

**Chromatographic separation of rare earths from aqueous and ethanolic
leachates of NdFeB and SmCo magnets by a supported ionic liquid phase**

Dzenita Avdibegovic[†], Koen Binnemans^{†*}

[†] KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. box 2404, B-3001 Leuven,
Belgium.

*Corresponding author:

Email: Koen.Binnemans@kuleuven.be

Electronic supplementary information (ESI)

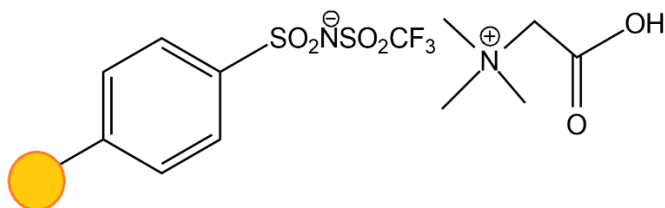


Figure S1. Supported ionic liquid phase (SILP) betainium sulfonate(trifluoromethanesulfonylimide) poly(styrene-*co*-divinylbenzene) [Hbet-STFSI-PS-DVB].

Characterization of magnet

The cylindrical magnets were ground in a disc mill (DM 200, Retsch, Germany) to a particle size of less than 1600 μm . Further particle size reduction was performed by ball milling (Pulverisette Premium 7, Fritsch, Germany) to a final particle size of less than 400 μm . The ball mill was operated using 10 mm grinding balls with a ball-to-powder ratio of 5/1 (g/g) at 800 rpm for 2 min. X-ray powder diffraction (XRD) patterns of the magnet powders were collected from 5° to 70° 2θ in Bragg-Brentano geometry on a Bruker D2 PHASER X-ray diffractometer equipped with a $\text{CuK}\alpha$ radiation, operating at a voltage of 30 kV and a current of 10 mA. Leaching experiments were performed using Thermo Fisher shaker (Type 462-0355).

Sample preparation for UV–VIS analysis

Neocuproine was used as the colorimetric agent for determining the presence of copper(I) in the ethanolic leachate of SmCo magnet.¹ An aliquot of 500 μL of the leachate was mixed with 2 mL of neocuproine solution (0.1 wt.%), 2 mL of sodium acetate buffer solution and 6.5 mL of milliQ water. The blank solution was prepared by the same procedure using 500 μL of ethanol instead of the ethanolic leachate of SmCo magnet. The sodium acetate buffer solution was prepared by mixing equal volumes of 6 mol L^{-1} of acetic acid and 5 mol L^{-1} of sodium hydroxide. For the UV–VIS measurement of iron in NdFeB and SmCo magnets, lixiviants (0.7 mol L^{-1} HCl in water or in ethanol) were used as blank solutions and for diluting the leachates. The ethanolic leachates were diluted 2000 times, and aqueous leachates 400 times prior to UV–VIS measurement of iron. For the UV–VIS measurement of cobalt, both leachates of NdFeB magnet (*i.g.* aqueous and ethanolic) and the aqueous leachate of SmCo magnet were measured without dilution. The ethanolic leachate of SmCo magnet was diluted with the blank solution 50 times prior to the UV–VIS analysis. The solution of iron(II) chloride measured by the UV–VIS absorption spectrometry was first dissolved in 0.7 mol L^{-1} HCl in water or in ethanol to a concentration of iron(II) of 530 g L^{-1} and the solutions were subsequently diluted 2500 times with aqueous or ethanolic blank solutions (lixiviants) prior to a qualitative UV–VIS analysis. For the qualitative analysis of iron(II) in the leachates of NdFeB magnet, 1,10-phenanthroline (0.12 wt.%) was used as a colorimetric agent. The samples were prepared by mixing 5 μL of NdFeB leachates with 1 mL of 1,10-phenanthroline solution, 1 mL of sodium acetate buffer solution and 7.995 mL of milliQ water. The blank solutions were prepared in the same manner, without the addition of the leachate.

