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Determination of Rare Earth Elements in Natural Water Samples – a Review of Sample Separation, Preconcentration and Direct Methodologies.

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Abstract

This review discusses and compares the methods given for the determination of rare earth elements (REE) in natural water samples, including sea, river, lake, tap, ground and waste waters as well as Antarctic ice. Since REE are at very low concentrations in natural waters, numerous different preconcentration methods have been proposed to enable their measurement. These include liquid liquid extraction, dispersive liquid-liquid micro-extraction and solidified floating drop micro-extraction. In addition to liquid-liquid extraction methods, solid phase extraction using commercial resins, resins made in-house, silica-based exchange materials and other solid media is also discussed. These and other techniques such as precipitation / co-precipitation and flotation are compared in terms of speed, preconcentration factors achieved, precision, accuracy and limits of detection (LOD). Some papers have discussed the direct determination of REE in these sample types. Some have used specialised sample introduction systems such as ultrasonic nebulisation whereas others have used a standard sample introduction system coupled with inductively coupled plasma mass spectrometry (ICP-MS) detection. These direct methods have also been discussed and compared.

Keywords: Rare Earth Elements; Natural Waters; Methods of Analysis; Review

1. Introduction

The rare earth elements (REE) are the 14 lanthanide elements with atomic numbers ranging from 57 (La) to 71 (Lu) that have similar chemical and physical properties as well as scandium and yttrium. They have been used widely in numerous industrial processes such as in the production of superconductors, supermagnets, catalysts, pigments in glasses, plastics, additives, medicines and cosmetics as well as fertilizers (1-3). Therefore, REE emission into natural

waters is increasing, which may result in a potential risk to the environment. In addition, they are accumulating in aquatic organisms and therefore have the potential to enter the food chain (4,5). Unlike many elements, e.g. As, Cd and Pb, REE are not considered to be priority environmental contaminants. However, they are known to induce adverse health effects such as the stimulation of crystallization of urinary stones (6). Attention has been paid to the effects of REE ions on environmental ecosystems. Sometimes, natural water systems become the “source” and “influx” of metal ions in the natural cycle of an environmental ecosystem. In particular, REE that have extremely similar chemical properties but that also have different abundance are good tracers and may be used to characterize functions in the macroscopical and microcosmic processes of natural water systems (7,8). Thus far, the extent of the bioavailability and toxicity of REE are still unclear (9). The REE have unique chemical properties during various processes such as chemical weathering and sedimentation. Their determination in natural waters is therefore useful from the geochemistry, limnology, oceanography and environmental science viewpoints (10).

Several different techniques have been used to determine REE in natural water samples. These include: Ultraviolet-visible spectrophotometry (UV-Vis) (11-13), molecular fluorescence spectrometry(14,15), neutron activation analysis (NAA) (16,17), capillary electrophoresis coupled with UV-Vis detection (CE-UV-Vis) (18,19), Adsorptive stripping voltammetry (ASV) (20), potentiometry (21), inductively coupled plasma-optical emission spectrometry (ICP-OES) (1,22,23); and the various forms of inductively coupled plasma-mass spectrometry (ICP-MS) (24,6,2), sector field inductively coupled plasma sector field mass spectrometry (SF-ICP-MS) (25-28) and inductively coupled plasma time-of-flight mass spectrometry (TOF-ICP-MS) (29-31). Different sample introduction methodologies, e.g. electrothermal vaporization into ICP-MS (ETV-ICP-MS) have also been described (7,32). However, REE in most natural waters exist at ng L^{-1} concentration levels, which falls below the LOD of most conventional instruments. All of the methods given above, with the exception of the varying forms of ICP-MS, (33,34) have higher LODs than the concentrations of REE in natural waters. Techniques such as ICP-OES typically have LODs at the $\mu\text{g L}^{-1}$ level. These are insufficiently low for the determination of REE in uncontaminated waters. In addition, the REE have numerous emission wavelengths (i.e. they are “line-rich”). Many of these wavelengths can cause spectral interferences to other REE. Other techniques have

