RECENT ADVANCES IN THE QUANTIFICATION OF LANTHANIDES

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SUMMARY

The latest developments in the off-line and on-line enrichment and quantification of rare-earth elements (REEs) are reviewed. These are discussed in the context of the present state of the art in REE enrichment,

separation and quantification, with the main emphasis focusing on ion-exchange HPLC- and CE-techniques.

INTRODUCTION

Since their discovery in 1839, rare earth elements (REEs) are still hard to purify. Consequently, the original interest on these elements was restricted to some peculiar scientific investigations. This drastically changed in 1891, when the Austrian chemist C. A. von Welsbach developed his ThO_2/CeO_2-based incandescent lamp. Nowadays, REEs are widely used for the fabrication of advanced materials such as high-performance magnets (e.*g*. $Nd_2Fe_{14}B$; $SmCo_5/Sm_2Co_{17}$), high-temperature superconductors, sensors, fluorescent materials, magneto-optical discs and batteries. More recently they have also attracted considerable interest in organic synthesis[1,2]. Additionally, because of their unique and almost identical chemical properties, rare earth elements (REEs) have proved to be a set of interesting and intrinsic tools for elucidating igneous rock petrogenesis and for interpreting processes of metasomatism, ore formation[3,4] and rock alteration[5]. Finally, they represent reactive intermediates in radioactive waste. The careful characterization (quantification) of each isotope represents a challenging, yet inevitable task. The term “rare earth elements” itself is misleading, since the relative abundance of REEs (without the radioactive Pm-147) in the outer earth’s crust ranges from 0.5 to 66 ppm. There exist over 100 different minerals that contain one or more rare earth elements; nonetheless, only 2 of them are of any ecological relevance, i.e. monazite, a (La, Th, Ln)-phosphate (Ln = any lanthanide) and bastnesite, a (La, Ln)-fluorocarbonate.

In terms of separation/purification one needs to distinguish between two major applications. The first is the large-scale production/purification of REEs for industrial purposes; the second entails the enrichment and quantification of REEs from complex mixtures, where they usually occur at low or ultra-low concentrations (fg/g – µg/g level). Since this review only intends to summarize recent results in the trace enrichment and quantification of REEs, the most prominent techniques for the large-scale production of pure REEs such as selective reduction/vacuum distillation[6] or gaseous complex-mediated vapor transport[7,8] will only be briefly mentioned.

CLASSICAL SEPARATION METHODS

Because the chemical properties of rare earth ions in aqueous solution exhibit only incremental variation with atom number[9], any of the traditional separation techniques must be multiply applied in order to achieve sufficient purity of each element. Among the most prominent classical approaches[10] are (i) fractionated precipitation as hydroxides based on the different basicity of the lanthanide ions, (ii) fractionated precipitation as oxalates, mixed sulfates ($Ln_2(SO_4)_3 \cdot Na_2SO_4$) or nitrates ($2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2$), (iii) change of oxidation state of Ln^{3+} (if possible[11]), *e. g.* Ce^{4+}, Eu^{2+}.

STANDARD SEPARATION TECHNIQUES

So far, separation/preconcentration of REEs has been accomplished *via* solvent extraction, ion exchange, chelating resins, and by sorption of neutral Ln-complexes onto C_{18}-silica[12-14], respectively. In order to elucidate the requirements and restrictions in trace REE enrichment and quantification, the advantages and disadvantages of each technique as well as the state of the art will be briefly summarized.

Solvent extraction[15-17]

For the practical, large-scale separation of REEs, solvent extraction is a serious competitor of ion exchange techniques. In particular the knowledge of the behavior of fission product REEs during reprocessing of spent nuclear fuel has contributed to an interest in the solvent extraction chemistry. For standard extractions, sulfonic acids, carboxylic acids (*vide infra*), β-diketones, hydroxyketones, hydroxyacids, hydroxyquinolines, pyrazolones, phenylhydroxylamines and in particular organophosphorus extractants (*e. g.* tri(n-butyl)phosphate, bis(2-ethylhexyl)phosphoric acid) are used. The latter one has also been successfully used in TLC separation of REEs[18]. More recently, "designed" ligands such as N,N'-dimethyl-N,N'-diphenyl-3-oxa-pentanediamide[19], 1-phenyl-3-methyl-4-benzoyl-5-pyrazone[20], N,N'-bis(5-nitrosalicilidene)ethylenediamine, N,N'-bis(5-nitrosalicilidene)-o-phenylene-diamine[21], and 3-phenyl-4-benzoyl-5-isoxazolone[22] are used. The correct combination of extraction pH, organic solvent and extractant very often results in satisfactory separations. Nevertheless, despite the ease of the entire procedure, all standard ligands generally suffer from insufficient selectivity and/or low extraction capabilities. This represents a minor problem in the case of comparably high REE concentrations or in the absence of large amounts of co-extractable metal ions. In this case, quantification of REEs may easily be accomplished even in the presence of minor amounts of other metal ions by means of graphite furnace AAS[23,24] DCP-AES[25], ICP-AES[23,26-28] or ICP-MS[29,30]. In the case where larger amounts in particular of transition metal ions are present, insufficient separation of the REEs from the rest of the matrix was often observed. In due consequence other separation techniques were developed.

Ion exchange-based extraction and enrichment techniques[31-33]

Ion-exchange-based techniques still represent state of the art procedures for many applications. With the exception of a few reports on the use of anion exchangers[34,35], (strong) cation exchangers are applied throughout. The use of high-capacity strong cation exchangers (*e. g.* 200 – 400 mesh Bio Rad® AG 50W-X8, Dowex 50 W X12, Chelex 100)[36-39] allows the separation of REEs at least from all other divalent metal ions. More sophisticated techniques entail the use of two independent columns. The first retains the REEs. These are eluted with EDTA and injected onto the second, Cu^{2+}-loaded column. Cu^{2+} replaces the REEs to form Cu^{2+}- EDTA, which is eluted off. The REEs, now bound to the cation exchanger, may be successively eluted by mineral acids or a complexing agent, e. g. 2-hydroxy-*i*-butyric acid (HIBA). Since the logK (K = equilibrium constant for complex formation) increase from La to Lu by approximately 25 %, a fractionation[40] or even separation, depending on lanthanide composition, column size, loading and concentrations, may be achieved. Despite its chemical simplicity, this approach suffers from long and tideous separation times, thus basically preventing any high sample throughput. Additionally, large eluent volumes are required, which makes additional evaporation steps necessary.

