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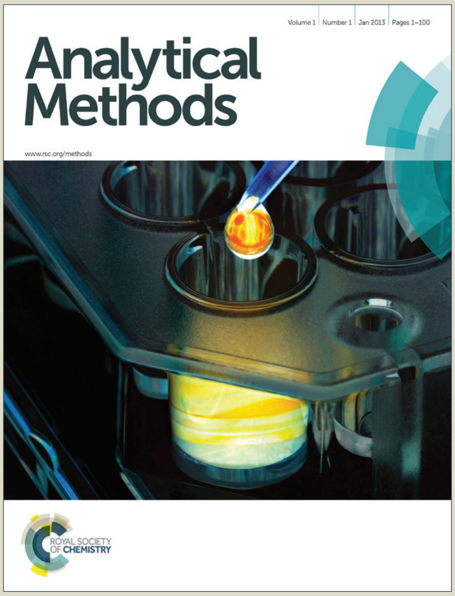

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Quantification of rare earth elements using cloud point extraction with diglycolamide and ICP-MS for environmental analysis

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Abstract

This article describes the development of a procedure for the bulk separation and determination of rare earth elements in soils by combining alkaline fusion, cloud point extraction, and inorganic mass spectrometry. The proposed cloud point extraction method uses a diglycolamide derivative as the chelating agent, which has a well-established affinity for rare earth elements. The method integrates bromine shielding to achieve efficient phase separation at highly acidic pH values. The methodology led to very low detection limits (0.2 to 30 ng/L), quantitative extraction (>97%) for soils, and a high preconcentration factor (up to 140). Decontamination factors were assessed for the most abundant elements, including trivalent ions such as Al^{3+} and Fe^{3+}. A reduction in concentration of up to 180-fold was measured for some elements. Quantitative recoveries for most rare earth elements in highly acidic conditions were achieved and validated using sediment reference material (NIST-2709a). There was excellent agreement between the expected and measured concentrations for all 16 rare earth elements evaluated. The superior analytical figures of merit enabled rare earth element determination at ultra-trace levels in environmental samples.

Keywords

Cloud Point Extraction, Rare Earth Elements, Soil, ICP-MS, Fusion

Introduction

Rare earth elements (REE) have important physical and chemical properties that make them suitable for many modern applications, including electronics, magnets, and fluorescence probes.[1] The mining industry is hence motivated to identify deposits, even marginal ones.[2] REE also have a nuclear origin, as they are also found as uranium and plutonium fission products.[3] The ability to quantify them both isotopically and in absolute quantities is essential in the assessment of nuclear fallout or nuclear emergencies. For example, during the Fukushima-Daiichi accident, significant quantities of cerium (^{144}Ce) and lanthanum (^{140}La) were released.[4] As REEs are typically found at trace levels in most environmental matrices, they often require a high degree of enrichment for proper quantification.[5]

Many strategies have already been proposed for the isolation of lanthanides from solid samples.[6] Methods with demonstrated extractive capabilities for soil samples garner the most interest, as they are expected to be compatible with simpler matrices. Common separation strategies such as liquid-liquid extraction (LLE)[7], chromatographic separation[8], and cloud point extraction (CPE)[9] have been developed to isolate and preconcentrate lanthanides from various environmental matrices. Until recently, focus was essentially on LLE and chromatographic approaches, as these techniques are well established for REE isolation.[10] However, these approaches are not without drawbacks. LLE, for example, uses large quantities of flammable, volatile, and often toxic solvents[11] but ion-exchange chromatography has limited REE capacities. Greener alternatives should be explored. An alternative to traditional liquid-liquid extraction is to replace the organic phase solvents with ionic liquids.[12] This alternative has shown great promise, however, the green potential of the most promising strategy for lanthanides so far is limited, as it uses a mixed solution of an ionic liquid in an organic solvent, such as dichloroethane.[13] Further development is required.

Analytical schemes using Extraction Chromatography (EXC) have also been developed for REE preconcentration.[14-19] Most of them were designed around diglycolamide (DGA) analogue resins. These resins have shown excellent affinities with REE and minor actinides using either N, N, N’, N’ – tetraoctyl diglycolamide (TODGA) or N, N, N’, N’ – tetra(2-ethyl-hexyl) diglycolamide (TEHDGA) as ligands. They demonstrated good selectivity for lanthanides over the rest of the matrix.[15, 17] For soil, a synergetic enhancement on the extraction of lanthanides in the presence iron as also been reported.[18] EXC using bis(2-ethylhexyl) phosphate as the ligand has also been commercialised for the extraction of REE. It is has been used for the determination of fission product components by measuring the lanthanide isotopic ratios.[16] In addition, EXC resins exhibit selectivity towards REE, enabling some level of separation with the other constituents of the matrix. Unfortunately, due to the bulky nature of the solid support used in EXC, large dead column volumes are observed, which translate to limited preconcentration factors.

