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Poly(7-oxanorborn-2-ene-5,6-dicarboxylate)-coated silica prepared by ring-opening metathesis polymerization for the selective enrichment of radioactive lanthanides

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Abstract

Block-*co*-polymers of norborn-2-ene and 7-oxanorborn-2-ene-5,6-dicarboxylate were prepared by ring-opening metathesis polymerization and used for the preparation of poly(norborn-2-ene)-*block*-(7-oxanorborn-2-ene-5,6-dicarboxylate)-coated silica materials. These sorbents were used for the selective extraction of lanthanides. The coated silicas exhibit an extraordinary good pH stability, are hydrophilic and therefore easily wettable by water alone and show high extraction efficiencies for lanthanides. The use of 200–400 mesh (20–40 μm) materials guarantees a facile handling in terms of back pressure. The extraction efficiencies of the new material for radioactive lanthanides were determined over a concentration range of 20 ng/l–250 $\mu\text{g}/\text{ml}$ by the enrichment of Pm-147 and Eu-152 from aqueous solutions. Breakthrough curves, the loading characteristics at different pH-values as well as recoveries for both Pm-147 and Eu-152 were determined by β liquid scintillation counting. The optimum pH for lanthanide extraction was found to be in the range of 3.5–5.5. The high extraction selectivity of the new sorbents for lanthanides was confirmed by recovery, HPLC as well as ICP-OES experiments. These investigations revealed that the retention of potentially interfering metal ions such as Mg^{2+} , Ca^{2+} , Ba^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} , Zn^{2+} by the new sorbent was less than 5% in all cases. Actinides such as UO_2^{2+} and Th^{4+} are quantitatively coextracted by the resin, yet do not interfere in β liquid scintillation counting. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Generally, the analysis of radioactive lanthanides has gained considerable interest for two main

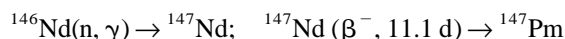
reasons. On the one hand, lanthanides possess a high cross-section target area for thermal neutrons, which makes their appearance in nuclear fuels and moderators highly unfavorable. On the other hand, lanthanides represent the major part of all nuclear fission products. Therefore, an in depth investigation of their occurrence and relative ratio is absolutely necessary. Due to the fact that besides of the lanthanides other, highly active isotopes of various

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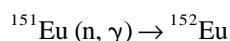
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elements are present, their *selective* separation prior to analysis is a major requirement.

Promethium is formed in the course of nuclear fission processes. The most prominent uranium-derived isotopes are Pm-145 (half-life, $t_{1/2}$ = 17.7 years), Pm-146 ($t_{1/2}$ = 5.53 years), Pm-149 ($t_{1/2}$ = 53 h), Pm-151 ($t_{1/2}$ = 28 h). Pm-147 (β^- , $t_{1/2}$ = 2.62 years) preferably forms from Nd-146 by neutron activation:



One of the most prominent Europium isotopes, Eu-152 ($t_{1/2}$ = 12.4 years), is formed from Eu-151, which shows a natural abundance of 47.77% with respect to Eu:



The quantification of lanthanides in the absence of any other transition metal ions may easily be performed by HPLC, e.g. using ion-chromatography [1–8] and RP-HPLC [9], or CE [10–13] and isotachopheresis [14]. Additionally, mass spectrometric methods [15] including isotope analysis have to be mentioned. Nevertheless, in the presence of sometimes large amounts of transition metal ions, the separation of lanthanides from their matrix is inevitable for any reliable quantification. So far, rare earth elements (REEs) have been extracted from aqueous solutions using solvent extraction. Xanthogenates [16–18] or other, designed ligands such as *N,N'*-dimethyl-*N,N'*-diphenyl-3-oxapentanediamide [19], *N,N'*-bis(5-nitrosalicydene)-*o*-phenylenediamine [20], 4-phenyl-4-benzoyl-5-isoxazolone [21] or 1-phenyl-3-methyl-4-benzoyl-5-pyrazone [22] have been used. In the case of comparably low amounts of REEs with respect to the other metal ions present, separation of lanthanides is preferably performed by ion-exchange procedures [23–26] followed by quantification by means of ICP-OES [27–30]. Despite the high recoveries (95–105%), which may be achieved by these techniques, they are still time consuming, entail the use of rather large amounts of chemicals and consequently significantly aggravate routine analyses, which require a maximum sample throughput.

