

Sorption of protactinium(V) on extraction chromatographic resins from nitric and hydrochloric solutions

V. Ostapenko^{1,2}  · I. Sinenko¹ · E. Arefyeva¹ · E. Lapshina² · S. Ermolaev² · B. Zhuikov² · S. Kalmykov^{1,3}

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Abstract Retention of Pa(V) on the extraction chromatographic resins (DGA, TRU, TEVA, UTEVA and octanol resin) produced by Triskem International Company has been studied. The capacity factor k' values of Pa(V) were determined in static experiments (batch technique) for a wide concentration range of nitric and hydrochloric acid solutions. The obtained data are useful to devise chromatographic separation of Pa(V) from other actinides.

Keywords Capacity factor · Protactinium · Radionuclide separation · DGA · TEVA/UTEVA · TRU

Introduction

Protactinium has a wide spectrum of applications. For example, the $^{231}\text{Pa}/^{230}\text{Th}$ ratio may be used for evaluation of migration processes in deep water circulation in Atlantic Ocean, providing a link between climate change and the rate of meridional circulation [1]. Pa is attractive for geology [2–4], nuclear forensics [5, 6]. Recently the

interest in application of ^{230}Pa for nuclear medicine has been demonstrated.

^{230}Pa partially (branching ratio is 7.8 %) decays to ^{230}U , which has a potential for targeted alpha-therapy (TAT) [7, 8] due to the decay chain of ^{230}U providing multiple alpha-particle emissions. ^{230}U may be utilized directly or as a parent of ^{226}Th ($T_{1/2} = 31$ min) in a generator system. However, resources of ^{230}Pa production are limited. One of the most perspective methods is irradiation of natural Th by protons. In [9] estimated the production yield for ^{230}Pa based on cross section measurements. It was shown, that clinically relevant amounts of ^{230}U can be produced at lower (<40 MeV) proton energies. At (70–200 MeV) energies ^{230}U can be produced together with ^{225}Ac and ^{223}Ra which are regarded as the most promising alpha-emitting radionuclides for TAT application. Besides ^{225}Ac , ^{223}Ra and $^{230}\text{Pa}/^{230}\text{U}$ the irradiation results in the formation of a large number of spallation and fission products including lanthanides needed to be eliminated.

Separation methods liquid–liquid extraction and ion exchange chromatography are usually used for isolation of Pa radioisotopes. Extraction behavior of Th(IV), Pa(V), U(VI) and Np(VI) from mineral acid solutions by triethylamine (TEA) was investigated in [10]. It was shown, that Th(IV), Pa(V), U(VI) demonstrate low distribution coefficients (<0.1) at high concentrations of H_2SO_4 . Addition of HCl and HBr to H_2SO_4 solutions enhances significantly the extraction of these elements. The authors [11] studied the extraction of Pa(V) by tributylamine (TBA) from oxalic, tartaric and phosphoric acid solutions. It was shown that Pa(V) may be effectively separated in a form of oxalic complex. Pa(V) is also quantitatively extracted by di-(2-ethylhexyl)phosphoric acid (HDEHP) from chloric and hydrochloric acid solutions [12].

✉ V. Ostapenko
ostapenkochem@gmail.com

¹ Lomonosov Moscow State University, Leninskie Gory 1, Moscow, Russia 119991

² Institute for Nuclear Research of Russian Academy of Sciences, 60th October Anniversary Prospect, 7a, Moscow, Russia 117312

³ National Research Center “Kurchatov Institute” (NRC “Kurchatov Institute”), pl. Akademika Kurchatova, 1, Moscow, Russia 123098

Anion exchange is also used for Pa separation [13], because the protactinium anionic complexes are formed in strong mineral acid solutions [14]. One of the most effective methods for Pa(V) separation is based on silica gel sorption [11]. The capacity factor of Pa(V) decreased three times in the presence of Th(IV) ions [15]. Water–alcohol solutions were investigated for separation of Pa(V), U(VI), Th(IV) and Np(VI) on silica gel [16].

Extraction chromatography combines advantages of liquid–liquid extraction and chromatography. However, experimental data describing Pa(V) separation using extraction chromatography from mineral acids are limited. Some of them are presented in [17, 18]. A novel approach to efficient separation of Pa(V) and Np(VI) was described in [19] with 1-octanol as an extracting agent. This approach significantly reduces waste (acidic and organic) and eliminates the need for HF and H₂SO₄. The present paper focuses on Pa extraction chromatographic behavior using DGA, TEVA, TRU, UTEVA, octanol resins (TrisKem Int.). Capacity factors of Pa were obtained for HNO₃ and HCl solutions in a wide range of acid concentration.

