PARTITION CHROMATOGRAPHY OF URANIUM AND FISSION PRODUCTS ON POROUS STYRENE–DIVINYLBENZENE COPOLYMER

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The preparation and the properties of the organic phase, *i.e.* of the macroporous copolymers of styrene with divinylbenzene swollen in the solutions of tertiary amines in xylene, were investigated and a comparison with gels swollen in TBP diluents was carried out. Equilibrium distribution of uranium and ^{106}Ru was followed in dependence on HNO_3 and HCl concentration in the aqueous phase. Conditions of the separation of uranium from some of its fission products on columns have been determined.

Extraction of uranium and fission products from nitric or hydrochloric acid solutions with tertiary long-chain amines was investigated in a series of papers[1-6]. For separations of uranium and its fission products by reversed phase chromatography tri-n-octylamine (TOA), tri-iso-octylamine (TiOA), or trilaurylamine (TLA) in combination with various carriers have been most often used. As a carrier for TOA Cerrai[7,8] and Testa[9,10] used cellulose, Akerman[11] and Kufeld[12] took silica gel, and Mikulski[13,14] and Stroński[15] employed Teflon. Kel-F was used for TOA by Hamlin[16] and for TLA by Petit-Bromet[17]. A copolymer of vinyl chloride and vinyl acetate in combination with TiOA is described by Pierce[18], while a copolymer of styrene and divinylbenzene was used for the separations of Am–Eu mixtures by Brown[19] and for Co–Ni separations by Clingman[20] in connection with special amines.

In this paper the copolymer styrene–divinylbenzene used differs from the above mentioned carriers by its evident porosity clearly manifested even in dry state, and by the different physical properties following from this fact.

EXPERIMENTAL

Chemicals and methods. Standard (S) and macroporous (P) styrene–divinylbenzene polymers were produced in the Research Institute for Synthetic Resins and Varnishes, Pardubice. Their properties were described in a number of papers[21,22]. A table of specific surface values, size of pores, *etc.* of macroporous samples was also published[23]. The amines (TOA, TLA — Schuchard, Munich, TiOA — Kodak, Liverpool) were purified by distillation at 10^{-1} Torr. For TOA fraction 175°–190°C, for TiOA fraction 160°C, and for TLA fraction 250–270°C was collected. The densities (g cm^{-3}) measured at 25°C were 0·8101 for TOA, 0·8152 for TiOA, and 0·8233 for TLA. The tertiary amines were used in the form of solutions in analytical grade xylene mixture or undiluted. The analytical content of amines was determined titrimetrically using Tomíček's method[24]; average value was 99·7% (all percentages are w/w). Radioactive isotopes ^{106}Ru—^{106}Rh,

^{95}Zr–^{95}Nb, ^{137}Cs were supplied by the Institute for the Investigation, Production, and Utilisation of Radioisotopes, Prague. ^{90}Y was obtained by separation on Dowex 50X-8 from ^{90}Sr, using 0·50M lactic acid at pH 3·8 for elution. Single radioisotopes were added in trace amounts to uranium solutions, either as nitrates or as chlorides. The analytical methods and the apparatus used were described earlier[22].

Procedure. For the study of the preparation and the properties of carriers swollen in amine solutions in xylene 0·5 g of copolymer was shaken with 2 ml of the amine solution for 24 h. The time was chosen on the basis of the results of a time-dependence investigation. The procedure during the preparation of copolymers swollen in TBP was similar except for the time of contact. After separation of the excess amine solution from the gel, using the method described in[22], the weight increase of the amine solution in the copolymer was determined, and the amount of amine in the gel was calculated after evaporation of the solvent. The ratio of phases in uranium distribution equilibrium experiments was in most cases 1 g of gel per 2 ml of aqueous phase, or 1 : 1, in the case of a liquid–liquid system. Other ratios are given in corresponding experiments. The time of contact was one hour. For column separations of uranium from single fission products a glass column (1·3 cm inner diameter) was used which was filled with the gel of the corresponding copolymer; the average height of the gel in the column was 11 cm; in some cases, when nitrate medium was used, the height of the gel column was 22 cm. The description of the column arrangement, its packing and free volume determination with a ^{137}Cs solution is given in[22]. The column was washed with several volumes of the corresponding acid and then a solution of elements in the same acid was sorbed on the top of the column; elution rate 0·119 or 0·059 ml cm^{-2} min^{-1}.

