Separation of Lanthanides by Ion Chromatography with Imprinted Polymers

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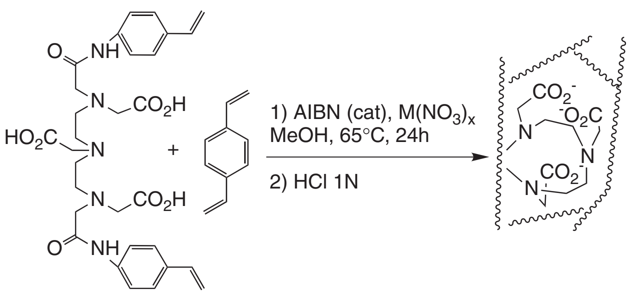
Several lanthanides were separated by ion chromatography with blank and imprinted polymers; the best resolutions were achieved over the latter one.

Nowadays, molecular imprinting-based materials prove to be efficient for high performance chromatographic separation of enantiomers, amino acids, peptides or biologically active compounds.[1] This technique was also dedicated to selective adsorption of metal ions, as described recently by the groups of Saunders[2] and Murray.[3] To obtain ion-selective resin, the choice of the appropriate chelating ligand is based not only on the charge, size and coordination number of the ion template but above all on the affinity with the cation which can be easily correlated with stability constants of metal-ion complexes.[4] According to this fact, DTPA-based polymers were synthetized as DTPA showed strong association constants towards lanthanides ($\log K_{\mathrm{La}} = 19.48$, $\log K_{\mathrm{Ce}} = 20.50$, $\log K_{\mathrm{Eu}} = 22.39$, $\log K_{\mathrm{Gd}} = 22.46$).[5] The Gd-imprinted solids exhibited higher selectivity towards $\mathrm{Gd^{(III)}}$ with respect to $\mathrm{La^{(III)}}$ than the corresponding blank polymer ($S_{\mathrm{Gd/La}} > 20$ and 6.3 respectively).[6] The loading capacity of the materials was low to moderate so that their applications on large scale were prohibited. However, development of such polymers as chromatographic sorbent is conceivable. Separation of lanthanides by high-performance chelation ion chromatography was recently described using a chromatographic column packed with iminodiacetate bonded to silica.[7] In this paper, we report a modified approach to prepare lanthanide-imprinted polymers and their use in ion chromatography. The bulk polymerisation is commonly employed to prepare imprinted polymers. Consequently, they have to be ground and sieved to give particles with a broad size distribution and irregular shape which lowered their performance as chromatographic support. To limit these disadvantages, we performed the preparation of the imprinted materials by dispersion polymerisation as previously described by Sellergren.[8]

Materials were prepared from diethylene triamine (*N*,*N*′) diacetamidostyrene triacetic acid (DTPA-like) as chelating monomer and divinylbenzene as crosslinker in the presence of $\mathrm{NaNO_3}$ (blank polymers) or $\mathrm{Gd(NO_3)_3{\cdot}6H_2O}$ (imprinted polymers) (Scheme 1).[9]



Scheme 1. Synthesis of imprinted material.

Table 1. Characteristics of custom-made polymers and batch extraction data

Polymer	C_{DTPA}[a] /μmol $\mathrm{g_{resin}}^{-1}$	S_{BET} /$\mathrm{m^{2-}\ g^{-1}}$	m /mg	$\%E_{\mathrm{La}}$[b]	$\%E_{\mathrm{Gd}}$[b]	$S_{\mathrm{Gd/La}}$[c]
B $\mathrm{blank_{(Na)}}$	340 (215)	40	20	10	30	4
I $\mathrm{imprinted_{(Gd)}}$	385 (280)	18	100	57	96	19

[a]from N elemental analysis, in bracket calculated from $\mathrm{H^+}$ exchange capacity; [b]$\%E = (C_{\mathrm{i}} - C_{\mathrm{f}})/C_{\mathrm{i}}) \times 100$; [c]$S_{\mathrm{Gd/La}} = D_{\mathrm{Gd}}/D_{\mathrm{La}}$ with $D = ((C_{\mathrm{i}} - C_{\mathrm{f}})/C_{\mathrm{f}}) \times m/V$ (m = mass of resin, V = volume of solution, C_{i} and C_{f} respectively initial and final concentrations of lanthanides solution).