A modern way of enrichment, which circumvents these problems, is the use of polymer immobilized

complexing ligands for solid-phase extraction [31–36]. Commercially available sorbents are either based on standard complexing ligands such as 8-hydroxyquinoline, EDTA or DTPA (diethylenetriaminepentaacetic acid) [37,38]. Unfortunately, these materials very often suffer from insufficient selectivity as basically all transition metal ions are coextracted. Modern sorbents such as TRU-Spec and EiChrom-materials contain a combination of sulfonate, phosphonate and carboxylate groups. As a consequence of the different pK_a values of these functional groups, their selectivity may be tuned by pH. Despite their rather favorable extraction properties for actinides, their selectivity in the extraction of lanthanides must still be considered as low. As a consequence of this rather unsatisfying situation, we focused on the development of a fast, reliable, quantitative and selective extraction sorbent for lanthanides.

The complexation capability of dicarboxylic acids such as oxalic acid for lanthanides has been known for a long time [39]. Recently, we presented a highly efficient material for the selective extraction of lanthanides based on a polymer-bound succinic acid [40–43]. This material was found to possess excellent selectivities for lanthanides, allowing their enrichment from complex mixtures such as rocks down to the ng/l level. Nevertheless, extractions by this sorbent had to be carried out within a rather narrow pH range (5.0–5.5) in order to obtain quantitative recoveries. To overcome these pH restrictions, a new ligand with a broader pH range of extraction was developed. Additionally, in order to reduce the high costs in the synthesis of pure polymer-based sorbents, we focused on the use of new polymer-coated carrier materials, which should allow for the preparation of kilogram-quantities of the new sorbent.

In this contribution, the use of such a new polymer-coated sorbent for the extraction of lanthanides is described. The new material is based on a commercially available silica-coated with poly(7-oxanorborn-2-ene)-co-(norborn-2-ene) (Fig. 1). Using the new sorbents, the highly efficient extraction of two radioactive lanthanides, Pm-147 and Eu-152, has been carried out. The loading characteristics as well as the selectivity of the new material will be discussed in detail.

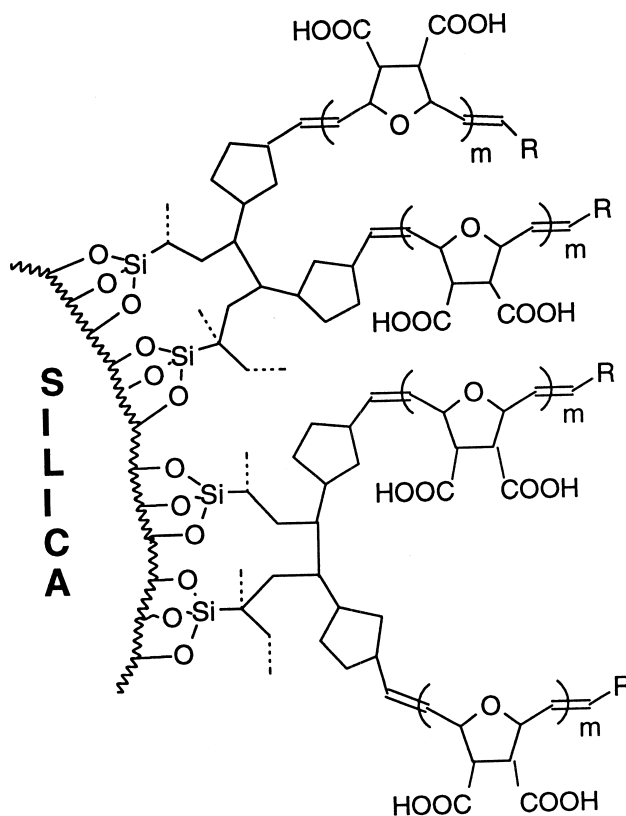


Fig. 1. Chemical structure of norborn-2-ene-block-7-oxanorborn-2-ene-5,6-dicarboxylic acid-coated silica.