RESULTS AND DISCUSSION

Preparation and the Properties of Copolymers Swollen in Tertiary Amine Solutions

The time-dependence of amine concentration in standard and macroporous copolymers was measured for copolymers with a 4%, 10%, and 25% content of divinylbenzene (DVB), for swelling with 8% of TOA in xylene, and for sorptions of undilute amine. From these dependences it follows that the amount of amine in copolymer after 24 h swelling differed very little from the values obtained in prolonged experiments, even in cases when standard copolymers were taken, the swelling of which in amine solutions is slower. For this reason the 24 hours interval was chosen for further experiments.

During the choice of a suitable gel for chromatographic separations it was necessary to follow the effect of the amine concentration in the original solution on the amount of amine in the gel of the corresponding copolymer. For this purpose macroporous or standard copolymers were chosen which contained 4%, 10%, 12% and 25% of DVB (P-4 or S-4 *etc.*, resp.; the adjoined number means the content of DVB in the copolymer). The dependence on concentration was observed in the range from 4% of amine solution in xylene up to undiluted TOA. The results for porous copolymers and S-10 are presented in Fig. 1 where the content of amine in the gel is represented in dependence on the concentration of amine in the original solution.

With increasing concentration of the amine in the original solution the amine concentration in the porous copolymer also increases, and although the amine solution is always more dilute in the gel than it was originally, the dependence is regular. The amount of amine always increases up to a certain maximum value depending on the degree of cross-linking (DVB content) of the corresponding copolymer. In more cross-linked samples (from 10% DVB up) a decrease in sorption is evident when undiluted amine is used. For a lower cross-linked copolymer (points ○) a decrease in amine concentration in the copolymer takes place earlier, *i.e.* between 43 and 69% of amine solution in xylene. For standard copolymers S-4, S-10, and S-25 the amount of amine in the gel is independent of the amine concentration in the original solution, and the values usually range under 5% of amine in the gel. Only the effect of 21% of amine solution produces relatively higher values for all three standard copolymers used, not exceeding, however, 7%. This dependence is demonstrated in Fig. 1 by copolymer S-10.

It is evident that standard copolymers are unsuitable for chromatographic purposes because of their low content of amine in the gel. In macroporous gels maximum content of amine in the gel was achieved by swelling of higher cross-linked copolymers in a 68·7% solution of TOA in xylene.
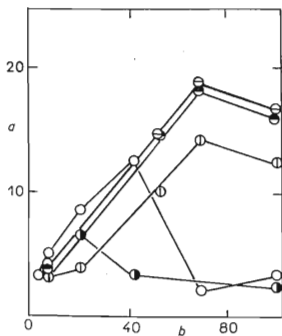

Fig. 1

Effect of TOA Concentration in Solution on Its Amount in Copolymer

a Weight% of TOA in gel, *b* weight% of TOA in the original solution (TOA/xylene), copolymers: ○ P-4, ◐ P-10, ⊖ P-12, ◗ P-25, ◑ S-10, (24 h).
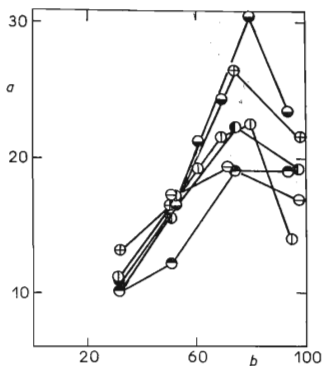
Fig. 2

Effect of TBP Concentration in Solution on Its Amount in Copolymer

a % of TBP in copolymer, *b* % of TBP in the original solution (TBP/xylene, TBP//dichloroethane); TBP/dichloroethane solution (3 h), copolymers: ⊖ P-12, ⊕ P-15, ◑ P-20, ◗ P-25; TBP/xylene solution (24 h), copolymers: ◐ P-10, ◗ P-15.

The question of a maximum concentration of substance in the gels of macroporous copolymers, or the question of the decrease of the substance concentration in the gel at a given concentration of this substance in the original solution was discussed[23] for similar concentration dependence when TBP solutions in solvents were used. For elucidation of the mentioned question some comparisons of gels obtained under the effect of TBP and amine solution are given. Some additional experiments for macroporous copolymers are given in Fig. 2.