One preconcentration/isolation strategy that has gathered attention in the last decade is cloud point extraction (CPE). CPE is a micellar extraction based on the hydrophobic nature of the micelle core. After the extraction of the hydrophobic compound, phase separation is achieved by modifying the temperature or the salt concentration in solution to induce the micelle aggregation.[20] Although CPE may lead to a high preconcentration factor, very few strategies have been developed for the total assessment of REE concentration in the environment.[9, 21-26]

As this technique does yield a high level of enrichment compared to other preconcentration techniques, CPE appears as a worthy alternative to the existing chromatographic approach, however, existing procedures show limitations as extraction occurs in slightly acidic pH, which is incompatible with digested solid samples. Though the method proposed by Ohashi *et al.*[24] shows good extraction in a more acidic media, (pH=3), higher concentrations of surfactant were needed to counter the effect of the acidic media on the extraction. Hence, with this approach, worse detection limits would be achieved as the preconcentration factor would be minimised and higher matrix effects would be expected from the amount of surfactant in solution.

The other CPE strategies for neutral-to-basic media mostly rely on non-selective agents for the extraction with demonstrated affinities for highly abundant metals, for example, iron in the presence of 8-hydroxyquinoline.[9, 27] For this reason, appreciable decontamination factors (DF) should not be expected and applicability in more complex matrices should not be assumed.

Furthermore, most of the CPE methodology has a demonstrated affinity with selected lanthanides, but the extraction is not demonstrated for all the REEs, which greatly hinders the application for total REE extraction.[21-26] Extraction for Sc and Y should not be assumed as they are outside of the lanthanide family and divergence in the reactivity may occur. The same caution should be raised for the extraction of REEs which exhibit alternative oxidation states. (i.e. Ce^{4+}, Eu^{2+}, Sm^{2+})[28]

This report presents the development of cloud point extraction using N,N,N',N' – tetraiospropyl diglycolamide ((i-pr)DGA) as a ligand, with the goal of enhancing the selectivity. The impact of acid concentration on extraction efficiency will also be investigated. The applicability of the proposed method will be validated with soil by using reference materials. Analytical figures of merit and decontamination factors from ions generating the most significant interferences will be determined. Finally, the method will also be compared to the existing CPE methods for REEs.

Experimental

Instrumentation

The mass spectrometer used for the REE sample measurements was an ICP-QQQ-MS (Inductively Coupled Plasma coupled to a Triple Quadrupole Mass Spectrometer) (Agilent 8800, Mississauga, ON, Canada). The optimised conditions for the measurement of REE concentrations are presented in Table 1. Note that the octopole reaction system was not used for this analysis. The phase separation process was enhanced using a centrifuge (Thermo Fisher Scientific Sorvall Legend XTR, Bremen, Germany). The centrifuge was also used in the soil sample preparation with the appropriate rotor for the volume of the samples. Soil samples were prepared using an automated fusion unit (M-4 fluxer, Corporation Scientifique Claisse, Québec, Canada).

The parameters used for the sample preparation via fusion are shown in ESI (Table S1)‡.

Reagents

High purity water with a resistivity of 18.2 MΩ•cm was produced in-house through a Milli-Q water purification unit (Millipore, Etobicoke, ON, Canada). Solutions of individual REE and Rh were purchased from SCP Science (Baie D'Urfé, QC, Canada). Throughout this experiment, rhodium was used as an internal standard during the mass spectrometric measurements. A stock solution of reagent grade Triton X-114 (Sigma-Aldrich Canada, Oakville, ON, Canada) was used as a surfactant in the CPE. Other reagents used for the system included: KBr (Anachemia Chemical, Montreal, QC, Canada), $KBrO_3$ (J.T. Baker Chemical co., Phillipsburg, NJ), and cetyl trimethyl ammonium bromide (CTAB) (Acros Chemicals, Ottawa, ON, Canada). These reagents were used as received, without further purification.

Reference materials of coastal origin IAEA-384 and soil of San Joaquin NIST-2709a were purchased from the International Atomic Energy Agency (IAEA, Monaco) and National Institute of Standards and Technologies (NIST, Gaithersburg, MD), respectively. Bauxite residue samples of unknown origin were provided by Rio Tinto Alcan (Montreal, QC, Canada). The DGA derivative was synthesised using a original procedure proposed by Horwitz *et al.*[17] for TODGA, modified by using the appropriate amine to yield (*i-pr*)DGA. The synthesis was performed using Sigma-Aldrich reagents (Sigma-Aldrich Canada, Oakville, ON, Canada). Purity was assessed via NMR spectroscopy using a Bruker AC 300 MHz NMR ^{1}H. (*i-pr*)DGA was dissolved in an aqueous solution of Triton X-114 to enhance its solubility. Sample fusion was performed using either lithium metaborate or a mix of lithium tetraborate and lithium metaborate, according to the nature of the sample. A flux/sample mass ratio of 3.4/0.5 was used throughout the experiment. The fused sample was then subjected to a silica condensation procedure[29] to eliminate silica and nebuliser clogging before being pre-concentrated by CPE.