Enrichment by chelating resins

One of the most promising approaches represents the use of chelating sorbents (resins) *if complex formation proceeds in a highly selective way*. In this case, REEs should be retained quantitatively, while all other interfering metal ions and matrix compounds are removed. Since REEs usually occur at comparably low concentrations (ng/g – µg/g level), the equilibrium constants for complex formation of REEs with the corresponding ligand must exceed those of all other metal ions with the same ligand by at least 7 orders (*sic!*) of magnitude, unless additional masking techniques are applied. Nitrogen-[41] or phosphorus-containing ligands[42,43] possess high affinities for all transition metals including REEs; nevertheless the selectivity for lanthanides is comparably low, thus leading to the coextraction of other metal ions[44-47]. Among the almost unlimited repertoire of potential ligands[48], those solely based on carboxylic acids appear to be the most promising ones. The complexation behavior of lanthanides with dicarboxylic acids is well documented[15,49-51] and has already been used in TLC[52], cation-exchange chromatography[53-60], RP-HPLC[61-63], isotachophoresis[64] as well as CE separations[65-70]. In consequence, carboxylic acid-based sorbents appeared to be of particular interest. Interestingly, weak (COOH-based) cation exchangers (WCXs) are not suitable for the selective enrichment of REEs. This is actually quite obvious, since dicarboxylic acids interact with REEs *via* chelation. Such a chelation is not possible in WCXs, due to the fact that such exchangers are prepared either from poly(acrylates) *via* hydrolysis or from PS-DVB supports *via* Friedel-Crafts acylation (Figure 1). Even poly(maleic acid) or poly(acrylic acid) homo- or copolymers[71] do not possess *gem-* or *vic-*carboxylic acids in *cis*-configuration, which is a basic requirement for chelation to proceed.

In order to create a sorbent containing *cis*-configured dicarboxylic acids, we therefore focused on the polymerization of functional monomers already containing the desired functional group.

MODERN SEPARATION TECHNIQUES

Synthesis of NDCA-based extraction resins

For resin preparation, we first aimed at the polymerization of *endo,endo-*[2.2.1]bicyclohept-2-ene-5,6-dicarboxylic anhydride (= norborn-2-ene-5,6-dicarboxylic anhydride = NDCA) (Figure 2). In principal, this monomer may be polymerized either *via* a Pd-mediated polyinsertion process or *via* ring-opening metathesis polymerization (ROMP)[72]. Using well-defined initiators[73], ROMP may be carried out in a strictly "living" manner and therefore offers an attractive access to well-defined polymers and block-copolymers. Consequently, we focused on this polymerization technique and

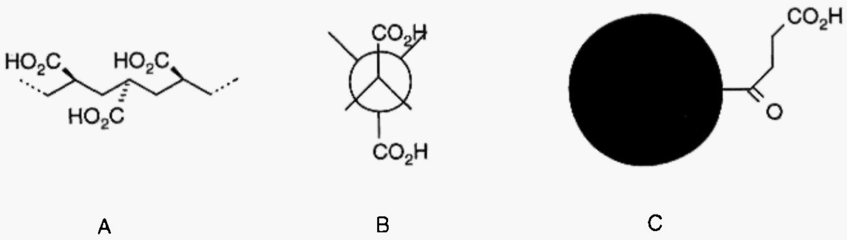
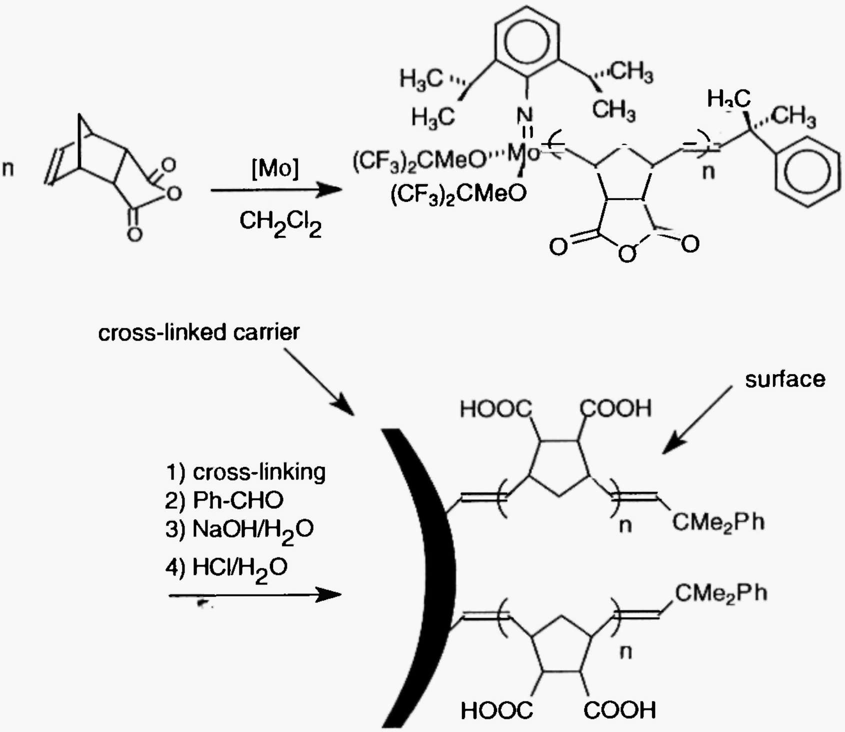


Fig. 1: Structure of ion exchangers prepared from poly(acrylic acid)-homopolymers or poly(acrylates) *via* hydrolysis (A), from poly(maleic acid) (B) and from PS-DVB supports modified *via* Friedel-Crafts acylation (C).