Whatever the type of polymerisation is, the concentration of the chelating monomer within the resin is slighly higher for the imprinted material compared to the blank one (Table 1). After acidic strippings, all the metal engaged during the polymerisation step was removed. The polymers were engaged in batch competitive extraction of lanthane and gadolinium in similar conditions to those described previously.[6] The mass of polymers used for these extractions was optimized to get the best selectivity in each case. A significant imprinted effect is observed, and similar selectivities towards the gadolinium are achieved with the imprinted polymers than those determined previously with resins synthetized in bulk polymerization.[6] La-imprinted resins were also prepared by dispersion polymerisation but moderate Gd/La selectivity were achieved ($S = 7.5$).[10] These solids were not further studied.

The solids were then evaluated for ion chromatography of a mixture of $\mathrm{Gd(NO_3)_3}$ and $\mathrm{La(NO_3)_3}$.[11] As expected, whatever the conditions of elution and the sorbent are, lanthanum was eluted first that confirmed it has lower association constant with support than gadolinium. Initial tests were performed with identical elution conditions (0.015 M (1M = 1 mol dm^{-3}) $\mathrm{HNO_3}$, 20 °C) with both resins. While Gd and La were co-eluted with blank polymer, a significant separation occured with imprinted one. The influence of $\mathrm{HNO_3}$ concentration and temperature of the column on the efficiency of the separation was studied for both supports to improve the ions separation. It has to be noticed that the retention time of sodium and lanthanum are close, which supposed that under these conditions, lanthanum does not interact significantly with the chelating ligand contrary to gadolinium.

The pH of the eluent was varied from 1 up to 1.82 at 20 °C, to determine its influence on the separation of the two lanthanides. At moderate $\mathrm{H^+}$ concentration, ($[\mathrm{HNO_3}] = 0.015\,\mathrm{M}$), strong complexation occured for both metals and the signals were not resolved when **B** was used as support. On the other hand, for high $\mathrm{H^+}$ concentration, Gd and La were eluted simultaneously to Na. Such phenomenon was already described for

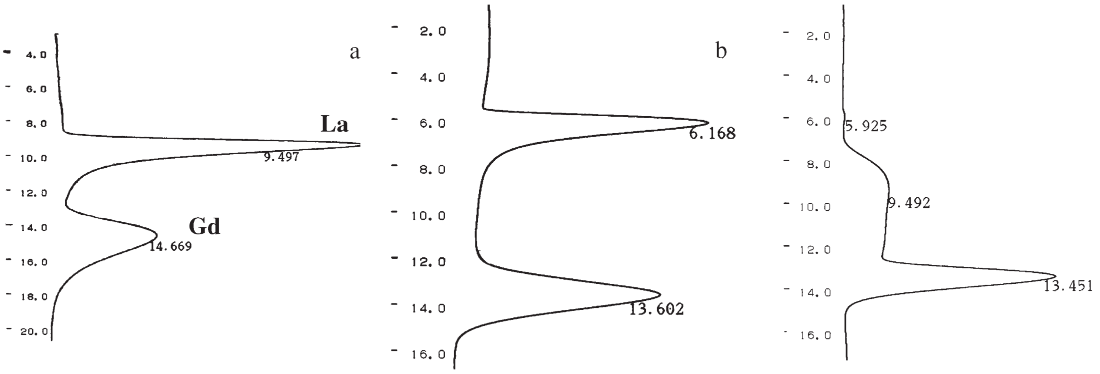


Figure 1. Chromatogram of Gd/La mixture. (a) blank polymer, 20 °C, flow-rate: 0.35 mL/min, eluent: 0.03 M HNO_3; (b) imprinted polymer, 20 °C, flow-rate: 0.5 ml/min, eluent: 0.02 M HNO_3, (c) imprinted polymer, 60 °C, flow-rate: 0.5 mL/min, eluent: 0.02 M HNO_3.

iminodiacetic acid, amino acids or aminopolycarboxylic-based support.[11] After optimisation, the highest resolution was achieved at pH 1.52 for **B** ($\alpha = 2.1$, Figure 1a) and 1.70 for **I** ($\alpha = 3.7$, Figure 1b).