Experimental

Chemicals

All chemicals and reagents were of p.a. quality or higher and used without additional purifications. Nitric acid (HNO₃), hydrochloric acid (HCl), perchloric acid (HClO₄) were obtained from Merck. Silicagel with particle size 100–160 and 100–400 μm were used. Extraction chromatographic resins DGA (N,N,N',N' tetroctyldiglicolamide as extracting agent), TRU (octylphenyl-N,N-di-isobutyl carbomoylphosphine oxide dissolved in TBP as extracting agent), TEVA (mixture of trioctyl and tridecyl methyl ammonium chloride as extracting agent), UTEVA (diamyl, amyolphosphonate as extracting agent) with 100–150 μm particle size and octanol (alcohols as extracting agent) with 50–100 μm particle size were used (all resins are produced by Triskem Int.).

²³³Pa

²³⁷NpO₂ was used for obtaining of ²³³Pa as decay product of ²³⁷Np. A sample of 20 mg ²³⁷NpO₂ was dissolved in concentrated HNO₃ and then evaporated to moist salts. The oxidation of ²³⁷Np^{+5,+4} to Np⁺⁶ was performed with concentrated HClO₄. Then neptunium was transferred to pentavalent state with small amount of sodium nitrite and an aliquot was measured on gamma-spectrometer and qualified by UV vis spectrophotometry. The total volume of ²³⁷Np solution was 20 mL and the activity ≈ 500 kBq.

Methods of ²³³Pa isolation

²³³Pa was separated from ²³⁷Np by extraction chromatography using TEVA and octanol resin and by sorption onto silica gel. Column conditions: $r = 0.4$ cm, $h = 8.5$ cm, $V = 4.3$ cm³. Silica gel [16], TEVA and octanol resin [19] were taken as sorbents for separation. All the sorbents were equilibrated with corresponding acid solutions during several hours.

Silica gel

Method 1

The silica gel (fraction 100–160 μm) was placed in 4 M HCl solution. Then the column was filled by pre-conditioned silica gel and of 1 mL of ²³⁷Np/²³³Pa stock solution was added. ²³⁷Np passed through the column in 4 M HCl with the flow rate of 0.08 mL/min. ²³³Pa was quantitatively adsorbed on the column under these conditions. The column was washed with 15 mL of 4 M HCl to remove the traces of ²³⁷Np. ²³³Pa was then eluted by 10 mL of 1:3 mixture of 4 M HCl and C₃H₇OH.

Method 2

The silica gel (fraction 100–400 μm) was placed in 6 M HCl solution. Then the column was filled by pre-condition silica gel and 1 mL of ²³⁷Np/²³³Pa stock solution was added. ²³⁷Np passed through the column in 6 M HCl with the flow rate of 0.3 mL/min. The column was washed with 15 mL of 4 M HCl to remove the traces of ²³⁷Np. ²³³Pa was eluted by 15 mL of mixture 6 M HNO₃: 0.6 M HF.

TEVA resin

The column was filled with TEVA resin and washed with 15 mL 9 M HNO₃. 1 mL of ²³⁷Np stock solution was added in the column. Then 60 mL of 9 M HNO₃ was passed through the column with the flow rate 0.4 mL/min to elute ²³⁷Np. The protactinium was eluted by 20 mL of 0.1 M HCl solution.

Octanol resin

The octanol resin was placed in 4 M HCl solution and left for several hours. ²³⁷Np was eluted by 30 mL of 9 M HCl solution at the flow rate of 0.2 mL/min [19]. Afterwards ²³³Pa was quantitatively eluted by 1 M HCl solution.

Capacity factors

Weight distribution ratios D_w for TRU resin, DGA resin, UTEVA, TEVA, octanol resin in wide range of acid concentration (from 0.01 to 9 M of nitric and hydrochloric acids) were determined in static conditions. The weight of sorbent sample was 50 mg. The aqueous phase containing known concentration of mineral acid solution and radioactive tracer was added to the sorbent and shaken during 3 h. After equilibration and filtration through a glass wool filter, aliquot 1 mL was measured by gamma-spectroscopy and the value of D_w was calculated:

$$D_w = \frac{(A_0 - A_s)}{A_s} \cdot \frac{V}{m} \quad (1)$$

In extraction chromatography, the capacity factor k' is commonly used instead of D :

$$k' = D \cdot \frac{V_s}{V_m} \quad (2)$$

$$D = D_w \cdot \frac{d_{\text{ext}}}{w_{\text{ext}}} \quad (3)$$

where A_0 —activity of aqueous phase before equilibration (cpm), A_s activity of aqueous phase after equilibration (cpm), W —weight mass of chromatographic material (g), V —volume of solution (mL), d_{ext} —density of extracting agent, w_{ext} —weight fraction of extracting agent. Details for converting D_w to k' are given in [18, 20].