2. Experimental

2.1. Columns and materials

The sorbent was prepared according to a previously published procedure [44]. Briefly, the material was synthesized as follows.

2.1.1. Poly(7-oxa-norborn-2-ene-5,6-dicarboxylic anhydride)-block-poly(norborn-2-ene)

7-Oxa-norborn-2-ene-5,6-dicarboxylic anhydride [45,46] (17.6 g, 104.8 mmol) was dissolved in methylene chloride and $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2\text{CHC}_6\text{H}_5$ [47,48] (436 mg, 0.53 mmol) was added. The mixture was stirred for 4 h resulting in a cloudy solution of the polymer. Norborn-2-ene (10.0 g, 106.4 mmol) was added and the mixture was stirred for another 2 h. For work-up, the polymer was

precipitated with pentane, washed with diethyl ether and dried in vacuo.

2.1.2. Polymer solutions

Distilled tetrahydrofuran (THF) was used throughout. After workup, polymers were stirred in THF for 2–3 days in order to be dissolved completely. Any hydrolysis of the anhydride during workup must be prevented, as this significantly aggravates or even impedes their subsequent dissolution in THF.

2.1.3. Vinylation of silica

The corresponding silica was refluxed for 12 h in toluene using a Dean-Stark apparatus in order to remove all water. Toluene was removed and silanization (10.0 g silica) was carried out under reflux in methylene chloride (200 ml) using vinyltrimethoxysilane (10 ml, 65.5 mmol). A reaction time of 2 h was found suitable. Finally, the solvent and excess

silyl reagent were removed by distillation, the material was subsequently washed with dry toluene and acetone and finally dried in vacuo.

2.1.4. Coating procedure

Vinylated silica 60 (10.0 g, 40–63 μm , 60 \AA pore diameter, 0.71–0.78 μl pore volume, specific surface 490 m^2 prior and 290 m^2 after coating) was placed in a round necked flask and a solution of poly(norborn-2-ene)-*block*-(7-oxanorborn-2-ene-5,6-dicarboxylic acid in THF (58 ml, 1 g/l) as well as AIBN (azo-bis-isobutyronitrile, 25% with respect to polymer) were added. The mixture was stirred vigorously for 1 h and subsequently sonicated for 1 h to remove all air bubbles. Finally the solvent was slowly evaporated (approximately 50 ml/h). Thermal cross-linking was carried out at $T=90^\circ\text{C}$ under vacuum within 12 h.

2.1.5. Determination of the capacity

A 200 mg amount of the corresponding coated material (anhydride-form) were stirred in 10 ml of a mixture of 0.05 *M* NaOH for 6 h. The resin was filtered off, washed with deionized water and the combined washings were titrated with 0.05 *M* hydrochloric acid using potentiometric end point indication. The capacity of the material determined by titration was 0.4 mequiv. H^+ /g.

2.1.6. pH stability

A 150 \times 4 mm column filled with the coated sorbent was treated with nitric acid and aqueous sodium hydroxide at pH values of 0–12. After careful washing with deionized water, the elution times and peak half-widths of 2-hydroxyquinoline and 4-hydroxyquinoline [44] were monitored. The

chromatographical properties of the sorbent remained constant within the investigated pH-range.

2.2. Standards

A Pm-147 standard (Isotope Products Labs, Burbank, CA, USA) with 182 kBq and a Eu-152 standard (Amersham Center, Harvel, UK) with 100 kBq (both calculated on basis of $t_{1/2}$ and the activity at the date of certificate) as well as lanthanide standards ($\text{Ce}(\text{NO}_3)_2$, $\text{Tm}(\text{NO}_3)_2$, $\text{Tb}(\text{NO}_3)_2$, $\text{Ho}(\text{NO}_3)_2$, $\text{Lu}(\text{NO}_3)_2$, each 1000 $\mu\text{g}/\text{ml}$) (Aldrich, Vienna, Austria) were used. Other metal salts were used in the form of the following salts: MgCl_2 , $\text{Ca}(\text{NO}_3)_2$, BaCl_2 , $\text{Al}(\text{NO}_3)_3$, MnCl_2 , FeCl_3 , $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{UO}_2(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_2$.

