irradiation of 10 mg of thorium(IV)-nitrate by thermal neutrons for 7 days in the nuclear reactor of the Nuclear Research Institute in Řež at a neutron flux of  $4 \cdot 10^{14}$  neutrons per  $\text{cm}^2$ . Protactinium was isolated from the target material by the method of Davydov and Palshin<sup>14</sup>. The stock solutions of protactinium in  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  were prepared by decomposition of the oxalic acid with concentrated nitric acid and 30% hydrogen peroxide followed by repeated evaporation with the respective acid. The acidity of the solutions was then adjusted to about 10–12M. These stock solutions were used after more than two weeks' storage at a room temperature to ensure equilibria between the individual complexes of protactinium.

Some properties of the various types of silica gel are given in Table I. Prior to experiments silica gel was fractionated by sedimentation in water and then purified by washing with concentrated hydrochloric acid and distilled water. The resulting products were dried at  $110^\circ\text{C}$  for 24 hours.

All acids used of the analytical grade purity. The solutions of hydrochloric acid of concentrations higher than  $11.5 \text{ mol l}^{-1}$  were prepared by additional saturation with gaseous hydrogen chloride.

## Procedure

The batchwise adsorption measurements in static conditions were performed by shaking 2 ml of the aqueous phase with 0.05 g of silica gel (granularity 0.10 mm) in polyethylene stoppered glass tubes. The solutions were prepared by mixing the respective components in the following order: distilled water, acid and the stock solution of protactinium. Unless it was otherwise stated, the stock solution of protactinium was added in the presence of silica gel.

The values of distribution coefficients,  $K_d$  (ml/g) were determined from the difference in the radioactivity before and after adsorption runs. The resulting data were the averages of two measurements.

TABLE I

Properties of the Used Kinds of Silica Gel

A Data of the manufacturer; B determined by the author using the argon sorption method BET.

Notation	Manufacturer	Spec. surface, $\text{m}^2/\text{g}$		Pore diameter, Å
		A	B	A
CH	Spolana, Neratovice, ČSSR	400	375	80
Gw	Grace GmbH Bad Homburg	350	340	115
Ge	Grace GmbH Bad Homburg	800	780	21
HR	E. Merck AG, Darmstadt	—	315	—

The sorption kinetic was measured under analogous conditions: the samples containing 0.1 g of silica gel (granularity 0.13 mm) were shaken with 4 ml of the aqueous phase. The moment of addition of protactinium was taken as the starting point of the sorption. Samples of 40  $\mu$ l were taken from the aqueous phase in adequate time intervals for the radioactivity measurements. The change of the ratio of the weight of the solid phase to the volume of the liquid phase can be neglected because of the small volumes of the samples (about 1% of the total volume of the liquid phase).

The concentration of protactinium in the aqueous phase was determined radiometrically using the NZQ 612 counter (Tesla) with NaJ(Tl) scintillator. The specific activity of used solutions was about  $5 \cdot 10^4$  cpm/ml, in kinetic studies the solutions ten times more concentrated were used. The statistic error of measurements was of about 5%. The deviations from the mean value of  $K_d$  did not exceed  $\pm 7\%$ . Experiments were carried out at the temperature  $22 \pm 2^\circ\text{C}$ .

## RESULTS

The effect of the mineral acid concentration of the values on  $K_d$  determined for the sorption of protactinium under static conditions are given in Figs 1–3.

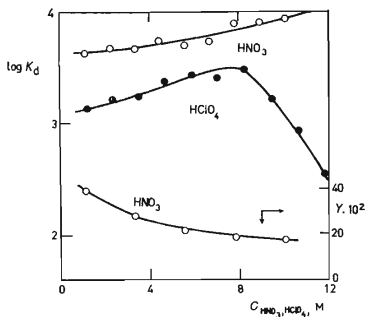


FIG. 1

The Distribution Coefficient of Protactinium as a Function of the Concentration of Nitric and Perchloric Acids

$C_{\text{HNO}_3}, C_{\text{HClO}_4}$  Initial molar concentration of  $\text{HNO}_3$  and  $\text{HClO}_4$ , respectively, in the solution;  $K_d$  the distribution coefficient;  $Y$  the fraction of protactinium sorbed on the walls of probes. The ratio of the liquid and solid phases  $V/m = 40$  ml/g, sorption time  $t = 75$  hours;  $T = 22 \pm 2^\circ\text{C}$ . Silica gel CH, granularity 0.10 mm.