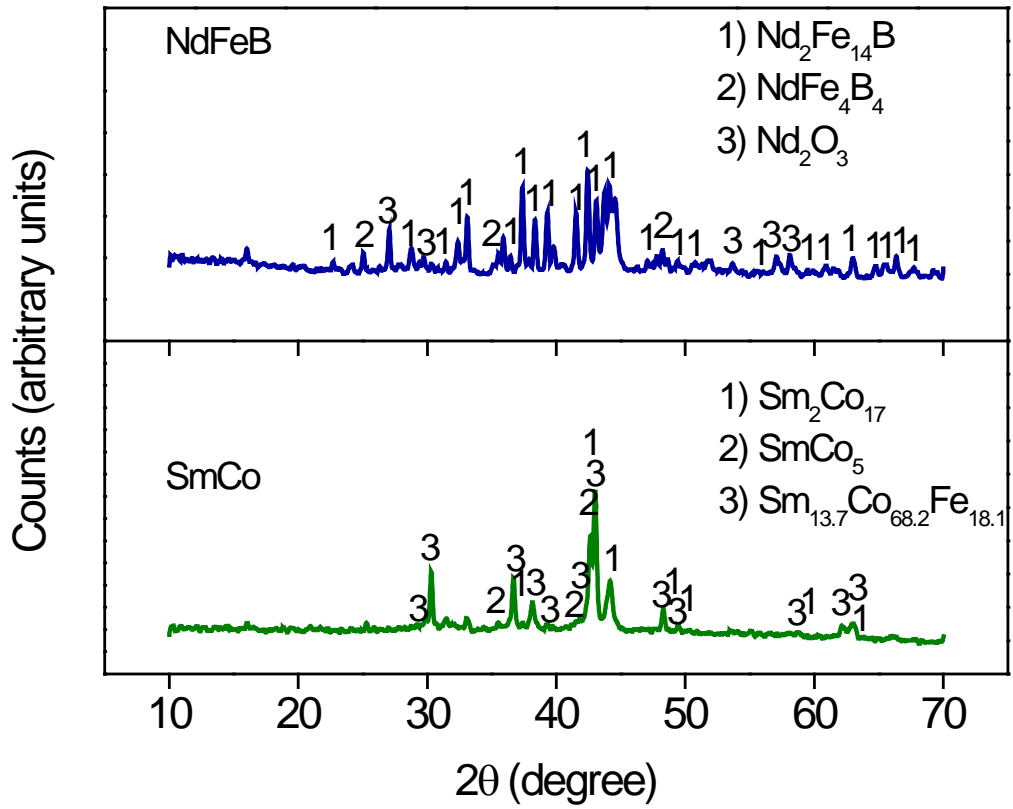


Figure S2. XRD diffractograms of NdFeB and SmCo magnet powders (<400 microns).

UV–VIS absorption spectra of copper(I)

Cuprous ions can be quantified by UV–VIS absorption spectrometry using neocuproine as a complexing and colouring agent.¹ The complex formed in the acidic media shows an absorption maximum around 465 nm without significant interferences from copper(II) or iron(II).¹

Ref: 1. X. Li, W. Monnens, Z. Li, J. Fransaer and K. Binnemans, *Green Chem.*, 2020, **22**, 417–426.