If concentration dependences for TBP in dichloroethane and TOA in xylene solutions are compared (Figs 1, 2) it may be seen that their course is similar. Concentration of the substance in the gel increases up to a certain maximum value and decreases for undilute TBP or amine. This is valid for more cross-linked copolymers for amine solutions (from P-10 up, for TBP from P-12 up). For less cross-linked copolymers maxi-
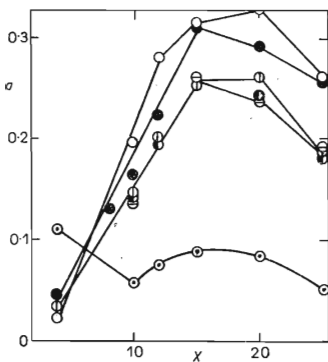

FIG. 3

Effect of Divinylbenzene Concentration in Copolymer on the Amount of Substance in Copolymer

a g amine or TBP per 1 g of dry copolymer, X weight of divinylbenzene in macroporous copolymer; ⊙ 8·3% of TOA in xylene, ○ 68·7% of TOA in xylene, ⊕ TOA, ⊖ TLA, ◐ TiOA, ● TBP (24 h).
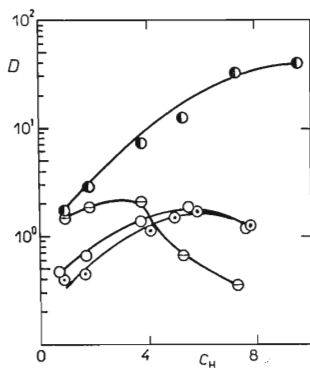
FIG. 4

Dependence of Distribution Ratio of Uranium and ^{106}Ru (D) on Equilibrium Concentration of Acid (C_H, mol l^{-1}) for Copolymer P-10

Distribution of uranium: aqueous phase 0·010M-UO$_2$(NO$_3$)$_2$ in HNO$_3$, organic phase ⊙ P-10 with 12·4% TOA (ratio org : aq = = 1 g : 2 ml), ○ solution of 12·4% TOA in xylene (1 ml : 1 ml); aqueous phase: 0·010M-UO$_2$Cl$_2$ in HCl, organic phase: ◐ P-10 with 12·4% TOA (0·5 g : 2 ml). Distribution of ^{106}Ru aqueous phase: 0·010M-UO$_2$Cl$_2$ + ^{106}Ru in HCl, organic phase: ⊖ P 10 with 12·4% TOA (1 g : 2 ml).

mum concentration of substances in gel is obtained when approximately 50% of sub-
stance solution in solvent is used. This is evident, for example, in Fig. 1 for P-4
(42% of amine solution) and in Fig. 2a in paper[23] (52% of solution TBP). The drop
in substance concentration in gel after a certain maximum may be explained in the
case of these less cross-linked polymers by the different behaviour of more or less
concentrated solutions of the mentioned extraction solvents in connection with dif-
fering physical properties of more and less cross-linked copolymers. The swelling
of a corresponding copolymer in a given solvent[23] is the prevailing factor in less
concentrated solutions of TBP or amine, determining the quantity of the substance
which will enter the copolymer. As less cross-linked copolymers swell more, we may
obtain for the same solution (for example for 50% of TBP in dichloroethane) a maxi-
mum amount of substance in the gels of copolymers P-2, P-4; with increasing amount
of DVB in the copolymer this amount diminishes (Fig. 4a in paper[23]). In the case
of amine solutions in xylene this decrease is evident in Fig. 3, though not as evidently
as in the case of TBP solutions.

Therefore, in more concentrated TBP or TOA solutions (approx. 70%) where
the effect of the extraction solvent prevails (in which the copolymer does not swell)
the swelling proper is negligible[23] and the solution behaves similarly as undilute
TBP or TOA. The effect of the specific surface and the size of pores in copolymers
play a role here, and the amount of TBP or of amine in copolymers grows with
increasing cross-linking (Fig. 3). As the absolute amount of this solution which enters
the less cross-linked copolymers is very low, a drop in substance concentration
in gel is evident for P-4 from Fig. 1, and for TBP solutions from Figs 2a, 2b in pa-
per[23]. More cross-linked copolymers in which a higher porosity or a higher specific
surface and larger pores play a more distinct role, take these more concentrated
solutions to a larger extent. At the same time the absolute amount of the solution
in copolymer increases and, hence, the concentration of substance in the gel as well.
A decrease takes place only in the case of undilute substance (Fig. 1 and 2) which
could be possibly explained by the high viscosity of undilute amines (for example
8·08 cp for TOA), which is in agreement with Small[24] who substantiates a similar
phenomenon for TBP in the same manner.