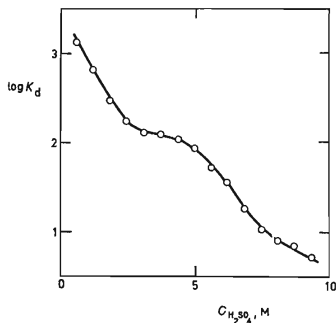


FIG. 2

The Distribution Coefficient of Protactinium as a Function of the Sulphuric Acid Concentration

$C_{\text{H}_2\text{SO}_4}$  Initial molar concentration of the sulphuric acid in the solution. All other notation and conditions are the same as in Fig. 1.

The highest uptake can be observed from the nitric or perchloric acid solutions. The  $\log K_d$  vs  $C_{\text{HNO}_3}$  plots show a slight increase with the concentration of acid in the range from 1 to 11M- $\text{HNO}_3$ . For the sorption from the perchloric acid solutions a pronounced maximum has been found at 8M- $\text{HClO}_4$ . The sorption of protactinium from the sulphuric acid solutions decreases with the increasing concentration of the acid. In the range of 3 to 7M- $\text{H}_2\text{SO}_3$  a distinct plateau can be observed. In the hydrochloric acid the values of  $K_d$  also decrease with the increasing  $C_{\text{HCl}}$ . However, a minimum was found in the range of 9 to 10M- $\text{HCl}$  and the further increase of the acid concentration causes again an increase of the sorption.

The sorption from the hydrochloric acid solutions has been studied in detail using several types of silica gel with different specific surface areas (or with different pore sizes). It has been found that the character of the dependence of  $\log K_d = f(C_{\text{HCl}})$  is practically the same for the sorption on silica gel with the medium-size and large-size pores. If silica gel with narrow pores is used for sorption from diluted solutions, the protactinium sorption is relatively smaller. However, in the concentrated solutions the values of  $K_d$  increase proportionally with the increasing specific surface of the silica gel.

The sorption of protactinium on silica gel from the hydrochloric acid solutions is most probably a reversible process. This is witnessed by the fact that during the desorption (in the course of 75 hours) practically the same results have been obtained as for sorption in the whole studied range of  $C_{\text{HCl}}$  so that it does not depend on the way by which the system reaches equilibrium. These data are not given in Fig. 3. Somewhat lower values of  $K_d$  (Fig. 3, curves 2 and 6) have been obtained for diluted solutions with  $C_{\text{HCl}} < 5 \text{ mol l}^{-1}$  if the protactinium solutions were put into the contact with silica gel 24 hours after their preparation. These therefore seem to depend on the length of the period of aging. The sorption of protactinium is, however, independent of the age of solutions if solutions of the concentration  $> 5\text{M-HCl}$  are

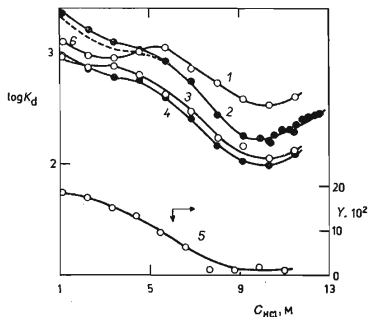


FIG. 3

The Distribution Coefficient of Protactinium as a Function of the Hydrochloric Acid Concentration

1 silica gel Ge, 2 silica gel CH, 3 silica gel Gw, 4 silica gel HR, 5 sorption on the probe walls, 6 (the dashed curve) — sorption on silica gel CH from solutions prepared 24 hours before the experiment.  $C_{\text{HCl}}$  the initial molar concentration of the hydrochloric acid. All other notation and conditions are the same as in Fig. 1.

used. It must be emphasized that protactinium stored in 11M-HCl or in 10M-H<sub>2</sub>SO<sub>4</sub> did not change its sorption properties in the course of two months.