2.3. Enrichment, recoveries and breakthrough curves

All stainless steel precolumns (10 \times 3 mm) and columns (60 \times 4 and 150 \times 4 mm) were packed at a pressure of 500 bar with the coated silica using a Knauer high pressure packing pump. For pH adjustments, an acetate buffer (acetic acid, sodium acetate, ionic strength 0.5) was used. For the enrichment of lanthanides, a flow of 2.5 ml/min was adjusted. The sorption behavior of the material for Pm-147 and Eu-152 was determined by passing mixed standards containing various $\mu\text{g}/\text{ml}$ quantities of Ce (inactive carrier) and 110–1665 kBq Pm-147 or 110–185 kBq Eu-152, respectively, over a 60 \times 4 mm column (Table 1). The effluents were collected in 5-ml portions and subsequently monitored by β liquid scintillation. For the determination of the maximum

Table 1
Recoveries for Pm-147 and Eu-152 on coated silica (pH=5.5)

Activity (Bq/ml)	Carriers ($\mu\text{g}/\text{ml}$ Ce+La)	Total loading ^a in μg (nmol)	Recovery (%)
1650 (Pm-147)	2.3	23 (165)	98
1632 (Pm-147)	12.2	117 (1180)	104
1487 (Pm-147)	102	102 (680)	98
1236 (Pm-147)	251.7	1130 (7530)	96
181 (Eu-152)	0	2.3×10^{-4} (1.5×10^{-3})	106
137 (Eu-152)	250	1125 (7500)	95

^a Total of all lanthanides.

loading (breakthrough curves), a 250 $\mu\text{g}/\text{ml}$ Ce standard spiked with the corresponding activity of Pm-147 and Eu-152, respectively, was used.

For recovery experiments, a 60×4 mm column was loaded as described above. Elution of the inactive carrier, Pm-147 and Eu-152 from the loaded columns was performed with 5% HNO_3 and the effluents were collected in 1 ml portions. Recoveries were calculated on the basis of the total number of counts (cpm) in all fractions and the total activity loaded onto the column. In all experiments, the eluted lanthanides were found in the first 2 ml. Unless stated otherwise, each extraction experiment was carried out twice ($n=2$).

2.4. Determination of the optimum extraction pH

A 5 ml volume of a mixed standard containing Ce, Sm, Tb, Yb (100 ng/ml each) were passed over a HPLC precolumn (10×3 mm) filled with the sorbent at different pH values (3.5, 4.0, 4.5, and 5.5). The column was washed with 5 ml of deionized water. Subsequent determination of the total amount of lanthanides sorbed onto the material was carried out by HPLC (UV-detection). For that purpose, gradient elution was started with 60 mM HIBA (hydroxyisobutyric acid) as a mobile phase reaching 400 mM within 30 min using 1-octanesulfonate as a modifier [8]. Separation of the four lanthanides was carried out on a standard RP-18 column (LiChroCart 125×4 mm, LiChrospher 100 RP-18, 5 μm , Merck, Darmstadt, Germany) performing post-derivatization with a 0.2 M aqueous solution of PAR [4-(2-pyridylazo)resorcinol, analytical-reagent grade, 99%, Fluka, Vienna, Austria] in 1.0 M acetic acid–3 M ammonium hydroxide. Extraction efficiencies were calculated from the corresponding peak areas in comparison to a directly injected standard.