In Fig. 2 the concentration-dependent function for TBP solution in xylene is given for co-
polymer P-10 and P-15. It is evident that by increasing the time of action the same course is
obtained for P-10 as in the case of TBP solutions in dichloroethane and for more cross-linked
copolymers, while when the operation lasted 3 hours the maximum amount of substance in gel
was equal to that in the case when TBP solutions in dichloroethane and less cross-linked co-
polymers were employed (Fig. 2b in paper[23]). In Fig. 3 the course of sorption of undiluted TOA,
TiOA, and TLA in dependence on the increasing amount of DVB is compared with that of TOA
solutions in xylene of various concentrations and in undiluted TBP. The dependence is the same
as for other substances with which copolymers do not swell (Fig. 4b in paper[23]). It is evident
that the absolute amount of amine in copolymer was practically identical for all amines used.

Finally it may be said that in order to obtain a suitable gel with a higher content of extraction solvent, more cross-linked macroporous copolymers and approximately 70% amine solutions or undilute amines should be used.

Equilibrium Distribution of Uranium and ^{106}Ru

The distribution of uranium and ^{106}Ru in dependence on the equilibrium concentration of nitric and hydrochloric acids in aqueous solution is presented in Fig. 4 and 5. The distribution ratio of uranium or of its fission product is the following: $D_U = [(C_0 - C)/C] (V/m)$ or $D_{Ru} = [(A_0 - A)/A] (V/m)$, where C_0 or A_0 are the initial concentrations of uranium or the initial radioactivity in the aqueous phase, C or A are equilibrium concentrations of uranium or the radioactivity in aqueous phase, V is the volume of the aqueous phase, and m is the weight of gel.

On Fig. 4 the distribution ratios of uranium and ^{106}Ru are presented when copolymer P-10 was used which contained 12·4% of TOA. This organic phase was prepared by the action of undilute TOA for 24 h. In Fig. 5 a similar dependence is represented, for the organic phase consisting of copolymer P-12 with a content of either 16·7% of TOA, prepared by the action of undilute TOA for 24 h, or with 18·9% of TOA and 13·6% of xylene, prepared by swelling in a 68·7% solution. For comparison the values D_U are presented on Fig. 4 and 5 during the distribution between 12·4% and 16·4% TOA solutions and nitric acid in liquid–liquid system.

The values of distribution ratios of uranium increase with nitric acid concentration and attain maximum values in both systems at equilibrium concentration of 5·5 to 6·0M-HNO₃. If the values D_U in the system copolymer–aqueous phase and the system
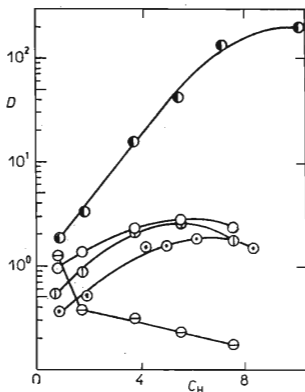

FIG. 5

Dependence of Distribution Ratio of Uranium and ^{106}Ru (D) on Equilibrium Concentration of Acid (C_H, mol l^{-1}) for Copolymer P-12

Distribution of uranium: aqueous phase — 0·010M-UO₂(NO₃)₂ in HNO₃, organic phase: ⊙ P-12 with 16·7% TOA (ratio org. : aq = 1 g : 2 ml), ○ P-12 with 18·9% TOA + + 13·6% xylene (1 g : 2 ml), ⊕ solution of 16·4% TOA in xylene (1·2 ml : 2 ml); aqueous phase 0·010M-UO₂Cl₂ in HCl, organic phase ◑ P-12 with 16·7% TOA (0·5 g : 2 ml). Distribution of ^{106}Ru: aqueous phase 0·010M-UO₂(NO₃)₂ + ^{106}Ru in HNO₃, organic phase ⊖ P-12 with 18·9% TOA + 13·6% xylene (1 g : 2 ml).

liquid–liquid are compared, it may be seen that in the latter case they are somewhat higher for the same TOA concentration (points ○, ◎ Fig. 4, points ⊕, ◎ Fig. 5), although the differences in Fig. 4 are very small. These differences may be caused by a slightly different expression of D_U in both systems. As under the effect of swelling more TOA enters the gel (Fig. 5, points ○), higher D_U values may be achieved by using an organic phase with a higher TOA content, which may be obtained if instead of undilute TOA, solution of TOA in xylene are used.