The data on the sorption of protactinium on the probe walls in the absence of silica gel are also given in Figs 1 and 3. Protactinium is significantly sorbed on glass only from diluted hydrochloric acid solutions. The sorption on glass from the nitric acid solution is somewhat higher in the whole range of concentrations studied. As can be seen from these results, the loss in radioactivity due to the sorption on glass does not significantly affect the above results. The sorption from nitric acid and perchloric acid was measured only for comparison and therefore the results will not be discussed.

In addition to these experiments also the kinetics of sorption and desorption from the hydrochloric and sulphuric acid solutions has been studied. The sorption kinetics of protactinium on silica gel CH is given in Fig. 4. The sorption is fastest in concentrated solutions. The differences are, however, small so that after 1–2 hours of mixing of the two phases the sorption equilibrium is achieved practically in all cases. Substantially slower kinetics has been observed for the sorption on silica gel with narrow pores (Fig. 5). In this case the equilibrium has been achieved only after 10–15 hours which is much more than for the silica gel CH.

The interpretation of certain results requires to find the dependence of the desorption kinetics of protactinium on the concentration of the acid from which pro-

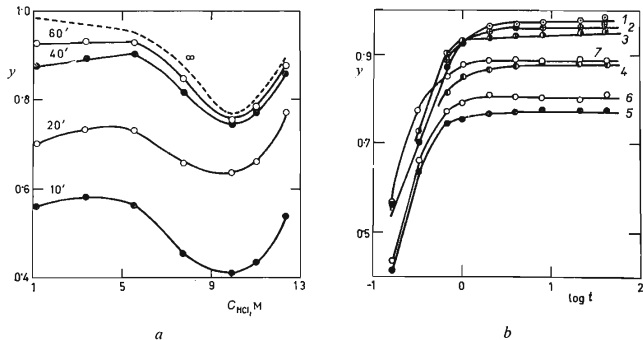


FIG. 4

The Sorption Kinetics of Protactinium on Silica Gel CH from the Hydrochloric Acid Solutions

$y$  The fraction of protactinium sorbed on silica gel,  $t$  the sorption time (hours),  $V/m = 40$  ml/g,  $T = 22 \pm 2^\circ\text{C}$ . *a*: The numbers at curves indicate the sorption time  $t$  (min), the dashed curve gives the mean value of  $y$  after a long shaking of the liquid and solid phases. *b*: 1 1.1M-HCl; 2 3.3M-HCl; 3 5.5M-HCl; 4 7.7M-HCl; 5 9.9M-HCl; 6 11M-HCl; 7 12.3M-HCl.

tactinium had been sorbed. The results obtained for the desorption by 9.9M-HCl are given in Fig. 6. It turns out that the sorption conditions have a substantial effect on the kinetics of desorption. The value of the distribution coefficient after a long-term desorption (*i.e.* in the equilibrium) is not influenced by the concentration of the solution used in sorption.

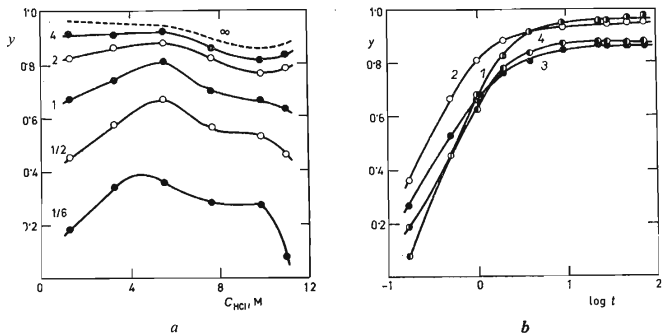


FIG. 5

The Sorption Kinetics of Protactinium on Silica Gel Ge from the Hydrochloric Acid Solutions

For the experimental sorption conditions *cf.* text to Fig. 4. *a*: The numbers at curves indicate the sorption time  $t$  (hours), the dashed curve gives the mean value  $y$  after a long shaking of the liquid and solid phases. *b*: 1 1.1M-HCl; 2 5.5M-HCl; 3 9.9M-HCl; 4 11M-HCl.