2.5. Selectivity and masking

Selectivity of extraction was checked by passing 50 ml of a mixture containing each 5 $\mu\text{g}/\text{ml}$ of Mg^{2+} , Ca^{2+} , Ba^{2+} , Al^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , U^{6+} , Th^{4+} over a 150×4 mm column packed with the sorbent (flow = 1 ml/min). The column was washed with 5 ml of deionized water. Elution of the column was achieved with 5% nitric acid. The

retention of the corresponding metal ion by the coated silica was determined by subsequent ICP-OES (inductively coupled plasma-optical emission spectroscopy) measurement (JY 38 Plus, Jobin Yvon, Division d'Instruments) of the effluent. As iron is extracted by the resin, it was masked using 5-sulfosalicylic acid. Masking efficiencies for iron were determined by HPLC as follows: To a solution containing 5 $\mu\text{g}/\text{ml}$ iron was added 5-sulfosalicylic acid (1 ml, 2% in water). The solution was passed over a HPLC precolumn which was then washed with 5 ml of deionized water. The total amount of the sorbed iron was determined by ICP-OES. Any negative influence of 5-sulfosalicylic acid on the retention of lanthanides was ruled out by mixing a 5 ml of a test lanthanide solution (50 ng/ml each of Tm, Tb, Lu and Ho) containing 84 $\mu\text{g}/\text{ml}$ iron with 100 mg 5-sulfosalicylic acid. The mixture was passed over the sorbent (pH 4.5). After rinsing with deionized water, the total amount of the sorbed metal ions was determined. Thus, only less than 1 μg of iron remained on the sorbent, corresponding to a masking efficiency of 99.8%. Recoveries for the test lanthanides (Ho, Lu, Tm, Tb) remained unaffected (95–105%).

2.6. Activity measurements

Activities of the Pm-147 and Eu-152 containing effluents and solutions were determined by means of liquid scintillation. For Pm-147, 1 ml portions of the effluent were mixed with 10 ml LSC Ultima Gold XR-solution and either screened on a Berthold BF 5000 using a C-14 window (1 min acquisition time, background C-14: 24 cpm) or either quantified on a Canberra Packard 2260 XL within a C-14 window with a 2σ -accuracy (background C-14: 2.9 cpm); efficiency = 0.91 based on C-14. For Eu-152, 1 ml portions of the effluent were mixed with 10 ml LSC Ultima Gold XR-solution and either screened on a Berthold BF 5000 using a window ≥ 5 keV (1 min acquisition time, background 28 cpm) or either quantified on a Canberra Packard 2260 XL within a window ≥ 5 keV with 2σ accuracy (background: 3.2 cpm), efficiency = 0.87 measured by efficiency tracing. The MDAs (minimum detector activities) for Eu and for Pm based on $\Delta 2\sigma$ were 0.1 Bq.

3. Results and discussion

3.1. Sorbents and extraction conditions

Ring-opening metathesis polymerization (ROMP) offers an attractive access to functionalized polymers, as it allows the polymerization of functional monomers. The synthesis may be conducted with high reproducibility as it avoids any polymer transformations. Consequently, the capacities of the final stationary phases are predetermined and reproducible. The preparation of other ROMP-based sorbents and some applications have been reported previously [40,42–44,49–53].

For the present investigations, silica-60 (200–400 mesh, 40–80 μm), coated with 5.8% poly(norbornene)-*block*-(7-oxanorborn-2-ene-5,6-dicarboxylic acid) was used. A detailed description for the preparation of the sorbent using ring-opening-metathesis polymerization (ROMP) as well as its mechanical and chemical properties is given elsewhere [44]. Fig. 1 gives an illustration of the material. As can be deduced from this illustration, the repetitive unit of the polymer consists of a succinic acid anellated to a tetrahydrofuran ring. The utilization of 7-oxa-norbornene-derivatives instead of norbornene-based monomers [42] enhances the hydrophilicity of the polymer surface, and therefore leads to an enhanced wettability of the resulting material. Consequently, no organic additives such as methanol or THF have to be added.

The use of coated silica supports which are suitable for solid-phase extraction (SPE) offers the advantages of a stable and cheap inorganic support as long as any hydrolysis process can strictly be avoided. Consequently, any coating must be thick enough to prevent chemical degradation of the carrier. Such an optimum copolymer layer in terms of stability was deposited on the surface of the silica carrier [44]. This coating forms an impermeous polymer layer, which provides excellent chemical stability versus bases and especially acids. As a consequence of the amount and chemical nature of the coating, the coated material was found to be entirely stable under acidic conditions (5% nitric acid) as well as up to a pH of ≥ 12 . Consequently, this allows for the reuse of a material after careful clean-up for many times without any loss in per-

formance. A further consequence of the chemical nature of the copolymer, which consists in part of a poly(dicarboxylic acid-derivatized tetrahydrofuran), is the high wettability of the resin, which makes a pretreatment with methanol prior to SPE no longer necessary.