Distribution ratios of uranium increase with growing concentration of hydrochloric acid and attain maximum values at high acid concentrations in the aqueous phase (Fig. 4 and 5, points ◖); they are higher by an order or magnitude than D_U in nitric acid. Distribution of [106]Ru in the case of hydrochloric and nitric acid has a similar course and D_{Ru} attain maximum values at lower concentrations of acids and then decrease with increasing acidity (points ⊖, Fig. 4 and 5). With 7·6M-HNO₃ the separation factor U/Ru (α) attains the value α = 14, or, with 7·4M-HCl the value α 90 (for copolymer P-10 with 12·4% of TOA in the gel, or for copolymer P-12 with 18·9% of TOA +13·6% of xylene in the gel).

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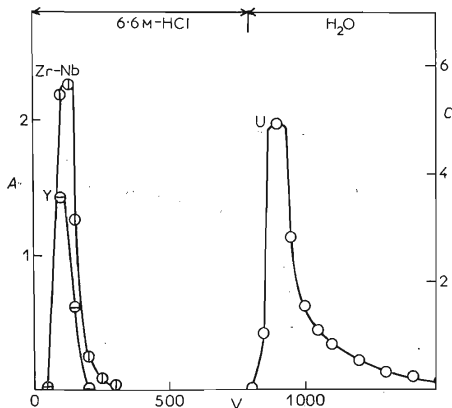
Separation of Uranium from ^{90}Y and [95]Zr—[95]Nb in HCl

A radioactivity (10⁴ c.p.m.), *C* uranium concentration (mg/ml), *V* eluent volume (drops); column (1·3 × 11 cm), copolymer P-10 with 12·4% TOA, flow rate 0·119 ml cm⁻² min⁻¹, sorption of 1 ml of 0·1M-UO₂Cl₂ solution with radioisotope in 7·6M-HCl, elution with 6·6M-HCl.
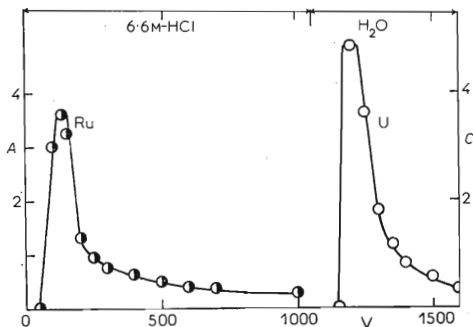
Separation of Uranium from ^{106}Ru in HCl

A Radioactivity (10^3 c.p.m.), C uranium concentration (mg/ml), V eluent volume (drops), column ($1 \cdot 3 \times 11$ cm), copolymer P-10 with $12 \cdot 4\%$ TOA, flow rate $0 \cdot 119$ ml/cm^2 min, sorption 1 ml of $0 \cdot 1$M-UO_2Cl_2 in $7 \cdot 6$M-HCl, elution with $6 \cdot 6$M-HCl.
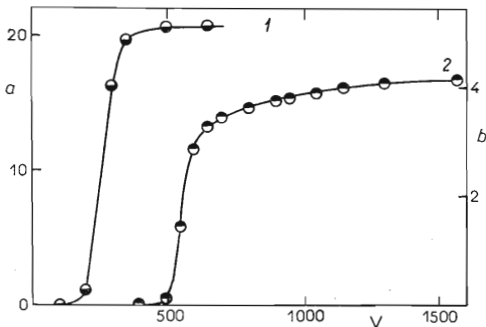
Break-Through Curves of Uranium

a Uranium concentration (mg/ml) for curve 1, b for 2, V eluent volume (drops); curve 1: $0 \cdot 10$M-UO_2Cl_2 in $7 \cdot 6$M-HCl, 2: $0 \cdot 020$M-UO_2Cl_2 in $6 \cdot 8$M-HCl; column ($1 \cdot 3 \times 11$ cm), copolymer P-10 with $12 \cdot 4\%$ TOA, flow rate $0 \cdot 119$ ml cm^{-2} min^{-1}.