CPE system

Aliquot samples with volumes of 6.5 mL were adjusted to approximately 1-3 M HNO_3 through the addition of acid. Typical parameters were calculated for the aforementioned sample solution volumes, even though a scaled-up version of the procedure could be used to perform the analysis on larger volumes. 100 µL of a solution of 0.01 M of CTAB was added to the aliquoted samples, followed by 400 µL of an aqueous solution containing 4.3 mM of the DGA derivatives dissolved in 22 mM of TTX-114. 0.15 mL of 0.1 M $KBrO_3$ and 0.5 ml of 0.2 M KBr were added to complete the CPE system.

After the addition of all reagents, the solution was left to stir in a sealed falcon tubes in an ice-water bath for 30 minutes to reach equilibrium. Following this equilibration period, the solution was left to settle until it reached room temperature. Then, the solutions were centrifuged at 4700 G for 10 minutes at a temperature of 20°C. Finally, the surfactant rich phase (SRP) was isolated from the supernatant by removing the latter phase. Both of these solutions were analysed by ICP-MS, following dilution with the appropriate molarity of HNO_3, without any other treatment.

A summary of the optimal CPE system conditions is presented in Table S2.[‡] Using these conditions, analytical figures of merit were calculated using the equations presented in ESI.[‡]

Results and discussion

Optimisation of CPE Conditions

Effect of the chelating agent

The choice of (*i-pr*)-DGA (structure shown in Fig. 1) as a ligand is based on the knowledge that numerous members of the DGA family have demonstrated affinity for REEs, especially the octyl derivative[30]. For CPE applications, the selection of a derivative with a shorter side chain is necessary to ensure a balance between hydrophilicity and hydrophobicity. First, sufficient hydrophilicity is needed to ensure interaction between the ligand and the analyte, while hydrophobicity is required to maintain the complex formed within the micelle resulting in a proper extraction. Therefore, the long chains of TEHDGA were dramatically shortened to enhance hydrophilicity, resulting in an increase aqueous solubility.[30, 31] The isopropyl chains were also chosen because of their branched nature, which is expected to impact the bite angle. This mimics the TEHDGA used in a commercial solid phase extraction cartridge.

Using (*i-pr*)DGA as a ligand, the method was highly efficient for lanthanide extraction as a plateau was obtained for a relatively low concentration of ligand (Fig. 2a) and was maintained as the ligand concentration increased. In fact, the extraction was quantitative for all lanthanides except for Gd. (Fig. 2a) A drop-off in extraction for Sm, Eu, and Gd compared to other lanthanides has already been reported using DGA analogues.[30] A DGA derivative using an isopropyl side chain attached to calixarene core, also showed some reduction of complexation for Gd [32] and lighter REEs in comparison to heavier REEs, which was not observed in our CPE system. This discrepancy could be attributed to the absence of a macromolecular structure, which restricts the possible molecular arrangement.

Extraction was attempted without a chelating agent to ensure that the extraction was in fact due to (*i-pr*)DGA and not to other components of the CPE method. Aside from Sc, the extraction was less than 5 % for all REEs, highlighting that the ligand is the driving force of the extraction process. This should translate into enhanced method selectivity (see Figures of Merit section). Furthermore, the increase in the ligand concentration did not impact the formation of micelles even at concentrations as high as 180 μM. For the other experiments, the (*i-pr*)DGA concentration was fixed at 165 μM. (see Table S2)

Effect of Bromate

Labrecque *et al.* recently demonstrated the use of bromate as an agent to induce the extraction of plutonium at highly acidic pH values.[33] Bromate, in the presence of an excess of bromide, comproportionates to form bromine, which efficiently shields the micelles from the disrupting effect of high-solids matrices in highly acidic conditions. The bromine formed has a tendency to stay at the water-micelle interface, due to its high polarisability. This results in an apparent constant chemical environment, which is desirable for the micelles. However, in our previous studies on plutonium, it was impossible to discriminate between the protective (via bromine formation) and oxidative role of bromine with Pu(IV). Since rare earth elements all exhibit a trivalent oxidation state (with the exception of Ce in specific redox conditions), the fact that extraction efficiency increases with the addition of bromate (Fig. 2b) confirms the protective effect of bromine on the micelles in highly acidic environments. Furthermore, the quantitative extraction of Ce also indicates that the presence of bromate is not sufficient to oxidise Ce^{3+} to Ce^{4+}. For the remaining experiments, $KBrO_3$ and KBr concentration were fixed at 1.5 mM and 10 mM, respectively.