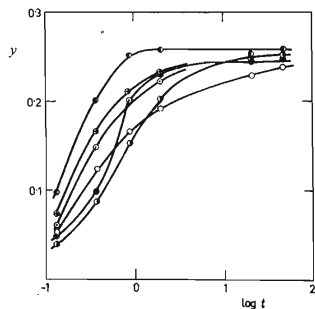


FIG. 6

The Desorption Kinetics of Protactinium Sorbed from the Hydrochloric Acid Solutions of Various Concentrations

$Z$  fraction of the desorbed protactinium;  $t$  the desorption time (hours),  $V/m = 40$  ml/g;  $T = 22 \pm 2^\circ\text{C}$ . Silica gel CH, granularity 0.13 mm. The hydrochloric acid concentration:  $\otimes$  1.1,  $\circ$  3.3,  $\bullet$  5.5,  $\ominus$  7.7,  $\circ$  9.9,  $\oplus$  12.0M. The desorption has been done in all cases with the 9.9M-HCl.

The sorption kinetics from the sulphuric acid solutions is presented in Fig. 7. The equilibrium is established within 30 minutes at the acid concentrations  $> 5\text{M-H}_2\text{SO}_4$ , in more diluted solutions within 2–3 hours. The change of the sorption rate appears in a relatively narrow region of the sulphuric acid concentrations in the region of the plateau of the curve in Fig. 2.

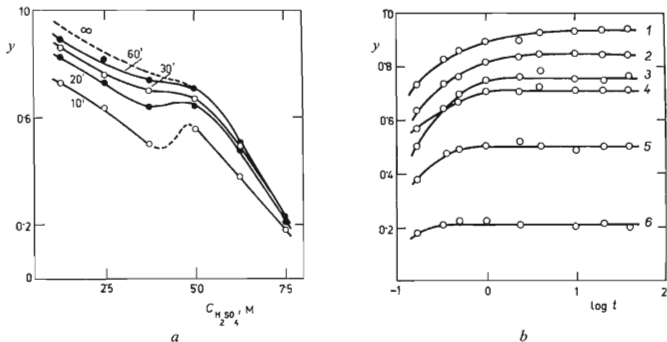


FIG. 7

The Sorption Kinetics of Protactinium on Silica Gel CH from the Sulphuric Acid Solutions

The sorption conditions were the same as in Fig. 4. *a*: The numbers at curves indicate the sorption time  $t$  (min), the dashed curve gives the mean value of  $y$  after a long shaking of the liquid and solid phases. *b*: 1 1.25M- $\text{H}_2\text{SO}_4$ ; 2 2.5M- $\text{H}_2\text{SO}_4$ ; 3 3.75M- $\text{H}_2\text{SO}_4$ ; 4 5.0M- $\text{H}_2\text{SO}_4$ ; 5 6.25M- $\text{H}_2\text{SO}_4$ ; 6 7.5M- $\text{H}_2\text{SO}_4$ .

## DISCUSSION

The mechanism of sorption, *i.e.* the processes of the adsorption of metal complexes present in the solution on silica gel, is not well known. Åhrland and coworkers<sup>15</sup> assume that the sorption on silica gel is due to a simple ion exchange. However, some other data obtained in sorption studies of the easily hydrolyzing elements<sup>16,17</sup> are incompatible with this assumption. According to Davydov<sup>8</sup>, protactinium is sorbed as neutral molecules formed in the hydrolytic reactions (so-called "hydrolytic sorption"). The relatively strong bond of hydroxo complexes of protactinium with silica gel is explained by Davydov as due to the ol-type bridges  $-\text{Si}-\text{O}-\text{Pa}-$ . Nevertheless, even the "hydrolytic sorption" cannot successfully explain all the experimental results. This refers especially to the plateau of the curve in 3–7M- $\text{H}_2\text{SO}_4$ , to the increase of  $K_d$  in the concentrated hydrochloric acid and to the results obtained in desorption studies.

This is why it seems worthwhile to find out a relation between the sorption and the properties of sorbate in the corresponding medium. However, only qualitative data are available on the behaviour of protactinium in mineral acid solutions, namely on the probable composition of the complexes and on the approximate concentration limits of the corresponding acid.