Then, the column temperature was studied. Generally, an increase of column temperature improves the kinetics of chelation and changes the impact of chelating exchange on the retention of cations.[13] Typical chromatograms obtained with Gd-imprinted sorbent at 20 and 60 °C are shown in Figures 1b and 1c respectively. Whatever the support, gadolinium and lanthanum exhibited different behaviour towards the temperature modification, while gadolinium is not affected with the increase of the temperature, the retention time of lanthanum increases with temperature and simultaneously the peaks become broader dramatically. The preorganisation of the functionnalized monomer within the resin affected dramatically its behaviour towards lanthanide. It can be supposed that when the temperature increased the lanthane, which has larger ionic radius than the gadolinium, diffused in the matrix and was chelated with the ligand, increasing so the retention time. However, due to its size, the equilibrium is probably low yielding a broad signal.

The best separation Gd/La by ion chromatography was performed using the Gd-imprinted resin at 20 °C with 0.4 mL/min of 0.02 M HNO_3 eluent. Using these conditions, the selectivity of separation Gd/La reached 4.2. The best separation Gd/La with the Na-templated resin was only 2.4.

The performance of **I** on the separation of several couples of lanthanide was then studied using the best conditions. Results are summarized in Table 2.

Europium salt having similar association constants towards polyaminoacides to gadolinium exhibited identical retention time when **I** was used as sorbent. Cerium nitrate gave intermediate retention time between La and Gd that can be correlated to the relative association constant with DTPA. So that, efficient separation can be performed. It has to be noticed that the separations Ce/Gd or Ce/Eu were not possible with **B** resin. We thought that during polymerization in the presence of gadolinium, the DTPA monomer adopts a defined geometry, which fits properly with the template ion. The ionic imprinted effect is not by itself alone responsible of the separation of the cations but its contribution is not negligible.

Table 2. Retention of lanthanide ions and selectivity of separation. Elution conditions: 0.02 M HNO_3, 20 °C, flow-rate 0.4 mL/min

Ln_1/Ln_2	k'_{Ln1} [a]	k'_{Ln2} [a]	α^{β}
La/Eu	0.03	1.3	4.2
Ce/Gd	0.14	1.3	2.5
Ce/Eu	0.14	1.3	2.5

[a] $k' = (t_{Ln} - t_0)/t_0$ with t_{Ln} = retention time of Ln and t_0 = retention time of Na; [b] $\alpha = 2(t_{Ln1} - t_{Ln2})/(w_{Ln1} + w_{Ln2})$ with w_{Ln} = baseline peak width.

In conclusion, it was shown that imprinted effect improved separation efficiency in high-performance ion chromatography. Further work has to be performed to optimize the separation and for example the use of eluents with different ionic strength must be studied. The comprehension of interactions between ligand and cation could help in the design of well-defined support.

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9 Diethylene triamine-(*N*,*N'*)-diacetamidostyrene triacetic acid (5 g, 8.4 mol), and sodium nitrate (2.14 g, 25 mol, 3 equiv.) were ultrasonicated in 260 mL of methanol. The solution was transferred in a three-necked round bottom flask equipped with a mechanical stirring and purged under argon. Divinylbenzene (19.5 mL, 134 mmol), and AIBN (30 mg) were added and the solution was heated at 65 °C at 500 rpm. After 20 h, the suspension was cooled and the polymer was filtered. The solid was shaken in methanol for 24 h and filtered. The polymer was washed with 1 M HCl (5 times) then water until neutral pH. The resin was dried under vacuum for 24 h in the presence of P_2O_5 and sieved from 25 to 50 μm to give 7.2 g of blank polymer. Similarly, the Gd-imprinted polymer was synthesised in the presence of $Gd(NO_3)_3 \cdot 6H_2O$ (1 equiv.).

10 Ph. D. Thesis Olivier Vigneau, n° 12–2002, University of Lyon, 2002.

11 The chromatographic column (260 mm × 5 mm) was packed with 1.2 g of resin by suspension method using a BIOCART pressure packing system increasing the flow of eluent from 0.1 up to 0.5 mL/min. After stabilisation, the stationary phase was 17 cm high whatever the polymer. All separations were duplicated and were reproducible.

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