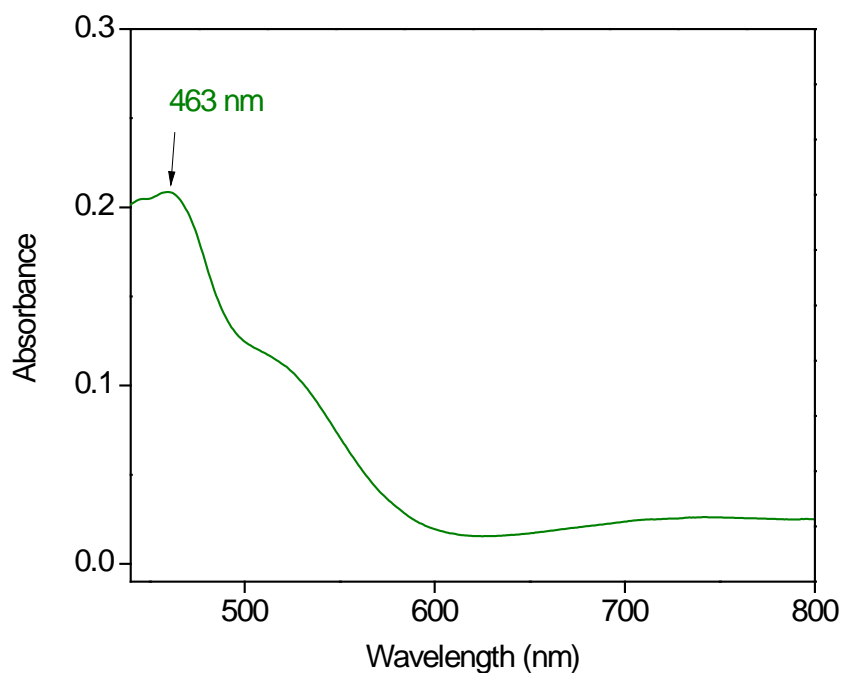


Figure S3. UV–VIS absorption spectra of copper(I) in the ethanolic leachate of SmCo magnet, in the presence of neocuproine.

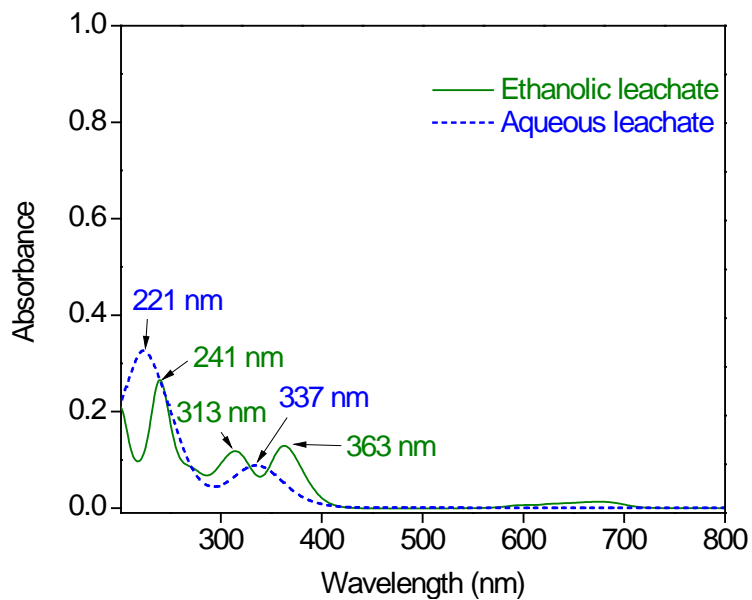


Figure S4. UV–VIS absorption spectra of the leachates of SmCo magnets with 0.7 mol L^{-1} HCl in water (aqueous leachate, dashed blue line), or with 0.7 mol L^{-1} HCl in ethanol (ethanolic leachate, full green line). Aqueous leachates were diluted 400 times, and ethanolic 2000 times.

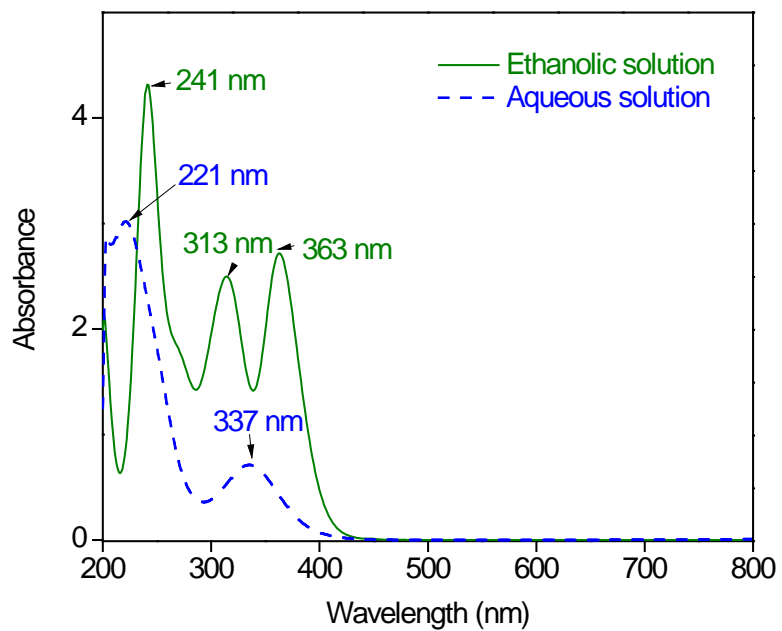


Figure S5. UV–VIS absorption spectra of iron(II) chloride dissolved in 0.7 mol L^{-1} HCl in water (aqueous solution), or in 0.7 mol L^{-1} HCl in ethanol (ethanolic solution).