Fig. 2: Structure of NDCA (A) and ONDCA (B).

new materials for solid-phase extraction (SPE) have been prepared by ring-opening metathesis precipitation copolymerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (DMN-H6) with NDCA, using the well-defined Schrock-catalyst $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$[74]. The resulting cross-linked polymers have been investigated in terms of influence of the polymerization sequence as well as of the stoichiometry on swelling behavior, surface area, capacity, accessibility of the functional groups, and their possible use in metal extraction, respectively. Due to the polymerization technique employed, the resin consists of a highly cross-linked interior with linear polymer chains of functional groups attached to its surface, thus forming a tentacle-type structure. This ensures a fast mass-transfer within the interphase as observed with similar resins[75]. The capacities of the different weak cation exchangers may be reproducibly varied over many orders of magnitudes (up to 10 mmol/g). Hydrolyses of the anhydride moiety yields the desired *cis*-configured *vic*-dicarboxylic acid functionality. The synthesis and the final structure of these resins are summarized in Scheme 1.



Scheme 1: Synthesis and structure of poly(NDCA-*co*-DMN-H6)-based resins.

Off-line REE-extraction with NDCA-based resins

Since poly(NDCA-*co*-DMN-H6)-based resins do not possess sufficient pressure stability, these materials may not be used as precolumn materials, but solely for off-line SPE experiments. For REE-enrichment, three different rock standard reference materials (SRMs), GSR-1 granite, GSR-2 andesite, GSR-3 basalt, were digested by fusion of the corresponding rock with lithium metaborate ($LiBO_2$) and subsequent dissolution in nitric acid[76]. As a consequence of the different compositions of the three investigated SRMs, the resulting digest showed different concentrations of the REEs as well as of SiO_2, Fe^{3+}, Al^{3+}, Mg^{2+}, and Ca^{2+}. A high capacity poly(NDCA-*co*-DMN-H6)-based resin (3.1 mmol/g) containing the desired *cis*-1,4-butandioic acid (succinic acid) units was used for the extraction of rare-earth elements (REEs) from rock digests. Extraction efficiencies measured by means of ICP-AES were found to be in the range of 90-100 % for standards containing 5 and 500 ng/mg of each REE, respectively, with relative standard deviations (RSDs) $\leq$ 6.6 % (Table 1a). The optimum extraction pH was found to be between 5.3 and 5.5. Masking of Fe^{3+} and Al^{3+} with 5-sulfosalicylic acid additionally enhanced the extraction selectivity of REEs from rock digests. Small amounts of methanol were added to prevent silicate from precipitation. Following this setup, REEs which occurred in the digest solutions in a range of 40 fg/g to 150 ng/g, were retained selectively with recoveries ranging for most elements from 75-110 %. RSDs were < 10 % for most of the REEs. A summary of these data is given in Table 1b. In-depth investigations by means of ICP-AES revealed excellent "peak purities", indicating an excellent selectivity of the sorbent (Figure 3). Nevertheless, the off-line set-up, the comparably broad range of recoveries (75 – 110 %) as well as the narrow pH range during extraction (5.3 – 5.5) made a "second generation" of *vic*-carboxylic acid resins highly desirable.

Synthesis of ONDCA-based extraction resins[77]

The main objective was to gain access to an on-line SPE-HPLC system for the quantification of REEs, in order to avoid the still time consuming off-line SPE process. In order to obtain such pressure-stable supports, research focused on silica-based materials. Copolymers of 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (ONDCA) and norborn-2-ene (NBE) with well-defined block sizes and molecular weights were prepared by ROMP using initiators of the type $Cl_2Ru(PR_3)_2(CHPh)$ (R = cyclohexyl). The linear polymers and copolymers were coated onto various vinylsilanized silica materials and subsequently cross-linked employing azobis-*i*-butyronitrile (AIBN) (Scheme 2). The coating procedure presented in this contribution leads in combination with the use of well-defined polymers and copolymers to more reproducible materials, as the amount of polymer and consequently the capacity (expressed in mmol/g) of the material is simply determined by weight. Nevertheless, coating conditions definitely strongly depend on the nature of the prepolymer used and special care must be taken in case of polymers bearing functional groups in order to prevent degradation or any other kind of change. In order to obtain an optimized support, the influence of particle size, pore diameter and volume, specific surface of the inorganic carrier, the influence of the block-sizes and amounts of coating on the chemical stability of the resulting materials as well as on the separation efficiency and selectivity have been studied extensively[77]. One important

Table 1a

Average recoveries (%) and rRSDs (σ_n%) for La-Lu (without Pm) on succinic acid derivatized resin (3.1 mequiv COOH/g, 300 mg); **mixed standard** containing 500 ng/g and 5 ng/g La-Lu (without Pm), respectively, in 1N HNO_3. pH = 5.5 (acetate buffer).

REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5 ppb	90.0	93.0	101.3	97.5	101.6	98.8	97.9	96.1	97.3	98.3	100.2	99.7	92.2	96.9
σ_n **(n=3)**	0.7	3.3	2.5	3.5	3.2	1.3	4.1	0.6	2.1	0.8	2.1	1.0	4.6	1.9
500 ppb	92.3	94.7	102.1	94.9	100.1	100.3	92.4	96.8	97.1	95.0	97.8	101.8	91.5	98.1
σ_n **(n=4)**	3.2	6.6	3.1	2.4	6.0	5.2	3.0	6.6	2.9	1.7	2.6	6.0	3.4	5.0

Table 1b

Average recoveries (%) and RSDs (σ_{n-1}, %) for La-Lu (without Pm) from granite, andesite, and basalt on succinic acid derivatized resin (3.1 mequiv. COOH/g, 250 mg), masking agents: 5-sulfosalicylic acid, MeOH (0.8 % v/v). pH = 5.5 (NaOH / acetate buffer). $^{1)}$ theoretical concentration after SPE procedure and elution. x) below l.q. according to DIN 32645[81].