3.2. Pm-147 and Eu-152 extraction

Solutions of $^{147}\text{Pm(III)}$ chloride and $^{152}\text{Eu(III)}$ chloride, respectively, containing 150–1670 Bq/ml as well as 0–250 $\mu\text{g/ml}$ of an inactive carrier were passed at a flow-rate of approximately 2.5 ml/min through a stainless steel cartridge filled with coated silica. The use of a 200–400 mesh material guaranteed a suitable backpressure of less than 0.5 bar. The effluent was collected and Pm-147 as well as Eu-152 were measured by means of β liquid scintillation counting. The loadings of Pm-147 and the corresponding recoveries are summarized in Table 1. As for Pm-147, sorption efficiencies at pH=5.5 were determined for Eu-152 (Table 1). Elution of the metal ions from a loaded column and simultaneous recycling of the material was performed using 5% nitric acid. Both lanthanides were eluted rapidly and quantitatively into the first 3 ml thus guaranteeing a rapid and convenient experimental setup. In both cases quantitative recoveries in a range of 96–106% were achieved.

The $\text{p}K_{\text{a}}$ values of succinic acid are 5.16 and 5.61, respectively. As lanthanides tend to precipitate at a $\text{pH} > 5.5$, an applicable extraction pH had to be determined. Due to the identical complexation behavior of lanthanides, this may conveniently be accomplished by monitoring the retention of a few rare earth elements by the sorbent. Solutions of 100 ng/ml of Ce, Sm, Tb and Yb were passed over a column packed with coated silica at pH values of 5.5; 5.0; 4.5; 4.0; 3.5; 3.0. In contrast to phosphate-based buffers, their acetate analogues were found suitable for buffering due to the low affinity of acetate to lanthanides. All lanthanides revealed a high affinity to the sorbent within a pH range of 3.5–5.5. The fact, that quantitative retention is observed at pH values smaller than the $\text{p}K_{\text{a}}$ strongly suggests a significant influence of the auxiliary oxygen ligand. At pH 3.0 a loss of roughly 25% for each lanthanide was observed. This broader applic-

able pH range of 3.5–5.5 for extractions compared to a previously published sorbent [42] significantly reduces the need for a careful buffering of the entire system, thus facilitating the entire setup. For convenience, extraction and breakthrough experiments were carried out at pH 5.5. The corresponding breakthrough curves for both Pm-147 and Eu-152 are shown in Figs. 2 and 3.

The extraordinary high affinity of the sorbent for lanthanides was additionally demonstrated by passing both pure Eu-152 standards as well as solutions spiked with inactive Ce over the resin. The neat Eu-152 standard solution contained an activity of 180 Bq/ml corresponding to a concentration of only 150 f/mol/l (23 ng/l). Spiked solutions were prepared up to a total lanthanide content of 250 $\mu\text{g/ml}$. Recovery values for this broad concentration range (seven orders of magnitude) varied within 96–106%. Keeping the comparably short analyses times of less than 5 min in mind, these data give an impressive

demonstration of the extraction potential of the new material.

In order to determine the maximum loading capacity at $C=250 \mu\text{g/ml}$, Ce-spiked solutions of Pm-147 as well as Eu-152 were passed through the cartridge. As might be expected, spiked ^{152}Eu and ^{147}Pm solutions show the identical maximum loading capacity of 4.3 mg metal per gram resin. Expressed in mg metal per milliequivalent (mequiv.) of functional groups the current value of 21.4 mg illustrates in comparison to 12.1 mg of lanthanide per mequiv. ligand on a poly(succinic acid) derivatized resin [42] the enhanced complexation capabilities of the new ligand. In terms of succinic-acid capacity, this value corresponds to a total coverage at the point of breakthrough of 14% of all ligands present. As already discussed briefly, the significantly stronger complexation is attributed to the presence of the additional ether-ligand in the five membered ring. As this tetrahydrofuran ring is in sufficient proximity to