The most probable composition of protactinium complexes depending on the hydrochloric acid concentration is as follows<sup>13</sup>:

1–3M-HCl	$\text{PaOOH}^{2+}$ , $\text{PaO(OH)Cl}^+$ , $\text{Pa(OH)}_3\text{Cl}^+$ , $\text{Pa(OH)}_2\text{Cl}_2^+$ , $\text{PaOHCl}_3^+$
~ 4M-HCl	$\text{PaOOHCl}_2$ , $\text{PaOCl}_3$ , $\text{Pa(OH)}_2\text{Cl}_3$ ,
5–10M-HCl	$\text{PaOOHCl}_3^-$ , $\text{PaOCl}_4^-$ , $\text{Pa(OH)}_2\text{Cl}_4^-$ , $\text{PaOCl}_5^{2-}$ , $\text{PaOHCl}_5^-$ , $\text{PaOHCl}_6^{2-}$
≥ 10M-HCl	$\text{PaOCl}_6^{3-}$ , $\text{PaCl}_6^-$ , $\text{PaCl}_7^{2-}$ , $\text{PaCl}_8^{3-}$

From the comparison of these results with Fig. 3 it follows that the highest values of  $K_d$  and at the same time also the lowest sorption rate have been found in that concentration range of the acid where the hydroxo complexes are the most abundant. On the other hand, the increase of adsorption in 10M-HCl is connected with the formation of non-hydrolyzed chloro complexes of protactinium.

From the overall course of sorption from the hydrochloric acid solutions and from the data on the sorption and desorption kinetics it can be concluded that at least two different kinds of protactinium complexes take part in the sorption. Their probable composition and the corresponding limits of acid concentrations can be estimated as follows:

In the region 1–10M-HCl neutral hydroxo chloro complexes of the type  $\text{Pa(OH)}_n \cdot \text{Cl}_{5-n}$  are being adsorbed. The value of  $n$  decreases gradually with the increasing acidity of the solution. At the same time the hydration of the complex increases and this seems to be main reason for the decrease of sorption. The lower sorption of protactinium on silica gel with narrow pores can be explained by the "grating effect". It seems that there is no definite limit between the individual  $\text{Pa(OH)}_n \cdot \text{Cl}_{5-n}$  complexes. Their adsorption shifts the chemical equilibrium in the solution. This shift is the higher the lower is their relative abundance. The effect of the gradual establishment of the chemical equilibrium is illustrated in Fig. 5a. In the first moments of sorption a small maximum is formed in dilute solutions and this is shifted toward higher concentrations of the hydrochloric acid. Because individual solutions were prepared by the dilution of the stock solution of protactinium already in the presence of silica gel, the curves in Figs 4–6 reflect not only the diffusion processes connected with the interphase transport of the sorbate but also some chemical processes. Comparing Fig. 4 and Fig. 5 we may conclude that the rate of the establishment of the chemical equilibrium is higher than the diffusion rate of the sorbate into the silica gel grains.



In the hydrochloric acid solutions of concentrations higher than 10M the complexes of the type  $\text{PaCl}_x^{5-x}$  ( $x = 6-8$ ) are predominant. It can be assumed that the increased sorption ability of protactinium in this medium is due to the sorption of associated molecules  $\text{H}_{x-5}\text{PaCl}_x$ . The high concentration of the hydrochloric acid is probably the reason not only for the formation of complexes with the high number of ligands and for the association of the chloroprotactinic acid, but also for their salting out into the solid.

Also the data of Fig. 6 indicate the sorption of several complex species. They indicate a "memory-effect" of silica gel for the concentration of the hydrochloric acid used for the sorption (the composition of the sorbed complex of protactinium). This effect has already been observed in the case of zirconium sorption<sup>15</sup>. It is remarkable that the desorption of protactinium sorbed from 9.9M-HCl is the slowest. There is no plausible explanation for this effect.

From the above mentioned results it follows that the sorption of protactinium is due to the molecular sorption of completely or partly hydrolyzed complexes as well as complexes not containing hydroxyl groups as ligands. Therefore Davydov's assumption on the formation of ol-bridges  $-\text{Si}-\text{O}-\text{Pa}-$  seems very improbable. A similar bond sorbate-sorbent would be rather stable and the desorption of protactinium would be hindered. Moreover, in concentrated solutions the conditions for olation are rather unfavourable. However, it is possible that ol-bridges are formed during the "aging" of sorbed protactinium, or, eventually, during the drying of silica gel with the sorbed protactinium.