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
granite	**conc [µg/g]$^{1)}$**	2.70	5.40	0.635	2.35	0.485	0.043	0.465	0.083	0.51	0.103	0.325	0.053	0.37	0.057
	recovery	101.4	95.2	115.2	80.2	77.5	94.7	93.8	84.5	86.9	104.3	95.8	92.4	110.8	100.5
	σ_{n-1} **(n=21)**	5.6	5.4	6.2	7.9	4.6	9.6	4.6	11.2	5.7	10.6	5.0	10.2	5.4	11.2
andesite	**conc [µg/g]$^{1)}$**	1.09	2.00	0.245	0.95	0.170	0.051	0.135	0.021	0.090	0.017	0.043	0.008	0.045	0.006
	recovery	120.6	94.8	103.0	85.7	90.6	89.2	79.7	x)	93.1	x)	x)	x)	86.6	x)
	σ_{n-1} **(n=21)**	6.6	2.7	6.7	2.8	4.0	3.0	7.8	x)	2.4	x)	x)	x)	3.0	x)
basalt	**conc [µg/g]$^{1)}$**	2.80	5.25	0.660	2.70	0.510	0.160	0.425	0.060	0.280	0.044	0.10	0.014	0.075	0.010
	recovery	98.0	93.0	121.9	88.1	84.7	93.5	100.8	74.6	91.4	102.2	82.1	x)	86.8	102.6
	σ_{n-1} **(n=19)**	5.3	4.0	10.5	5.4	5.2	7.0	4.6	16.1	6.6	10.9	7.5	x)	7.9	23.3

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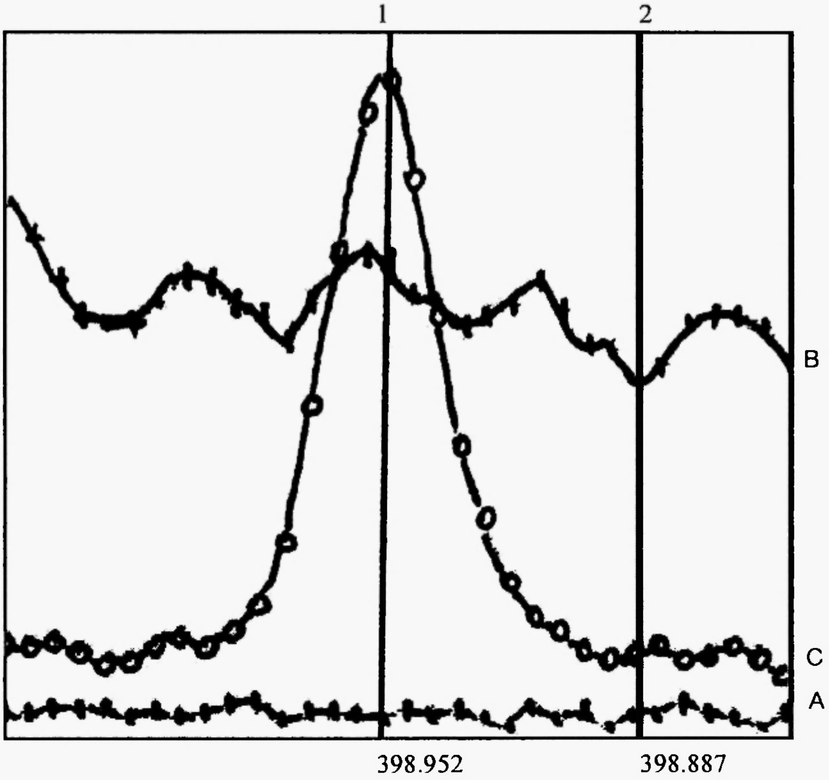
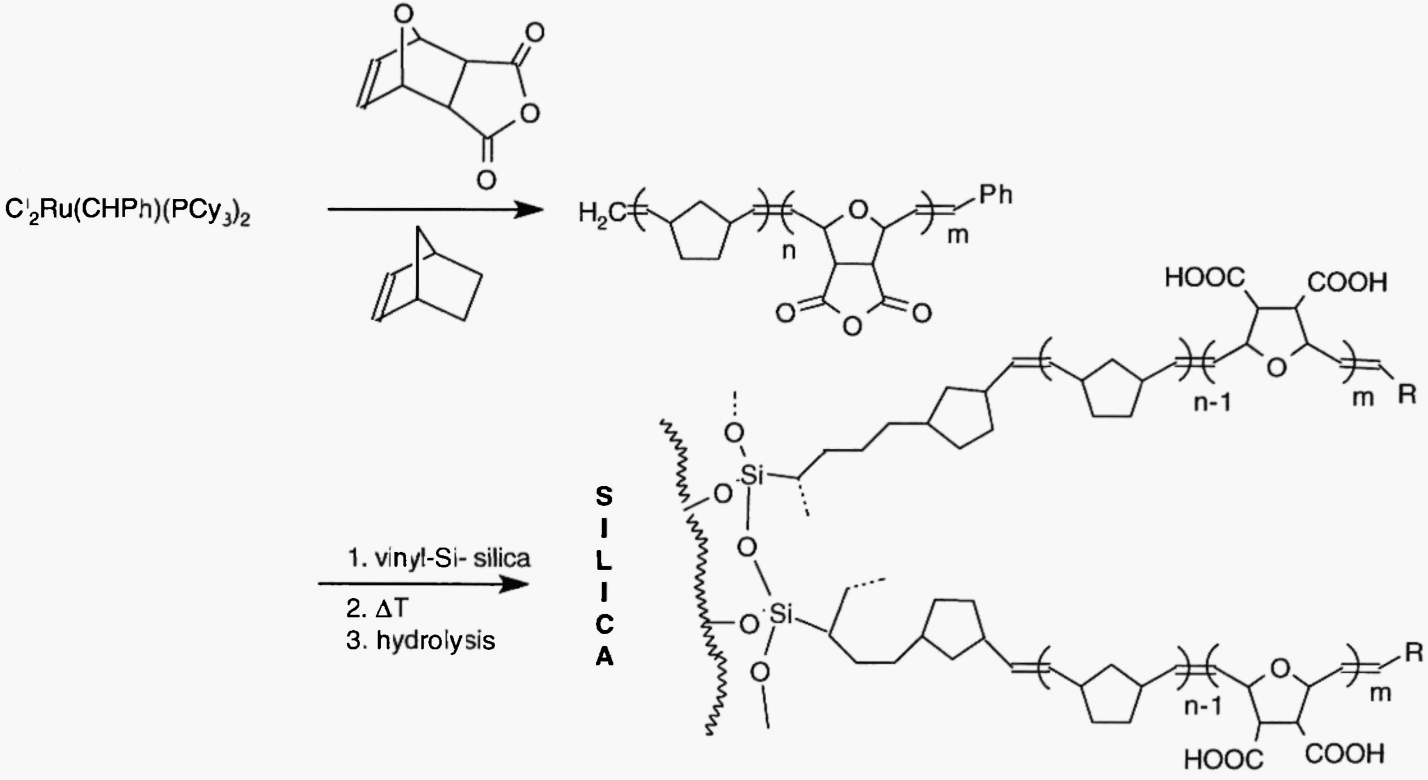