Effect of the nature and concentration of the acid

Tests were performed to determine the impact of the type of acid (HNO_3 and HCl) on extraction, as well as at which concentration it is maximal. (Fig. 2c and 2d) Extraction was quantitative between 0.1 and 2 M, independently of the nature of the acid. Extraction also decreased drastically above the aforementioned concentration for both acids.

The quantitative extraction behaviour observed in acidic conditions is much better than other CPE systems which operate in neutral-to-basic media (Table 1). Indeed, it was demonstrated that acidic conditions increase the selectivity of CPE by decreasing the number of ions that were chelating with the ligand,[34, 35] which should have a direct impact on the decontamination factor. Furthermore, the acidic character of the CPE solution significantly reduced the potential formation of hydroxide, thus decreasing the precipitation of those hydroxides in the coacervate. For the remaining experimentation, acid concentrations were fixed between 1 and 2 M HNO_3.

Effect of the surfactants

Tests were performed to determine the optimal concentration of both the cationic and non-ionic surfactants. (fig. 2e and f) CTAB was added, as it has a demonstrated ability to enhance the solubility of polar molecules. It was also presupposed to be an efficient way to tune the cloud point temperature of the system. However, as illustrated in Fig 2e, the presence of CTAB had little effect on extraction efficiencies, suggesting that with the current experimental conditions, the cloud point temperature was already tuned to the appropriate temperature. Nonetheless, small quantities (100 mM) were added to the extraction system, as it can induce a charge in the micelles, creating repulsion of the micelles and of the ion in solution[36], which is a desirable feature in digested solid samples.

TTX-114 was chosen as a non-ionic surfactant due to its near-ambient cloud point temperature (CPT) and its well-established physical properties and behaviour in an extractive system.[20] The response in extraction efficiencies as a function of TTX-114 concentration are in agreement with the established critical micelle concentration (cmc) of 0,8 mM. In fact, the best results are obtained when the surfactant concentration approaches this value. However, extraction is possible for concentrations below the cmc, which could be due to the addition of CTAB. Although parameters are shown to be optimised individually, the multivariate nature of such a system cannot be denied. Furthermore, at higher concentrations of surfactant, the CPT was shown to increase, thus diminishing the extraction efficiency.[24] For the remaining experimentation, surfactant concentrations were fixed at 100 µM for CTAB and at 1.07 mM for TTX-114.

Analytical Figures of Merit

The proposed methodology combines cloud point extraction and ICP-MS, enables low detection limits (Table 2), selectivity (Table 3), and high recoveries for environmental samples (Table 4-5). Details of its features follow. While most published CPE methodologies for REE yielded quantitative extraction efficiency similar to that reported for the proposed approach (>97%), they generally lack the high level of preconcentration achieved here (>140). This is due to the fact that large volumes of surfactants are required to maintain the stability of the micellar structure in acidic conditions. The *in situ* formation of Br_2, which acts as a protective barrier to significantly enhance stability, reduces the amount of surfactant needed. This directly translates to a smaller coacervate phase and thus a higher preconcentration factor.

When comparing CPE methodologies for REE, the type of sample matrices on which the separation is performed must be taken into consideration. With the exception of the approach proposed by Li and Hu[9], all other published CPE methodologies targeted liquid samples, avoiding the issue of compatibility with chemical dissolution approaches. In this study, borate fusion was investigated as a chemical dissolution strategy. The main reasons for selecting this dissolution method over acid digestion were its robustness, high analytical throughput, and ability to completely dissolve soil samples, including refractory fractions.

The latter aspect is critical as it has previously been demonstrated that lanthanide oxides are also refractory; [37] they could therefore be found in undissolved residues, and this resulted in an underestimation of the REE content. Detection limits (Table 2) were determined for solutions containing borate fusion flux, representative of digested soil samples. The reported detection limits are lower than those of previous CPE methods by up to 2 orders of magnitude, and are lower than those obtained from direct analysis of an $LiBO_2$ matrix by ICP-MS (0.9 to 400 ng L^{-1}). These results provide evidence that the developed method is effective at preconcentrating REEs and reducing potential interference. However, as expected, the method showed detection limits slightly higher than the ones calculated for pure acid solutions (0.1 to 30 ng L^{-1}). As the detection limits for the CPE approach are lower than the ones from direct analyses of the flux solutions, it also indirectly demonstrates that the proposed method leads to the exclusion of many of the major constituents of the matrix. This is confirmed by the assessment of decontamination factors. (Table 3) Even if the proposed method was developed with the objective of providing preconcentration for solid environmental matrices, it could be used for liquid samples with little modification.