UV–VIS absorption spectra of iron(II)

In order to further confirm the oxidation state of iron in the aqueous and ethanolic leachates of magnets, a qualitative UV–VIS absorption study using 1,10-phenanthroline as colouring agent was performed. The complex formed between iron(II) and 1,10-phenanthroline in acidic media shows an absorption maximum at 512 nm, with very low interference of iron(III). The recorded absorption spectra of the formed complex in the aqueous and ethanolic leachates of NdFeB and SmCo magnets additionally confirmed the presence of iron in the divalent state (Figure S6).

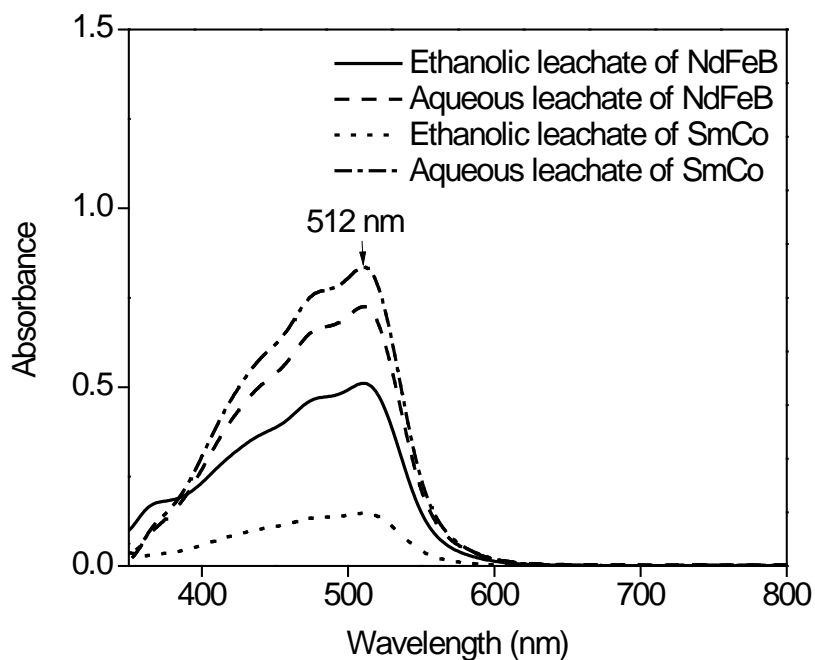


Figure S6. UV–VIS absorption spectra of iron(II) in the aqueous and ethanolic leachates of NdFeB and SmCo magnets, in the presence of 1,10-phenanthroline.

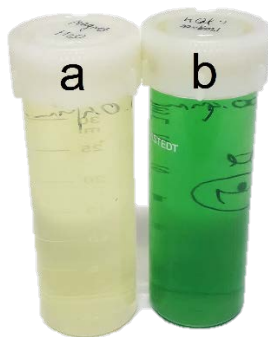


Figure S7. Leachates of NdFeB magnet: a) aqueous solution, and b) ethanolic solution. Aqueous leachates were obtained by leaching of magnets with 0.7 mol L^{-1} HCl in water and ethanolic leachates by leaching with 0.7 mol L^{-1} HCl in ethanol.

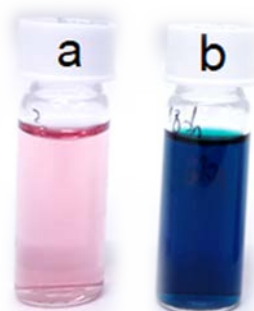


Figure S8. Leachates of SmCo magnet: a) aqueous solution, and b) ethanolic solution. Aqueous leachates were obtained by leaching of magnets with 0.7 mol L^{-1} HCl in water and ethanolic leachates by leaching with 0.7 mol L^{-1} HCl in ethanol.