Fig. 3: ICP-OES signal for La (from granite). (1) on-peak quantification (λ = 398.952 nm), (2) background position (λ = 398.887 nm). **A**: deionized water, **B**: rock digest, **C**: interference-free La-signal after clean-up and preconcentration step.

finding was that the high hydrophilicity of the ONDCA-containing copolymer ensured a strong interaction of the mobile phase with the material even in the absence of any organic solvent content.

Especially in the case of silica-based materials, certain stability criteria had to be addressed and fulfilled. On one hand, any coating must be thick enough to prevent chemical degradation of the carrier. On the other hand, the coating may not be too thick, as this significantly further reduces the



Scheme 2: Synthesis of poly(ONDCA- *block*-NBE)-coated silica

chromatographic surface and consequently leads to significantly reduced extraction efficiencies. Due to the high average molecular weights of the polymers, a loss of pore volume and specific surface area was observed. Thus, the specific surface (σ) of silica with 100 Å or 300 Å materials showed a loss in σ of approximately 20 %. The optimum coating thickness with regard to the accessibility of the carboxylic acid groups was found to be in the range of 50 - 120 $\mu g/m^2$. This amount allowed an almost quantitative interaction (80- 100 %) of the carboxylic acid groups with the mobile phase (as determined by acid/base titration) without sacrificing the chemical stability of the support ($0 < pH < 14$).

On-line REE-extraction with ONDCA-based resins[78]

The new poly(ONDCA-*block*-NBE)-coated silica-based sorbents turned out to be highly useful in the on-line preconcentration of lanthanides from rock digests and their subsequent RP-ion-pair HPLC separation. The new sorbent shows high extraction efficiencies for lanthanides within an enhanced pH-range for extraction of 3.5 – 5.5. This extraction pH represents a crucial point in the enrichment of metal ions. As a consequence of the solubility products (pK_s) of $Fe(OH)_3$ (38.6) and the pK_a-values of succinic acid (5.16 and 5.61, respectively), a pH higher than 5.5 had to be strictly avoided. In order to determine the lowest working pH, sorption experiments were carried out at pH 3.0 - 5.5. These investigations, performed with a test set of four different lanthanides (Ce, Sm, Tb, and Yb), revealed a constant, quantitative extraction between pH 3.5 and 5.5. This represents an improvement to poly(NDCA-*co*-DMN-H6)-based materials reported previously[76] (*vide supra*), where extractions had to be carried out at pH 5.4 ± 0.1. These significantly improved complexation capabilities of the new ligand are attributed to the presence of the additional ether-ligand in each five-membered ring, which results from ROMP of ONDCA and that is not present in the poly(NDCA-*co*-DMN-H6) system. Based on the known complexation behavior of lanthanides with dicarboxylic acids[15,49,50], the extraction of lanthanides is therefore believed to proceed *via* complexation of a metal ion by the two *vic*-dicarboxylate groups *and* the additional oxygen in the 5-membered ring (Figure 4). This is supported by the finding that, despite their lower carboxylic acid content, coated silica sorbents based on poly(ONDCA-*block*-NBE) allow higher loadings than NDCA-based polymer beads. For these investigations, the corresponding values for the maximum REE-

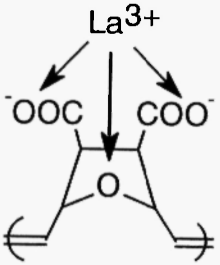


Fig. 4: Proposed complexation mechanism.

loadings were deduced from the corresponding breakthrough curves. Since sorption capacity for REEs was sufficiently high with both large and small diameter silica sorbents and the use of a coated silica with larger particle diameters did not influence the resulting separation, we focused on the use of coated Silica 60 in order to contribute to a cheap SPE-material. In SPE experiments, a precolumn size of 4 x 60 mm was found sufficient for quantitative REE extractions. Recoveries found for a REE standard are summarized in Table 2a.