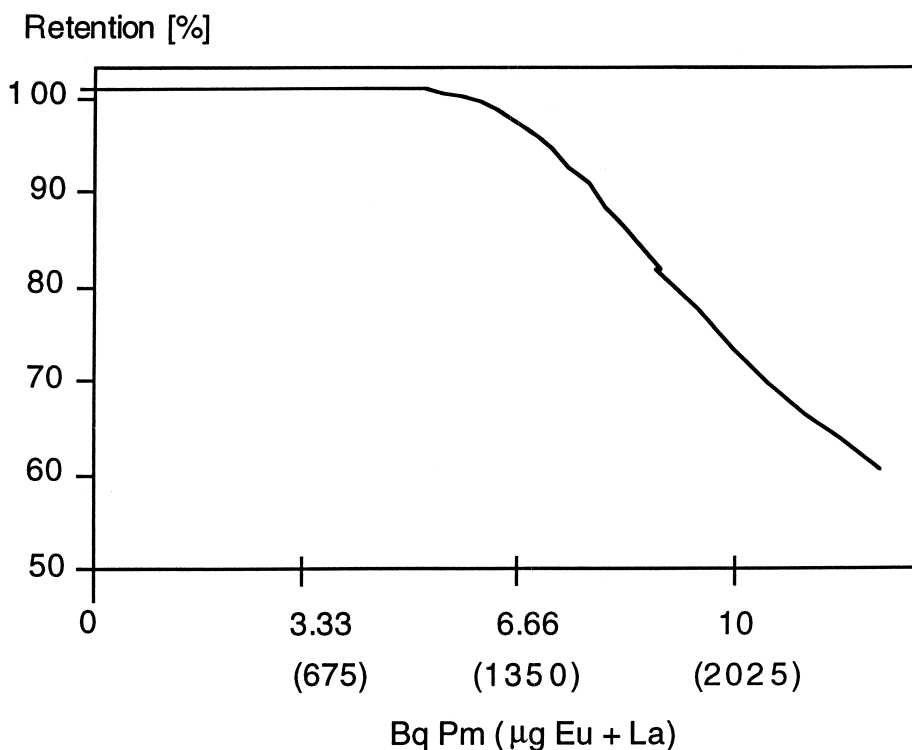


Fig. 2. Breakthrough curve for a mixed standard containing 1236 Bq Pm-147/ml and 250 $\mu\text{g/ml}$ Ce on coated silica (pH 5.5).