The selectivity is an important feature of CPE as matrix ions can greatly interfere with measurement. In fact, the presence of Ba has been proven to induce interference for masses between 145 and 155 (Nd, Sm, and Eu) due to the formation of oxide/hydroxide, which limits trace determination.[19] Furthermore, the presence of high-solids matrices affects the plasma, as a result of the high mass loading. Decontamination factors are a parameter of choice to measure the method selectivity. DF represents the ratio of the concentration of an element in the aqueous phase on the one in the coacervate. For example, a DF of 2 indicates that 66% of an analyte remains in the aqueous phase, a proportion that could increase to 95% for a DF of 20. The proposed method successfully removes ions from the matrix and provides fractions less loaded with inorganic ions than the initial sample, as displayed by the DFs (Table 3). Such DFs are particularly interesting as one of the main drawbacks of the use of lithium fusion as a digestion strategy is that it induces a high concentration of lithium and boron into the solution. As the DF for Li^+ and B^{3+} are high (>50), this tends to minimise the level of these ions in the nebulised solution.

Furthermore, high DFs are obtained for the most abundant alkaline earth and transition metals analysed. For Ba and Zn, DFs are lower; their concentrations in solution approach the detection limits, which hamper the calculation of a more precise DF. Finally, even with their analogous oxidation states, ions such as Fe^{3+}, Cr^{3+}, and Al^{3+} were not found to interfere in the extraction of REEs and showed excellent DF(>50). Samples of coastal sediments (IAEA-384) and soils (NIST-2709a) were measured to confirm that the REE recoveries were high for samples of different origins.

To confirm the method's performance, two approaches were tested: standard addition, and validation through the use of a reference material. The standard addition approach showed that the extraction yields are quantitative (>94%) for all REEs except Sc in the IAEA-384. (Table 4) This behaviour is expected as lighter REEs tend not to bind as strongly with DGA derivatives.[30] For NIST-2709a, recoveries assessed by standard addition displayed high extractions (>90%) for all REEs except La, Ce, and Tb.

The proposed CPE strategy was used to quantify REEs in various environmental matrices. (Table 5) REE concentrations from nanograms to tens of milligrams per kilogram were measured in the digested samples. For NIST-2709a, agreement was obtained between the experimental data, and reference and information values.[38] Quantitative results from bauxite residues show concentrations of REEs comparable to those reported in Indian bauxite[39], but approximately one order of magnitude lower than those reported by Wagh and Pinnock for Jamaican bauxite residues.[40] Furthermore, the determination of REEs in these samples shows the potential applicability of the CPE methodology in industrial waste and effluent.

The concentrations of lanthanides in IAEA-384 determined by our approach were similar to those reported by Dupuy *et al.* [41] in samples collected in the region. The lanthanide profile they observed also matched the one determined over the course of this analysis.

Conclusions

A new cloud point extraction method was developed for the preconcentration and subsequent analysis of rare earth elements in solid environmental samples by ICP-MS. This method, compatible with digested environmental matrices, results in quantitative recoveries, as validated with a standard reference material, and a high preconcentration factor. There are many other potential applications for this preconcentration approach. These include the determination of precise isotopic signature of REEs, which could confirm nuclear anthropic contamination, and recycling of REEs from *e*-waste.

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Notes

The authors declare no competing financial interest.

References

1. A. R. Jha, *Rare Earth Materials: Properties and Applications*, CRC Press, 2014.
2. G. Gunn, *Critical Metals Handbook*, Wiley-Blackwell, 2014.
3. A. Pitois, L. A. de las Heras and M. Betti, *International Journal of Mass Spectrometry*, 2008, 270, 118-126.
4. H. Mala, P. Rulik, V. Beckova, J. Mihalik and M. Slezakova, *Journal of Environmental Radioactivity*, 2013, 126, 92-98.
5. M. Ferrat, D. J. Weiss and S. Strekopytov, *Talanta*, 2012, 93, 415-423.
6. B. Zawisza, K. Pytlakowska, B. Feist, M. Polowniak, A. Kita and R. Sitko, *Journal of Analytical Atomic Spectrometry*, 2011, 26, 2373-2390.
7. J. Tang and C. M. Wai, *Analytical Chemistry*, 1986, 58, 3233-3235.
8. J. N. Connelly, *Geochemistry Geophysics Geosystems*, 2006, 7, 9.
9. Y. J. Li and B. Hu, *Journal of Hazardous Materials*, 2010, 174, 534-540.
10. C. A. Lucy, L. Gureli and S. Elchuk, *Analytical Chemistry*, 1993, 65, 3320-3325.
11. I. Billard, A. Ouadi and C. Gaillard, *Analytical and Bioanalytical Chemistry*, 2011, 400, 1555-1566.
12. A.-V. Mudring and S. Tang, *European Journal of Inorganic Chemistry*, 2010, DOI: 10.1002/ejic.201000297, 2569-2581.
13. A. N. Turanov, V. K. Karandashev and V. E. Baulin, *Russian Journal of Inorganic Chemistry*, 2008, 53, 970-975.
14. J. N. Connelly, D. G. Ulfbeck, K. Thrane, M. Bizzarro and T. Housh, *Chemical Geology*, 2006, 233, 126-136.
15. J. Florek, F. Chalifour, F. Bilodeau, D. Lariviere and F. Kleitz, *Advanced Functional Materials*, 2014, 24, 2668-2676.
16. M. L. Geagea, P. Stille, M. Millet and T. Perrone, *Science of the Total Environment*, 2007, 373, 404-419.
17. E. P. Horwitz, D. R. McAlister, A. H. Bond and R. E. Barrans, *Solvent Extraction and Ion Exchange*, 2005, 23, 319-344.