Quantification of REEs via on-line SPE-RP-HPLC[78]

In principal, the lowest values for l.d. and l.q. may be achieved by ICP-OES[43] rather than by HPLC using post-column derivatization. This definitely needs to be addressed. Nevertheless, the large amounts of interfering ions present in rock samples, from which REEs need to be separated prior to any quantification, justify the development of an HPLC-based system. Among other potential post-derivatization reagents (PDRs, *e. g.* chlorophosphonazo III[59,63], 2-arsono-benzolazo-2'-chromotropic acid disodium salt (neothorine = arsenazo I[53]), bis-(2-arsono-benzolazo)-2,7-chromotropic acid (arsenazo III)[54,57,58,61,62,79,80] or 4-(2-pyridylazo)resorcinol (PAR)[54-58,60], arsenazo III and PAR were chosen for the complementary molar extinction coefficients (ε) of the corresponding REE-complexes. In order to obtain optimum REE separations by means of HPLC, one basic requirement was the instantaneous and quantitative elution of all analytes sorbed onto the precolumn. For these purposes, a gradient separation system consisting of hydroxyisobutyric acid (HIBA) and sodium octadecylsulfonate was found suitable[58], despite the fact that Y and Dy are not baseline-separated under these conditions. It is worth

Table 2a

Recoveries (%) and RSDs (σ_{n-1}, %) for a La-Lu standard(without Pm, 50 ng/mL each) after enrichment on poly(ONDCA-*block*-NBE)-coated silica-60. pH was adjusted to 4.0 using NH_4OH and an acetate buffer (pH = 4, I = 0.5). n = 3, unless stated otherwise.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy+Y	Ho	Er	Tm	Yb	Lu
recovery[5]	100	98	101	97	101	102	97	99	98	101	102	103	103	100

Table 2b

Recoveries (%) and RSDs (σ_{n-1}, %) for La-Lu (without Pm) from GSR-3 basalt after enrichment on poly(ONDCA-*block*-NBE)-coated silica-60. pH was adjusted to 4.0 using NH_4OH and an acetate buffer (pH = 4, I = 0.5). n = 3, unless stated otherwise.

Conc [µg/g][1]	56	105	13.2	54	10.2	3.2	8.5	1.2	27.6	0.88	2.0	0.28	1.5	0.19
ng REE[2]/ reagent	140/A	263/A	66/P 198/A	135/A2 70/P	153/A	48/A	42.5/P 128/A	60/AP	69/A	44/P	10/P 100/P	-	7.5/P	-
recovery	104	103	100	103	99	94	103	98	103	94	98	[x]	95	[x]
σ_{n-1}	2	2	7	4[3]	4	0	4[3]	2	3	1	3	-	2	-

[x] Below limit of quantification according to DIN 32645 [46]. [1] REE-content in rock, [2] amount of REE (ng) enriched by the precolumn, [3] n = 5, [4] σ_{n-1} (n = 3) ≤ 2 %. A = arsenazo III, P = PAR.

Table 2c

Recoveries (%) and RSDs (σ_{n-1}, %) for La-Lu (without Pm) from GSR-1 granite after enrichment on poly(ONDCA-*block*-NBE)-coated silica-60. pH was adjusted to 4.0 using NH_4OH and an acetate buffer (pH = 4, I = 0.5). n = 3, unless stated otherwise.

Conc [µg/g][1]	54	108	12.7	47	9.7	0.85	9.3	1.65	72.2	2.05	6.5	1.06	7.4	1.15
ng REE[2]/ reagent	135/A	270/A	191/A 64/P	118/A	146/A 49/P	43/A	47/P 140/A	8/P 83/A	181/A	10/P 31/A	33/P 98/A	53/A	37/P 111/A	58/A
recovery	99	100	99	103	97	98	100	97	100	112	99	106	103	99
σ_{n-1}	4	0	7	6	5	2	5	4[3]	6	7	3	4	5	5

[x] Below limit of quantification according to DIN 32645 [46]. [1] REE-content in rock, [2] amount of REE (ng) enriched by the precolumn, [3] n = 5, [4] σ_{n-1} (n = 3) ≤ 2 %. A = arsenazo III, P = PAR.

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mentioning that recent reports[61] described the use of a similar eluent consisting of HIBA and glycolic acid that allows the separation of these two elements. Nevertheless, Gd and Eu coelute under these conditions. So far, a baseline separation of all REEs has only been achieved by CE-techniques[70]. Unfortunately, CE techniques entail some restrictions in terms of on-line enrichment, thus preventing their use so far. For the enrichment step, rock digests were modified with 5-sulfosalicylic acid in order to mask Fe^{3+} and Al^{3+}. Since especially granites possess a high Si-content and since *ortho*-silicic acid shows a minimum in solubility around pH = 5, methanol was added to prevent the formation of polysilicic acid. The entire solution was adjusted to a pH of 4.0 and passed over coated silica-60-packed precolumns (60 x 4 mm). Since the concentrations of REEs in granite and basalt vary over more than two orders of magnitude, different amounts of rock-digests as well as two different PDRs with different sensitivities had to be applied for a complete quantification. In this context it is worth mentioning, that the limits of quantification as determined by DIN 32645 [81] were found to be 4 times lower for PAR compared to arsenazo III. Consequently, PAR was used for the quantification of REEs occurring at low concentrations (e. g. Ho in GSR-3 basalt), while arsenazo III was used for REEs occurring at high concentrations (e. g. La, Ce, Dy+Y, etc.). Recoveries and RSDs obtained from GSR-1 granite and GSR-3 basalt after on-line SPE-gradient RP-ion-pair chromatography are summarized in Tables 2b and 2c. As can be deduced therefrom, almost quantitative recoveries (97 – 103 %) were obtained for most REEs. Except for Pr, Dy+Y and Ho, RSDs were within a range of 2 – 5 %. The quantification of Ho was aggravated by Th, which is quantitatively coextracted by the precolumn (*vide infra*). According to DIN 32645 [81], the Tm- and Lu-content in GSR-3 basaltic rock was found to be too low for quantification; nevertheless, half-quantitative determinations with recoveries of 95 – 105 % and r.s.d. $\leq$10 % of these two REEs were possible.