Blank experiments

A sample of aqueous phase containing known concentration of mineral acid solution and radioactive tracer was shaken during 3 h without sorbents. After passing through a glass wool filter, 1 mL of solution was measured by gamma-spectroscopy. A part of activity lost anywhere (the surface of labware, the filter, etc.) was obtained and then taken into account for calculation of k' measured under the same conditions.

Gamma-ray spectroscopy

Gamma-ray spectroscopic measurements were performed using a high purity Ge-detector GR 3818 Canberra Ind. (USA). Software Genie 2000 for spectrum processing was applied. Eluate from each column was collected in 1 mL flasks and ^{237}Np and ^{233}Pa were registered via gamma-peaks 86.47 and 311.90 keV, respectively.

Results and discussion

In aqueous solutions, Pa(V) forms mono-oxo cation PaO^{3+} having strong tendency to hydrolysis, polynuclear species formation as well as complexation with various anions. In

general, formation of Pa complexes in nitric acid may be presented as $\text{Pa}(\text{OH})_x(\text{NO}_3)_y^{5-x-y}$ ($x + y \leq 8$, where 8 is coordination number of Pa(V)). Cationic complexes $\text{Pa}(\text{OH})_3\text{NO}_3^+$ or $\text{Pa}(\text{OH})_2\text{NO}_3^{2+}$ are dominant in 1–2 M HNO_3 and gradually transform to neutral and anionic species [21] with $\text{Pa}(\text{OH})_2(\text{NO}_3)_4^-$ as a main species in concentrated HNO_3 [22]. In case of hydrochloric acid, complexes $\text{PaO}_x(\text{OH})_y\text{Cl}_z^{5-x-y-z}$ ($x = 0-2$, $y = 0-4$, $z = 0-8$, $x + y + z \leq 8$) were considered [11, 23]. Positive charge of complexes was observed up to 3–4 M HCl [24, 25]. In more concentrated HCl, oxo-chloride ions PaOCl_4^- , PaOCl_5^{2-} and PaOCl_6^{3-} were regarded as more probable rather than chloride complexes PaCl_6^- , PaCl_7^{2-} and PaCl_8^{3-} [26, 27]. Variety of Pa speciation results in a lack of reliable published data necessary for common separation techniques (liquid extraction, ion exchange, extraction chromatography).

According to the earlier published data [28] TEVA, TRU, DGA and UTEVA resins could be applied for protactinium separation. Since Pa(V) can adsorb not only onto the resins but also onto any surface of labware, the blank experiments were carried out. The losses of Pa(V) up to 15 % was found in both HCl and HNO_3 solutions of concentration range 0.01–0.1 M. Then the values of losses diminished gradually to 10 % along with increasing the acidity of solution. The obtained Pa(V) losses were taken into account when the values of capacity factor k' were calculated.

The values of capacity factor k' for Pa(V) with TEVA resin as a function of HCl or HNO_3 concentration are plotted in Fig. 1. The k' values significantly increase for HCl, as well as HNO_3 , concentrations above 3–4 M. Such behavior is in the agreement with Pa(V) speciation in highly concentrated mineral acids in which anionic complexes are formed that are sorbed by the positive

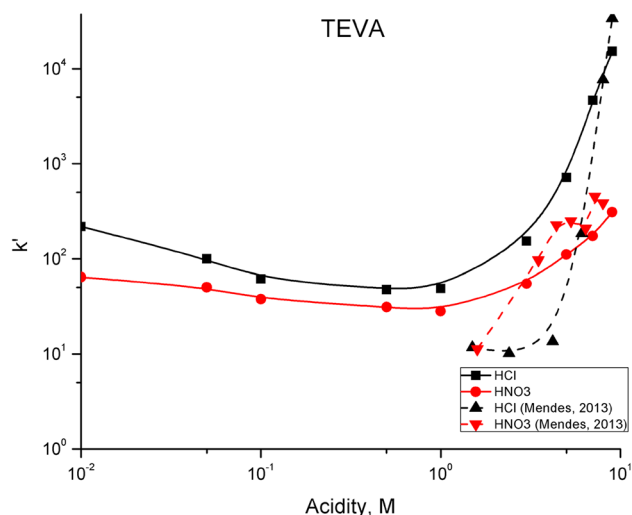


Fig. 1 Capacity factors for Pa with TEVA resin determined in HCl and HNO_3 solutions