18. E. P. Horwitz, D. R. McAlister and A. H. Thakkar, *Solvent Extraction and Ion Exchange*, 2008, 26, 12-24.

19. K. E. Jarvis, A. L. Gray and E. McCurdy, *Journal of Analytical Atomic Spectrometry*, 1989, 4, 743-747.

20. L. Koshy, A. H. Saiyad and A. K. Rakshit, *Colloid and Polymer Science*, 1996, 274, 582-587.

21. F. D. Depoi, F. R. S. Bentlin, M. F. Ferrao and D. Pozebon, *Analytical Methods*, 2012, 4, 2809-2814.

22. A. Favre-Reguillon, M. Draye, G. Lebuzit, S. Thomas, J. Foos, G. Cote and A. Guy, *Talanta*, 2004, 63, 803-806.

23. A. Mustafina, J. Elistratova, A. Burilov, I. Knyazeva, R. Zairov, R. Amirov, S. Solovieva and A. Konovalov, *Talanta*, 2006, 68, 863-868.

24. A. Ohashi, T. Hashimoto, H. Imura and K. Ohashi, *Talanta*, 2007, 73, 893-898.

25. S. E. Pepper, D. R. Peterman, T. J. Tranter and B. M. White, *Journal of Radioanalytical and Nuclear Chemistry*, 2009, 282, 909-912.

26. A. Perez-Gramatges and A. Chatt, *Journal of Radioanalytical and Nuclear Chemistry*, 2006, 269, 491-497.

27. K. Pytlakowska, V. Kozik and M. Dabioch, *Talanta*, 2013, 110, 202-228.

28. N. G. Yakovlev, V. N. Kosyakov and G. M. Kazakova, *Journal of Radioanalytical Chemistry*, 1982, 75, 7-16.

29. A. Gagne, J. Surette, S. Kramer-Tremblay, X. X. Dai, C. Didychuk and D. Lariviere, *Journal of Radioanalytical and Nuclear Chemistry*, 2013, 295, 477-482.

30. S. A. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chemical Reviews*, 2012, 112, 1751-1772.

31. S. A. Ansari, P. N. Pathak, V. K. Manchanda, M. Husain, A. K. Prasad and V. S. Parmar, *Solvent Extraction and Ion Exchange*, 2005, 23, 463-479.

32. K. Matloka, A. Gelis, M. Regalbuto, G. Vandegrift and M. J. Scott, *Dalton Transactions*, 2005, DOI: 10.1039/b513745d, 3719-3721.

33. C. Labrecque, L. Whitty-Leveille and D. Lariviere, *Analytical Chemistry*, 2013, 85, 10549-10555.

34. N. N. Meeravali and S. J. Jiang, *Journal of Analytical Atomic Spectrometry*, 2008, 23, 854-860.

35. J. A. Baig, T. G. Kazi, A. Q. Shah, M. B. Arain, H. I. Afridi, S. Khan, G. A. Kandhro, Naeemullah and A. S. Soomro, *Food and Chemical Toxicology*, 2010, 48, 3051-3057.

36. M. D. Bezerra, M. A. Z. Arruda and S. L. C. Ferreira, *Applied Spectroscopy Reviews*, 2005, 40, 269-299.

37. K. L. Nash and M. P. Jensen, in *Handbook on the physics and chemistry of rare earths*, eds. K. A. Schneider and L. Eyring, Elsevier, Amsterdam, 2000, vol. 28, p. 315.

38. E. A. Mackey, S. J. Christopher, R. M. Lindstrom, S. E. Long, A. F. Marlow, K. E. Murphy, R. L. Paul, R. S. Popelka-Filcoff, S. A. Rabb, J. R. Sieber, R. O. Spatz, B. E. Tomlin, L. J. Wood, J. H. Yen, L. L. Yu, R. Zeisler, S. A. Wilson, M. G. Adams, Z. A. Brown, P. L. Lamothe, J. E. Taggart, C. Jones and J. Nebelsick, ed. N. T. Note, U.S. Government Printing Office, Washington, DC, 2010.