In order to rule out coextraction of transition metals which potentially form colored complexes with either of the PDRs, a mix containing 5 μg/ml of Zn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, Al^{3+}, Ca^{2+}, Ba^{2+}, UO_2^{2+} and Th^{4+} was passed over a precolumn (Figures 5a and 5b). Elution was with HIBA, and the eluate was checked by ICP-OES. Besides thorium, which was coextracted quantitatively (100 %), UO_2^{2+} and Cu^{2+} were also retained rather strongly (75 and 20 %, respectively), yet only small amounts (1 - 6 %, Table 3) of all other investigated cations were found to be bound onto the precolumn. Group II metals and Cd do not form colored complexes either with PAR or with

Table 3

Overview over the retention characteristics of spin-coated precolumn materials for interfering cations in the presence of 5-sulfosalicylic acid and methanol. Retention determined by ICP-OES. For values for the beaded resins refer to lit. [76].

element	Zn	Ni	Cd	Co	Mn	Mg	Cu	Al	Ca	Ba	Fe	U¹⁾	Th¹⁾
retention [%]	3.9	2.0	6.3	3.9	2.7	2.1	20.1	1.8	4.4	3.4	1.0	75.0	100.0

¹⁾ determined by RP-ion pair-HPLC.

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arsenazo III and therefore do not impede the quantification of REEs. Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} only form colored complexes with PAR and interfere with Dy+Y, Eu, Sm and Ce due to similar retention times within the REE-chromatogram. Nevertheless, their influence may be omitted by using arsenazo III. Only Th^{4+} and UO_2^{2+} form colored complexes with PAR and especially with arsenazo III. This basically prevents the total elimination of the interference of these two ions, if they are present at concentrations > 10 µg/g. In the case of GSR-1 granite which possess a Th-content of 54 µg/g, it consequently influences the mean recovery value (112 %) as well as the RSDs (7 %) for Ho (7 %). In GSR-3 basaltic rock, which shows a reduced Th-content of only 6 µg/g, good recovery values of 98 % with low RSDs (3 %) were obtained for this element.

Extraction of radioactive REEs with ONDCA-based resins[82]

In order to check out the extraction capability of the new sorbents at ultra-low concentrations, extraction experiments were carried out with radioactive REEs. For these purposes, solutions (pH = 5.5) of $^{147}Pm^{3+}$ chloride and $^{152}Eu^{3+}$ chloride, respectively, were passed at a flow rate of approximately 2.5 ml/min through a stainless steel cartridge filled with coated silica (200-400 mesh material). Elution of the metal ions from a loaded column and simultaneous recycling of the material was performed using 5 % nitric acid. 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 4. Both lanthanides were

Table 4

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

activity [Bq/ml]	carriers [µg/ml Ce+Ln]	total loading[1] 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

[1] total of all lanthanides.

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eluted rapidly and quantitatively into the first three milliliters thus guaranteeing a rapid and convenient experimental setup. The extraordinary high affinity of the sorbent for lanthanides was demonstrated by passing neat Eu-152 standards containing an activity of 180 Bq/ml, corresponding to a concentration of only 150 fmol/l (23 ng/l) over the sorbent. Complementarily, spiked solutions were prepared up to a total lanthanide content of 250 µg/ml. Recovery values for this broad concentration range (7 orders of magnitude) varied within 96- 106 %. Keeping the comparably short analyses times of less than 5 minutes in mind, these data give an impressive demonstration of the extraction potential of the new material.

CONCLUSIONS

New and highly efficient sorbents based on poly(NBE-*co*-DMN-H6) and poly(ONDCA-*block*-NBE)–coated silica for off-line SPE-ICP-OES and on-line SPE-HPLC of lanthanides have been developed. In terms of recoveries, reproducibility, costs and ease of handling the latter one represents by far the superior system. Extraction efficiencies with poly(ONDCA-*block*-NBE)–coated silica materials are quantitative in a concentration range of at least 0.2 ng/ml -250 µg/ml. Generally, an extraction pH of 3.5 - 5.5 is applicable. The materials are stable within a pH-range of 0- 14, and may be recycled many times. Recoveries for most REEs from different types of rocks, which