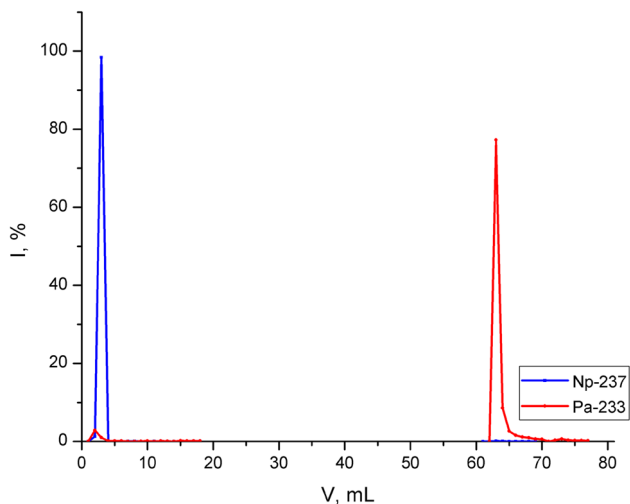


Fig. 2 Separation of ^{233}Pa from ^{237}Np by TEVA resin. Sorption ^{237}Np in 9 M HNO_3 ; sorption ^{233}Pa in 0.1 M HCl

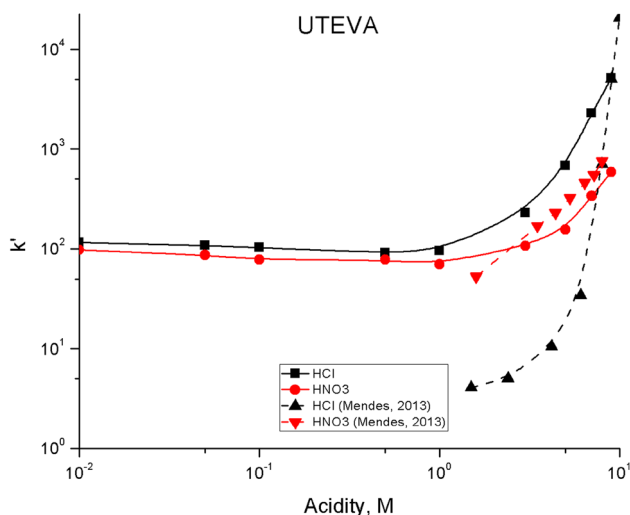


Fig. 3 Capacity factors for Pa with UTEVA resin determined in HCl and HNO_3 solutions

quaternary ammonium groups of TEVA resin. The data reported are compared to that reported by Mendes et al. [28] recalculated here using the ratio of the density of stationary phase, d_{ext} , and the weight fraction, w_{ext} , of extracting agent impregnated onto the inert support as proposed by Horwitz et al. [29]:

$$k' = D_w \cdot \frac{v_s}{v_m} \cdot \frac{d_{\text{ext}}}{w_{\text{ext}}} \quad (4)$$

The data from both our study and reported by Mendes [28] demonstrate the similar tendency.

The data of k' values were used for the choice of conditions of column separation of ^{233}Pa from ^{237}Np (Fig. 2).

It was shown that combination of 9 M HNO_3 and 0.1 M HCl solution resulted in a complete isolation of ^{233}Pa .

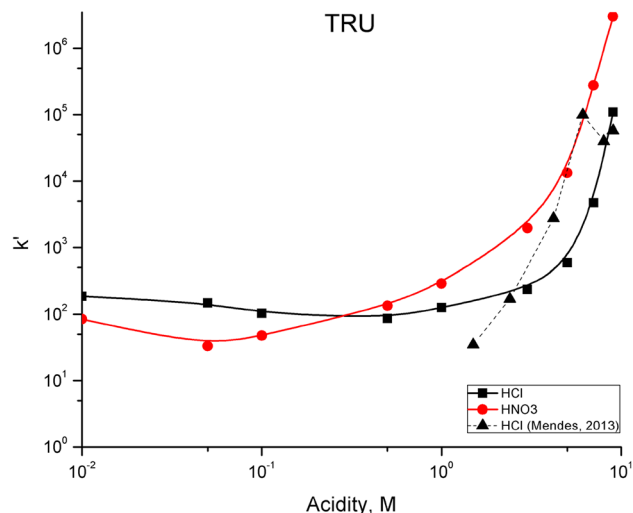


Fig. 4 Capacity factors for Pa with TRU resin determined in HCl and HNO_3 solutions