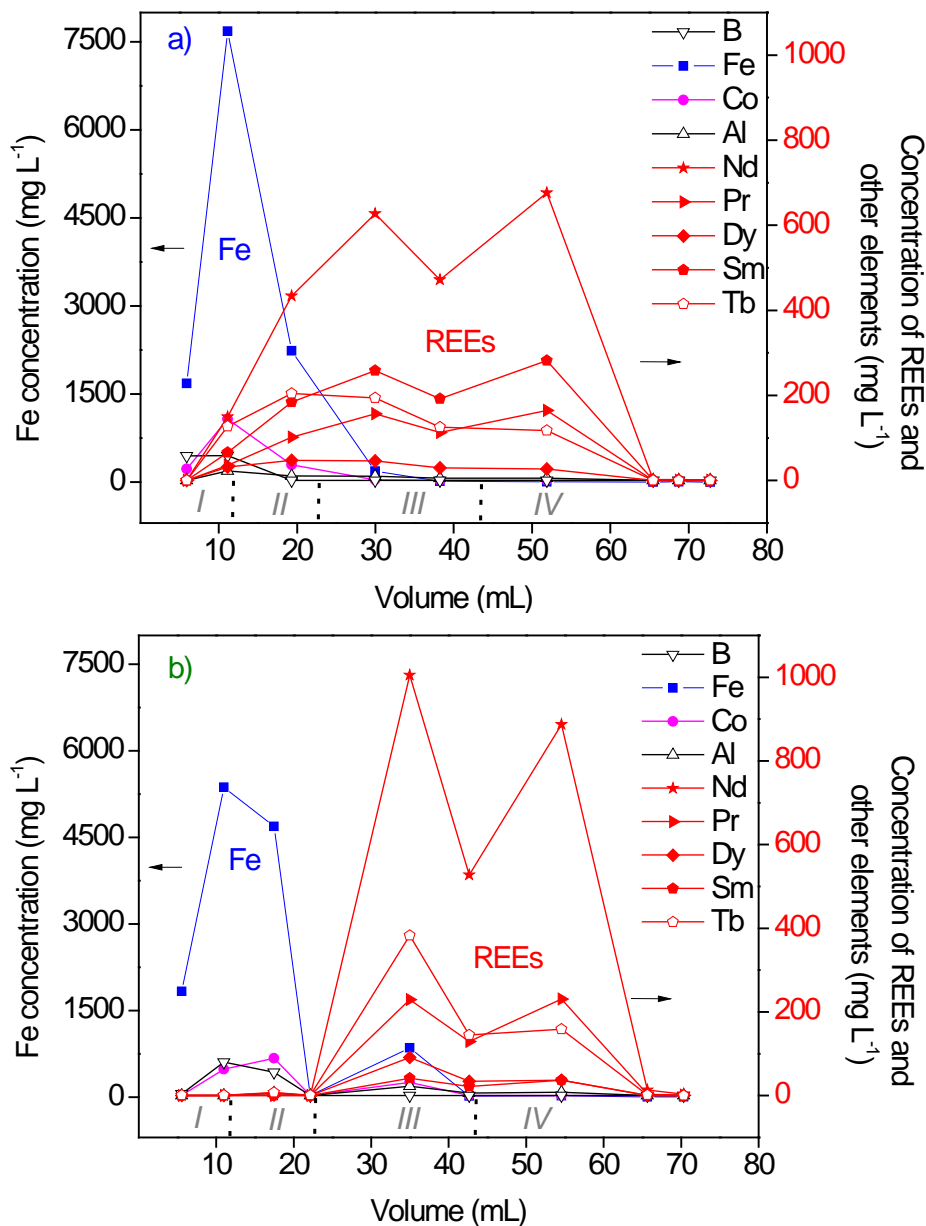


Figure S9. Chromatographic separation of elements from a) aqueous leachates or b) ethanolic leachate of NdFeB magnets. Mobile phases: *I*) 10 mL of aqueous a) or ethanolic b) leachate of NdFeB magnet, *II*) 10 mL of 0.3 mol L⁻¹ HCl for the aqueous leachate (figure a), or 10 mL of ethanol for the ethanolic leachate (figure b), *III*) 20 mL of 0.5 mol L⁻¹ of HCl, *IV*) 30 mL of 1.5 mol L⁻¹ of HCl. Flow rate of leachates was 0.1 mL min⁻¹, and of eluents 0.5 mL min⁻¹. Dotted lines mark the change of the mobile phase.