39. Abhilash, S. Sinha, M. K. Sinha and B. D. Pandey, *International Journal of Mineral Processing*, 2014, 127, 70-73.

40. A. S. Wagh and W. R. Pinnock, *Economic Geology*, 1987, 82, 757-761.

41. C. Dupuy, P. Vidal, R. C. Maury and G. Guille, *Earth and Planetary Science Letters*, 1993, 117, 89-100.

Table 1 : ICP-MS conditions used for rare earth elements analysis

Tune Parameters

Parameter	Value	Parameter	Value
Plasma parameters		**Acquisition**	
Plasma Mode	Hot	Monitored masses	45, 89, 103, 139, 140, 141, 146, 153, 157, 163, 165, 166, 169, 172, 175
Plasma Gas Flow Rate	15.1 L·min-1	Reading mode	Peak hoping
Auxiliary Gas Flow Rate	0.7 L·min-1	Detector mode	Pulse counting
Makeup Gas Flow Rate	0.44 L·min-1	Integration time	120 msec
RF Power	1500 W	Dwell time	12 msec
Reflected Power	>5 W		
Lense Parameters (volts)		**Q1 parameters (volts)**	
Extract 1	6.7	Q1 bias	-8.0
Extract 2	-230	Q1 pre-filter bias	-44.0
Omega Lens	27.2	Q1 post-filter bias	-26.0
Q1 Entrance	-3		
Q1 Exit	2		
Cell focus	-1.0		
Deflect	13.8		
OctP RF	150		
Energy Discrimination	5.0		

Table 2: Analytical Figures of Merit for the proposed methodology in comparison with other published CPE approaches for REE preconcentration and analysis.

Type of Sample	Instrument	LOD (ng/L)	Preconcentration factor	Extraction Efficiency (%)	Reference
Soils	ICP-MS	0.2 to 30	>140	>97	This work
River Water	ICP-OES	2 to 103	15	91 to 100	Depoi *et al.*[21]
Tea leaves and mushroom	ICP-OES	69 to 600	5-9	quantitative	Li and Hu[9]

LOD = Limit of detection.

Table 3: Decontamination factors of various ions found in solid environmental matrices (average for NIST-2709a and bauxite residues) digested by lithium fusion

Element	Decontamination Factor n=8
Al^{3+}	61 ± 4
B^{3+}	53 ± 3
Ba^{2+}	> 20
Ca^{2+}	36 ± 3
Cr^{3+}	180 ± 50
Fe^{3+}	53 ± 4
Li^{+}	57 ± 9
Mg^{2+}	171±17
Mn^{2+}	25.8 ± 0.2
Sr^{2+}	65 ± 14
Ti^{4+}	63 ± 15
Zn^{2+}	> 24

Table 4: REE recoveries determined by standard addition in environmental samples using CPE.

Element	Recovery (% ± SD)	
	IAEA-384 n=4	NIST-2709a n=4
Sc	78 ± 2	107 ± 9
Y	103 ± 4	94 ± 10
La	94 ± 9	78 ± 12
Ce	96 ± 9	84 ± 11
Pr	99 ±5	103 ± 14
Nd	101 ± 10	92 ± 13
Sm	99 ± 5	90 ± 13
Eu	99 ± 4	97 ± 11
Gd	98 ± 5	101 ± 13
Tb	99± 4	86 ±12
Dy	99 ± 4	92 ± 12
Ho	100 ± 4	93 ± 12
Er	98 ± 4	99 ± 12
Tm	99 ± 4	102± 12
Yb	97 ± 4	100 ± 13
Lu	98 ± 4	99 ± 11

Table 5: Concentration (mg kg^{-1}) of REEs in environmental matrices and reference material

Element	NIST-2709a (n =4)[a]		Bauxite residue (n = 4)	IAEA-384 (n = 4)
	Measured	Expected[38]		
Sc	11.8 ± 0.6	11.1 ± 0.1.	50 ± 1	10 ± 5
Y	12.1 ± 0.2	N.A.	71 ± 1	2.0 ± 0.8
La	20 ± 4	21.7 ± 0.4	50 ± 1	19 ± 2
Ce	43 ± 4	42 ± 1	93 ± 1	0.22 ± 0.05
Pr	5.4 ± 0.4	N.A.	8.8 ± 0.4	0.052 ± 0.009
Nd	22 ± 2	*17*	28.2 ± 0.9	0.04 ± 0.009
Sm	4.3 ± 0.2	*4*	5.9 ± 0.4	0.017 ±0.004
Eu	0.9 ± 0.1	0.83 ± 0.02	1.3 ± 0.4	0.014 ± 0.001
Gd	4.3 ± 0.2	3.0 ± 0.1	8.0 ± 0.3	0.032 ± 0.005
Tb	0.50 ± 0.02	*0.5*	1.3 ± 0.4	0.030 ± 0.003
Dy	3.2 ± 0.4	*3*	11.2 ± 0.3	0.020 ± 0.003
Ho	0.60 ± 0.06	N.A.	2.3 ± 0.2	0.029 ± 0.003
Er	2 ± 0.4	N.A.	8.5 ± 0.3	0.018 ± 0.002
Tm	---[b]	N.A.	1.3 ± 0.2	0.017 ± 0.002
Yb	2.0 ± 0.2	*2*	10.3 ± 0.3	0.012 ± 0.004
Lu	0.5 ± 0.09	*0.3*	1.2 ± 0.2	0.016 ± 0.005

N.A. – not available

a. Values in italic are information values

b. Tm was used as a recovery tracer

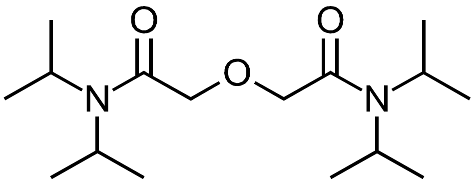

Figure 1: Structure of the (*i-pr*)-DGA ligand.