*Column Separation of Uranium from Some Fission Products*

The separations of uranium from single fission products were carried out on the column described in the section on procedure. A 0·1M solution of uranyl chloride or nitrate, containing a trace amount of a fission product, was sorbed on the top of the column and eluted with the corresponding acid. The results for copolymer P-10 with 12·4% TOA in hydrochloric acid and for fission products ^{90}Y, ^{95}Zr—^{95}Nb, ^{106}Ru are given in Fig. 6, 7. The separation is quantitative because the radioisotope is eluted with 6·6M-HCl practically immediately after the free column volume, and after separation uranium can be eluted with water.

On Fig. 8 the break-through curves of uranium are evident when the mentioned copolymer and 0·020M and 0·10M-UO$_2$Cl$_2$ solutions in 6·8M and 7·7M-HCl are used. They served for the determination of column capacity and the number of theoretical plates[26] N of the column. In the given medium the column capacity (1·3 × 11 cm) was equal to 0·209 to 0·212 mmol of uranium per 1 g of TOA, and N is equal to 123 in the first case (0·020M) and 45 in the second. For nitric acid medium the separation of uranium and its fission products is demonstrated in Fig. 9 where the elution of uranyl nitrate and ^{95}Zr—^{95}Nb is given.

Although the mentioned radioisotope is practically not extracted by the amine concentration employed and in the given acidity range, a satisfactory separation could not be achieved because lower values of distribution ratios of uranium are insufficient for its maintenance on the column and uranium is eluted practically immediately after the fission product even with 6M acid. An improvement in the position of the uranium peak does not take place even on increasing the height of the filling in the column or by using another copolymer with a higher amine content, or even by using a different amine (TLA); this is evident from Fig. 10 (points ◑ – ◔, or points ◑ – ○). An increase of the copolymer column produces a decrease in the peak width Δ from 460 to 100 drops (Δ was considered as a c/c_{max} concentration equal to e^{-1}); an improvement of the peak width may be achieved by using a co-

Fig. 9

Separation of Uranium from ^{95}Zr—^{95}Nb in HNO$_3$

A Radioactivity (10^4 c.p.m.), C uranium concentration (mg/ml), V eluent volume (drops); column (1·3 × 11 cm), copolymer P-12 with 18·9% TOA + 13·6% xylene in 1 g of gel, flow rate 0·119 ml cm^{-2} min^{-1}, sorption 1 ml of 0·1M-UO$_2$(NO$_3$)$_2$ with radioisotope in 6·3M-HNO$_3$, elution with 6·3M-HNO$_3$.
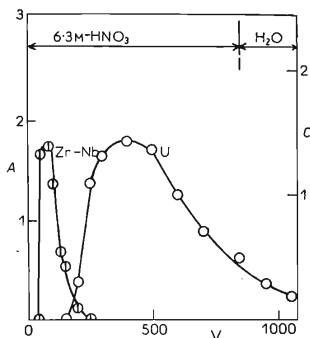
polymer with a higher TLA content (Δ is decreased from 460 to 300 drops); in all instances, however, uranium is eluted too rapidly, so that the results are not comparable with the separations in hydrochloric acid medium.
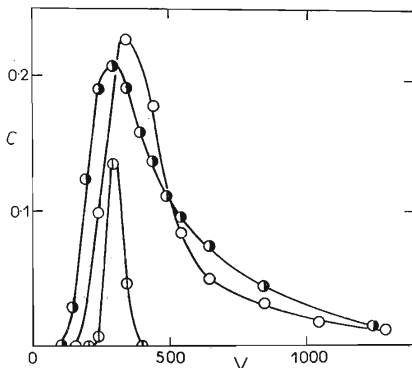

Fig. 10

Elution of Uranium in HNO_3

C Uranium concentration (mg/ml), V eluent volume (drops); sorption of 1 ml of 0·010M-$UO_2(NO_3)_2$ solution in 6·0M-HNO_3, elution with 6·3M-HNO_3, flow rate from 0·053 to 0·086 ml cm^{-2} min^{-1}, column (1·3 × 11 cm), copolymer: ◐ P-12 with 18·9% TOA + 13·6% xylene, ○ P-15 with 20·8% TIA; column (1·3 × 22 cm), copolymer: ◉ P-12 with 18·9% TAO + 13·6% xylene in 1 g of gel.

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