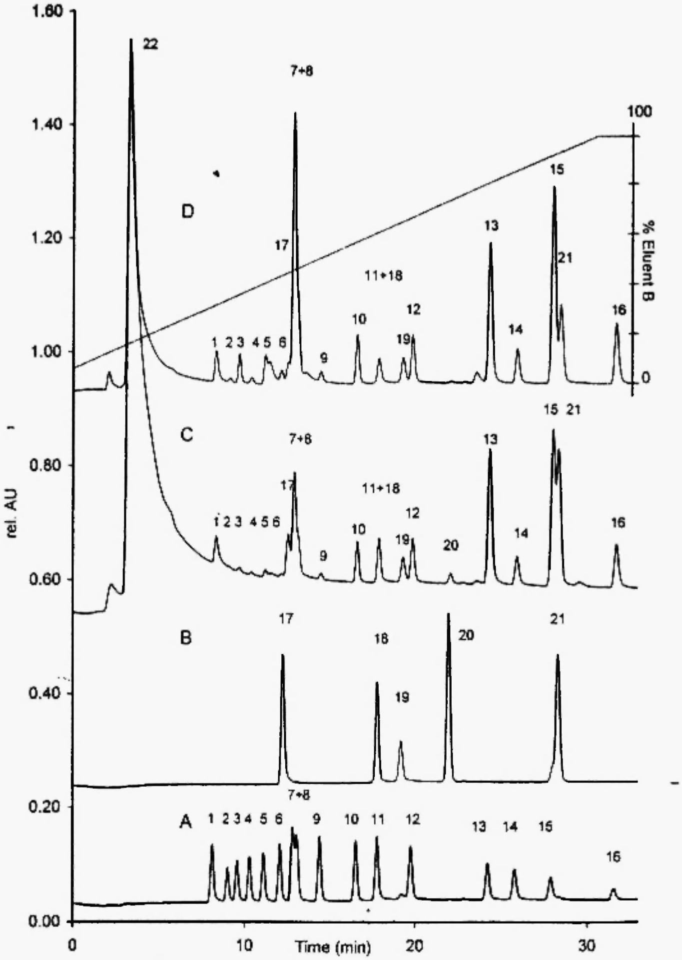

Fig. 5a: RP-ion-pair HPLC of lanthanides and interfering transition metal ions after on-line SPE using **PAR**-derivatization. For chromatographic conditions refer to the experimental section. **A**: lanthanide standard (inj. vol. 10 µl, c = 10 µg/ml each); **B**: Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} standard (inj. vol. 20 µl, c = 10 µg/ml each), **C**: GSR-3 basalt digest, **D**: GSR-1 granite digest. **Peak order**: Sc^{3+} (1), Lu^{3+} (2), Yb^{3+} (3), Tm^{3+} (4), Er^{3+} (5) Ho^{3+} (6), Y^{3+} (7), Dy^{3+} (8), Tb^{3+} (9), Gd^{3+} (10), Eu^{3+} (11), Sm^{3+} (12), Nd^{3+} (13), Pr^{3+} (14), Ce^{3+} (15), La^{3+} (16), Cu^{2+} (17), Zn^{2+} (18), Ni^{2+} (19), Co^{2+} (20), Mn^{2+} (21), Fe^{3+} (22).

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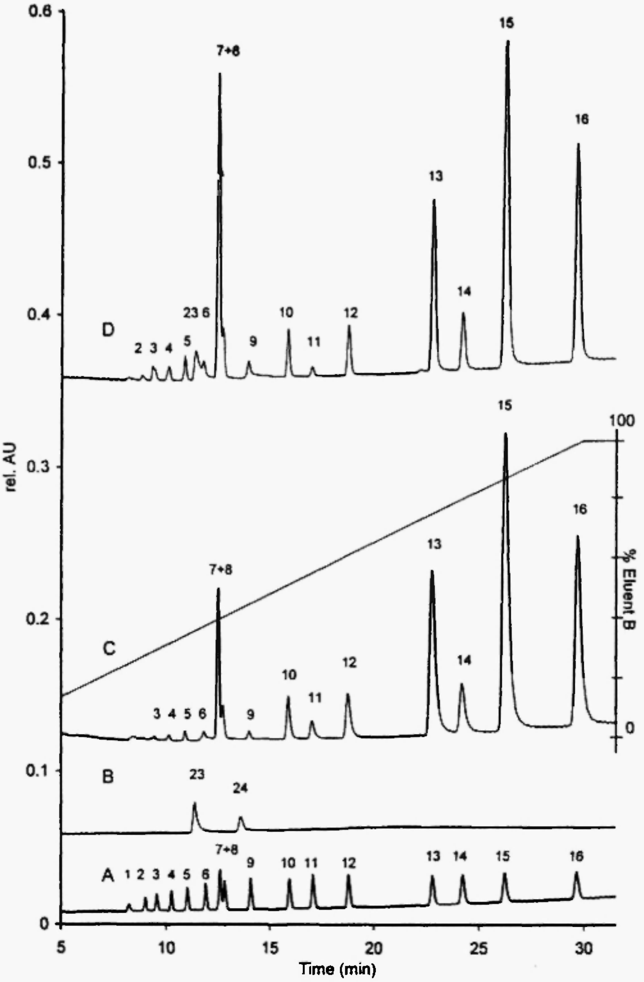

Fig. 5b: RP-ion-pair HPLC of lanthanides and interfering transition metal ions after on-line SPE using **arsenazo III**. For chromatographic conditions refer to the experimental section. **A**: lanthanide standard (inj. vol. 10 µl, c = 10 µg/ml each); **B**: UO_2^{2+} and Th^{4+} standard (inj. vol. 10 µl, c = 20 µg/ml each), **C**: GSR-3 basalt digest, **D**: GSR-1 granite digest. **Peak order:** Sc^{3+} (1), Lu^{3+} (2), Yb^{3+} (3), Tm^{3+} (4), Er^{3+} (5) Ho^{3+} (6), Y^{3+} (7), Dy^{3+} (8), Tb^{3+} (9), Gd^{3+} (10), Eu^{3+} (11), Sm^{3+} (12), Nd^{3+} (13), Pr^{3+} (14), Ce^{3+} (15), La^{3+} (16), Th^{4+} (23), UO_2^{2+} (24).

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differed significantly both in their REE-content and in the concentration of the major elements, were found to be in the range of 97 – 103 %. With the exception of Th^{4+} and (UO^{2+},$^{)}$, a negative influence of any coextracted metal ion (Th^{4+}, Al^{3+}, Fe^{3+} and Cu^{2+}) may be ruled out. Therefore, in summary, the present system is the first that allows a fast, convenient and highly reproducible quantification of REEs by a simple method. It is believed to represent an attractive alternative to standard, time-consuming preparative-scale ion exchange off-line enrichment procedures. In the absence or in the presence of low concentrations ($\leq$ 5 µg/g rock) of interfering transition metal cations, the total analysis time for one run (including preconcentration) is less than 1 hour. In the presence of higher concentrations of these transition metal ions, two runs with two different PDRs have to be performed.

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LIST OF ABBREVIATIONS

WCX	weak cation exchanger
PS-DVB	poly(styrene-*co*-divinylbenzene)
REEs	rare earth elements
CE	capillary electrophoresis
HPLC	high-performance liquid chromatography
RP	reversed-phase
TLC	thin layer chromatography
HIBA	2-hydroxy-*i*-butyric acid
EDTA	ethylenediamine tetraacetate (disodium form)
AAS	atomic absorption spectroscopy
DCP-AES	direct current plasma atomic emission spectroscopy
ICP-AES	inductively-coupled plasma atomic emission spectroscopy
ICP-MS	inductively-coupled plasma mass spectrometry

ROMP	ring opening metathesis polymerization
NDCA	norborn-2-ene-5,6-dicarboxylic acid
DMN-H6	1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene
ONDCA	7-oxanorborn-2-ene-5,6-dicarboxylic acid
NBE	norborn-2-ene
σ	specific surface area
SRM	standard reference material
RSDs	relative standard deviations
PDR	post-derivatization reagent
l.d.	limit of detection
l.q.	limit of quantification

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