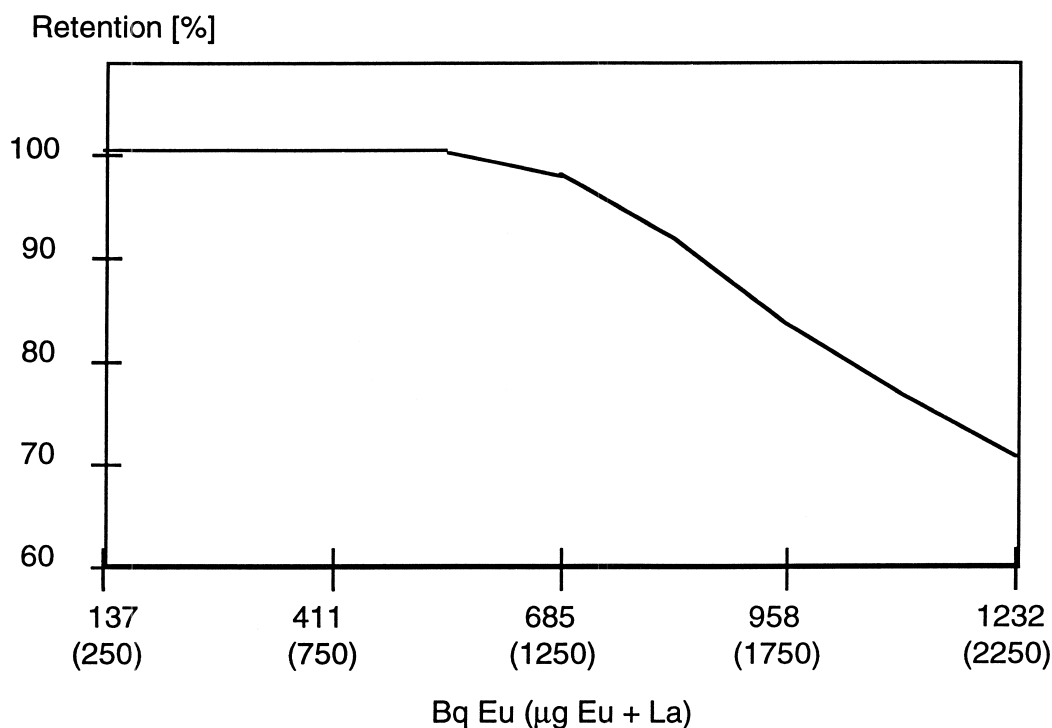


Fig. 3. Breakthrough curve for a mixed standard containing 137 Bq Eu-152/ml and 250 $\mu\text{g/ml}$ Ce on coated silica (pH 5.5).

the two carboxylic acid ligands, an additional site of complexation is generated. Based on the known complexation behavior of lanthanides with dicarboxylic acids [54,55] as well on the sorption experiments, the extraction of lanthanides is believed to be based on the complexation of a metal ion by the two *vic*-dicarboxylate groups and the additional oxygen in the 5-membered ring (Fig. 4).

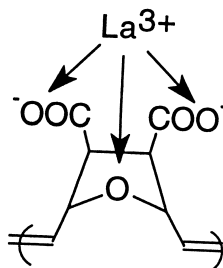


Fig. 4. Proposed complexation of lanthanides by the ligand.

3.3. Selectivity

The selectivity of the sorbent for lanthanides in the presence of other metal ions was investigated. Investigations revealed, that similar to poly(norborn-2-ene-5,6-dicarboxylate)-based materials many metal and transition metal ions (e.g. Mg^{2+} , Ca^{2+} , Ba^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}) are not extracted by the new ligand. Thus, solutions of Mg^{2+} , Ca^{2+} , Ba^{2+} , Al^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} were passed at a concentration of 5 $\mu\text{g/ml}$ for each element over the sorbent. Starting solution, the effluent as well as the eluent (using 5% of nitric acid) were counterchecked for metal sorption by means of ICP-OES. In each case, the extraction efficiencies for these transition metal ions were in the range of 3 to 5%. Nevertheless, some transition metal ions (e.g. Al^{3+} , Fe^{3+}) and especially actinides (UO^{2+} , Th^{4+}) undergo complexation with succinic acid derivatives. In order to enhance the selectivity [42], 5-sulfosalicylic acid was used as a masking agent (especially for Fe^{3+} and

Al³⁺). As expected, masking of iron and aluminum was found to be quantitative within experimental error (<1%), while the new material still exhibited the same extraction efficiency for lanthanides and both actinides.

4. Conclusion

A new highly efficient sorbent for the extraction of lanthanides has been developed. Extraction efficiencies are almost quantitative in a concentration range of 20 ng/l up to 250 µg/ml. Elution may be performed in a quantitative way using 5% nitric acid. Generally, an extraction pH of 3.5–5.5 is applicable. In the presence of larger amounts of iron and aluminum, the optimum sorption pH was found to be in the range of 4.5–5.5 in order to prevent precipitation of Fe(OH)₃ and Al(OH)₃, respectively. No significant co-complexation of other transition metal ions by the ligand was observed except for UO²⁺, Th⁴⁺, Al³⁺ and Fe³⁺. The latter two may selectively be masked using 5-sulfosalicylic acid. The material itself is stable within a pH range of 0–12, may rapidly be recycled and reconditioned and therefore represents an attractive material for the rapid and quantitative extraction or screening of radioactive lanthanides from complex mixtures.

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