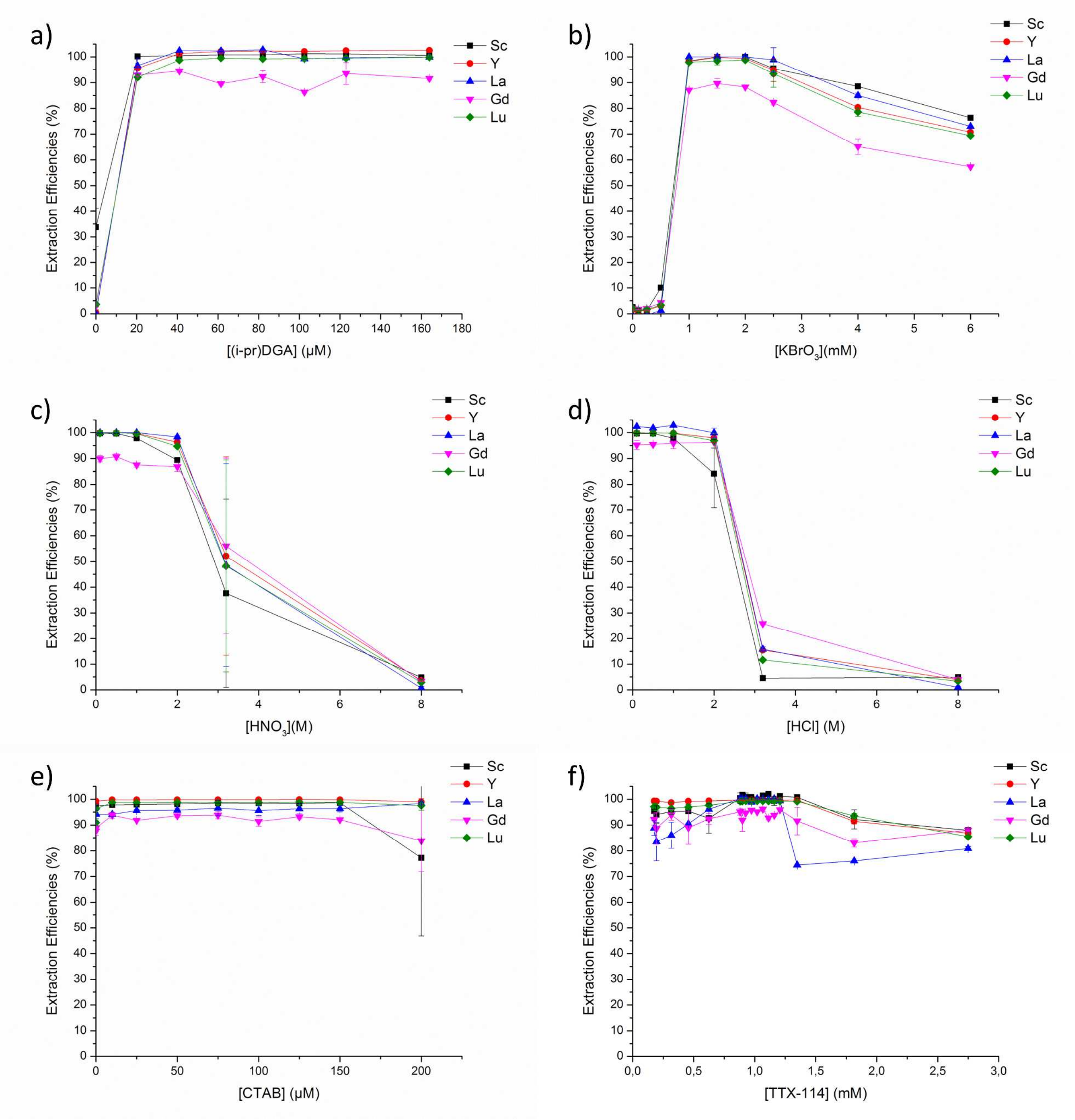

Figure 2 Influence of various parameters [a) ligand, b) $KBrO_3$, c) nitric acid, d) hydrochloric acid, e) CTAB and f) TTX-114 concentrations] on the extraction of selected REEs with other parameters being kept constant (at the concentration shown in Table S2), using nitric acid. The optimal conditions used are represented as a dashed line.