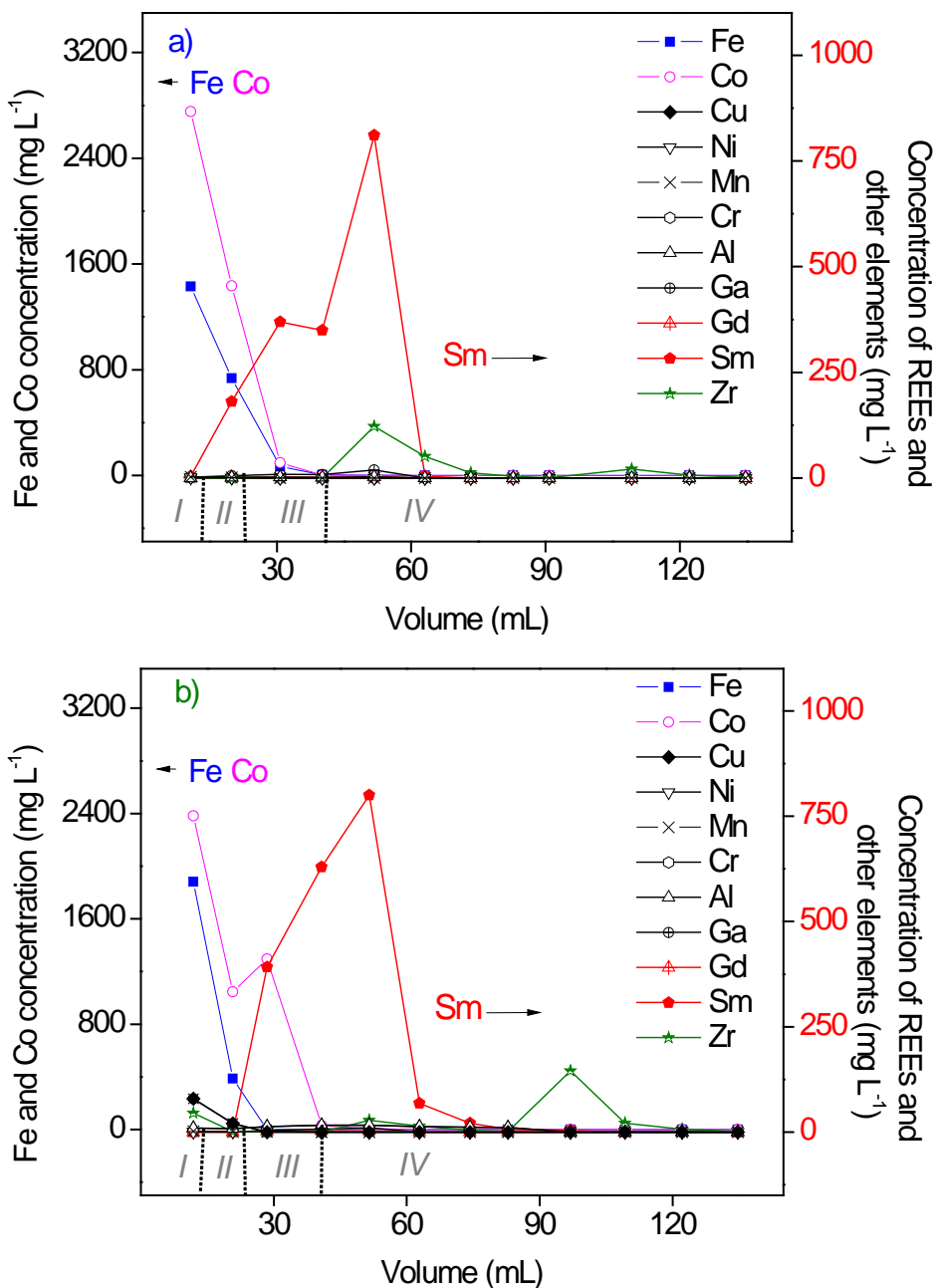


Figure S10. Chromatographic separation of elements from a) aqueous or b) ethanolic leachates of SmCo magnets. Mobile phases: *I*) 10 mL of aqueous or ethanolic leachate of SmCo magnet, *II*) 10 mL of 0.3 mol L⁻¹ HCl for the aqueous leachate (figure a), or 10 mL of ethanol for the ethanolic leachate (figure b), *III*) 20 mL of 0.5 mol L⁻¹ of HCl, *IV*) 95 mL of 1.5 mol L⁻¹ of HCl. Flow rate of leachates was 0.1 mL min⁻¹, and of eluents 0.5 mL min⁻¹. Dotted lines mark the change of the mobile phase.