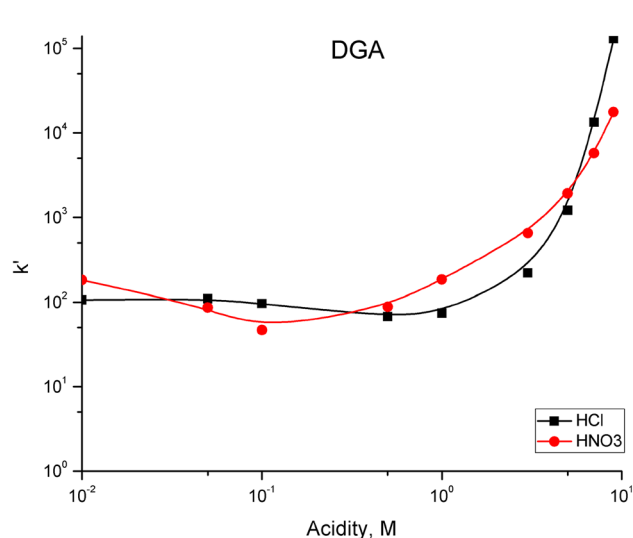


Fig. 5 Capacity factors for Pa with DGA resin determined in HCl and HNO_3 solutions

Comparing to the silica gel separation, the present method allows us to avoid using such chemicals as HF or alcohols.

The values of capacity factor k' for Pa(V) with UTEVA, TRU and DGA depending on HCl or HNO_3 concentration are presented in Figs. 3, 4, 5. The resins show strong affinity to Pa(V) in solutions of both acids with concentration above c.a. 5 M. Moreover, the maximal k' values for TRU and DGA in HCl reach 10^5 , which may be useful for further design of separation schemes. The character of k' value dependency in HNO_3 medium is similar, excepting that maximal k' values are systematically lower for TEVA and UTEVA than ones in HCl medium. This could be explained by the fact that the equilibrium in strong HCl solutions is essentially shifted towards formation of strong

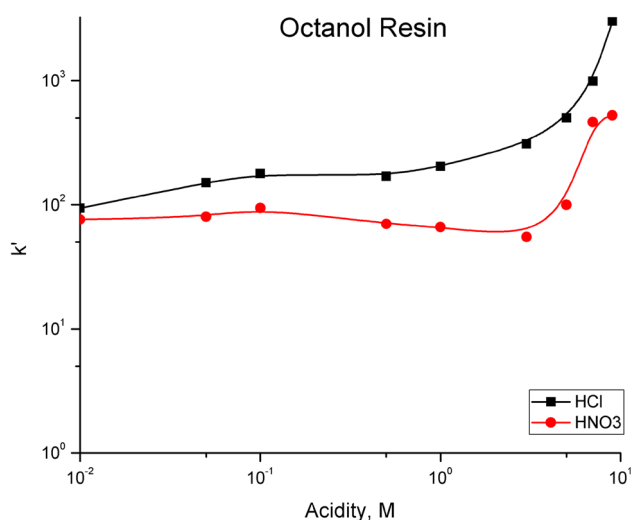


Fig. 6 Capacity factors for Pa with octanol resin determined in HCl solutions

multi-charged anionic complexes [26, 27], whereas in concentrated HNO_3 solutions, a noticeable part of cationic and neutral complexes exist together with anionic ones.

A new extraction chromatographic sorbent octanol resin was tested and the k' values for Pa in HCl solutions were obtained (Fig. 6). Moderate growth of k' values in the range of diluted HCl solutions may be attributed to the bonding of hydroxo-chloride complexes of Pa(V) with a hydroxyl group of 1-octanol while the increased k' values in concentrated HCl solutions correspond to effective interaction via chelating mechanism.

Conclusions

Despite of that behavior of various lanthanides and actinides on extraction chromatographic resins are well studied and reported, the reliable published data for Pa(V) remain scarce. The present work were determined the capacity factor k' for Pa(V) on extraction chromatographic resins, namely, TRU, DGA, UTEVA, TEVA and octanol resin at different HCl and HNO_3 concentrations (from 0.01 to 9 M). The obtained k' values were compared to ones available in literature. The data allow choosing the optimal conditions for chromatographic separation of Pa(V) from elements with similar chemical properties, and the separation of Pa(V) from Np(V) on TEVA was demonstrated. Extraction chromatographic resins are also promising for development of radionuclide generator, for example, $^{230}\text{Pa}/^{230}\text{U}/^{226}\text{Th}$ having practical potential for TAT.

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