At the present time the solutions of protactinium in sulphuric acid are much less studied than the chloride solutions. It is therefore much more difficult to seek a correlation between the amount of protactinium bound in complexes and its sorption. In the analysis of the results obtained for the sorption of protactinium from 3-7M  $\text{H}_2\text{SO}_4$  (Fig. 2) the horizontal section on the curve connected with the change of sorption rate (Fig. 7) is notable. Other analogous elements (Nb, Ta) behave similarly during the sorption on silica gel<sup>17</sup>. From the work<sup>18</sup> it follows that in the above-mentioned region of  $C_{\text{H}_2\text{SO}_4}$  the hydration of bisulphate anions  $\text{HSO}_4^-$ , that prevail at these concentrations of the sulphuric acid, sharply decreases. Therefore the characteristic shape of the curve in Fig. 2 can be explained by the sorption of neutral bisulphato complexes of protactinium that can be characterized by a lower number of water molecules in its hydration shell. This assumption is corroborated by the fact that the maxima plateau on curves of  $\log K_d = f(C_{\text{H}_2\text{SO}_4})$  in the sorption of niobium, tantalum and protactinium are all in approximately the same region of  $C_{\text{H}_2\text{SO}_4}$  regardless of the differences in the chemical nature of these elements. In more diluted solutions of the sulphuric acid we may expect - similarly as in the hydrochloric acid - the sorption of mixed hydroxosulphato complexes. In contrast to the solutions in hydrochloric acid, in the sulphate solutions protactinium is not salted out but the sorption ratio decreases practically to zero.

The author would like to express his gratitude to Dr C. Konečný for valuable comments to this work and to Dr M. Poděšíl and Mrs V. Novotná for their readiness to help with the measurements of the specific surfaces of sorbents.

## REFERENCES

1. Salutsky M. L., Shaver K., Elmlinger A., Curtis M. L.: J. Inorg. Nucl. Chem. 3, 289 (1956).
2. Hardy J. C., Scargill D., Fletcher I. M.: J. Inorg. Nucl. Chem. 7, 257 (1958).
3. Moore J. G., Rainey R. H.: Proc. of the Protactinium Chemistry Symposium, Gatlinburg, Tennessee, April 25–26, 1963; USAEC Rep. TID 7675 (1963).
4. Spicyn V. I., Ďáčková P. A.: Dokl. Akad. Nauk SSSR 134, 1111 (1965).
5. Sakanoue M., Abe M.: Radioisotopes Tokyo 16, 645 (1967); NSA 22, 8196 (1968).
6. Spicyn V. I., Ďáčková R. A., Kamenskaja N. A.: Dokl. Akad. Nauk SSSR 184, 379 (1969).
7. Scherff H. L.: Radiochim. Acta 2, 141 (1964).
8. Davydov A. V., Marov I. N.: *Sbornik Soosaždenie i Adsorbicija Radioaktivnych Elementov*, p. 134. Izd. Nauka, Moscow 1965.
9. Davydov A. V., Marov I. N.: Palej P. N.: *Physico-Chimie du Protactinium*, No 154, p. 181, CNRS, Paris 1966.
10. Davydov A. V., Mjasojedov B. F., Novikov Yu. P., Palej P. N., Palšin E. S.: *Trudy Komissii Anal. Chim.* 15, 64 (1965).
11. Davydov A. V., Marov I. N. Palej P. N.: *Ž. Neorg. Chim.* 11 1316 (1966).
12. Palshin E. S., Myasoyedov B. F., Davydov A. V.: *Analitičeskaja Chimia Protaktinia*. Izd. Nauka, Moscow 1968.
13. Guillaumont R., Bouissieres G., Muxart R.: *Actinides Rev.* 1, 135 (1968).
14. Davydov A. V., Palšin E. S.: *Trudy Komissii Anal. Chim.* 15, 368 (1965).
15. Ahrlund S., Grenthe I., Noren B.: *Acta Chem. Scand.* 14, 1059 (1960).
16. Caletka R., Kyrš M.: *This Journal* 29, 1150 (1964).
17. Caletka R.: *Radiochimia* 12, 448, 554 (1970).
18. Högfeldt E.: *Acta Chem. Scand.* 14, 1627 (1960).

Translated by Z. Prášil.