either short linear range, e.g. any absorption-based technique, such as UV-Vis or atomic absorption. Another problem with atomic absorption-based protocols is that they have historically been single element only; i.e. they can determine only one analyte at a time. The advent of multi-element, simultaneous atomic absorption instruments should overcome this drawback. Other methodologies, e.g. those that rely on the formation of a complex followed by UV-Vis detection or molecular fluorescence are notoriously prone to interferences. Since the REE have similar chemical properties, they are all likely to react in a similar manner in the presence of a complexing agent. Differentiating between the REE can therefore be troublesome. Other techniques, e.g. NAA can be quite sensitive for some REE. However, specialised facilities that are not widely available are required. Even ICP-MS will struggle to determine analytes at the ng L⁻¹ level, especially in samples with a problematic matrix, e.g. seawater. However, ICP-MS is usually the preferred technique to determine REE because of its high sensitivity, selectivity, multi-element analysis ability and wide linear range. It should be noted though that determination of REE using ICP-MS can be confounded by spectral interferences that include the oxides of the lower mass analytes on some of the higher mass ones. Examples include ¹⁴⁰Ce¹⁶O⁺ on ¹⁵⁶Gd⁺, ¹⁴¹Pr¹⁶O⁺ on ¹⁵⁷Gd⁺, ¹⁵⁹Tb¹⁶O⁺ on ¹⁷⁵Lu⁺. In addition, the oxides of barium can also be problematic, e.g. ¹³⁵Ba¹⁶O⁺ and ¹³⁷Ba¹⁶O⁺ on ¹⁵¹Eu⁺ and ¹⁵³Eu⁺, respectively. This list is by no means exhaustive. Further details of interferences observed during the determination of REE can be found elsewhere in the literature (35). Despite the advantages over many of the other techniques, a preconcentration and matrix separation step is often necessary even for ICP-MS determinations. Different preconcentration and matrix elimination methods have been employed to facilitate the determination of REE in water samples. These methods include liquid-liquid extraction (LLE) (15,36), Liquid-liquid-liquid micro-extraction (LLLME) (19), solid phase extraction (SPE) (22, 37), co-precipitation (10), precipitation (41), flotation (13), cloud point extraction (CPE) (42), dispersive liquid-liquid micro-extraction (DLLME) (43,5), solidified floating organic drop micro-extraction (SFODME) (32), dispersive solid phase extraction (D-SPE) (3,44) and membrane separation (11,14).

In addition to the chemical separations listed above, an electroanalytical method (20) (carbon paste electrode followed by adsorptive stripping voltammetry) and counter-current chromatography (CCC) (45) have also been used to either preconcentrate REE and / or separate them from the sample matrix. The relative merits of each of these will be discussed in future sections.

Some specialised sample introduction systems also facilitate the analysis. For example ultrasonic nebulization (USN), a micro-flow nebulization/desolvation sample introduction system or a low flow micro-concentric nebulizer connected with an ICP-MS instrument may possibly enable direct analysis of natural waters for the determination of REE ions without recourse to preconcentration methods. These devices are therefore not time-consuming and minimise the risk of contamination of the samples during a preconcentration procedure.

A few review articles have focused on the determination of REE ions in different sample types. Advances in the extraction and separation of REE using ionic liquids (46), flow injection on-line preconcentration procedures with detection using ICP-MS with a TOF mass analyser (30) and sample preparation methods and advanced techniques for the determination of REE in various matrices (e.g. biological, environmental and geological as well as in advanced materials) (47) have been published. This last example also covered sample digestion procedures as well as direct analysis of samples for REE determination. The present review focuses on the analysis of waters and therefore encompasses numerous detection techniques rather than only one or a few. Similarly, since REE are most likely to be at low concentration in these sample types, the range of preconcentration methods used is more diverse.

In this review we discuss and compare the preconcentration methods and direct methods reported for the determination of REE in natural water samples, including seawater, river, lake, tap, ground and waste waters as well as Arctic / Antarctic ice. This review has concentrated on those methods developed since 2000, but some of the key papers prior to that are also discussed. In addition, the review is of the methodologies developed rather than a comprehensive review of the analysis of water. Therefore, numerous papers that have determined REE in seawater worldwide using identical systems have

been omitted, since these would be of more interest to marine chemists and oceanographers rather than analytical chemists. Since REE concentrations are usually very low in natural waters (at the ng L^{-1} level), accurate, precise, rapid and reliable methods are required for their accurate determination. Figure 1 depicts the relative number of papers describing the determination of REE in natural waters as a percentage per type of instrumental technique, the type of preconcentration method and, where solid phase extraction was used, the type of the solid support used. It is clear that ICP-MS is the most popular and effective instrumental technique used for the detection of REE while solid phase extraction has been the preferred preconcentration method. The number of published papers determining REE in natural waters as a function of the year is given in Figure 2. It is clear that the determination of REE in natural waters is becoming an increasingly popular area of study in recent years.

2. Direct Determination of REE

In general, the determination of REE in natural waters, even using ICP-MS, is difficult because their concentrations are extremely low and are often below the instrumental LODs. As discussed throughout this review, to overcome this problem, many on-line or off-line preconcentration and matrix elimination procedures have been proposed and published in the literature. However, many of them are time consuming and there is always a risk of contamination. Therefore, some workers have used specialist sample introduction systems such as ultrasonic nebulization (USN), microflow nebulization/desolvation sample introduction systems or low flow micro-concentric nebulizers. Such systems may introduce sample more efficiently and hence, enhance sensitivity; which may enable direct analysis of some sample types. In addition, desolvation devices (normally a component of USN), ETV sample introduction and special nebulisers, decrease the potential for oxide-based interferences; a bane of REE determination using ICP-MS. However, because of the ultra-trace concentrations of REE in many sample types, it should be noted that although these techniques can improve the sensitivity, they will enable only some samples to be analysed successfully. Many of the specialised sample introduction systems do not separate the analyte from the matrix and hence, although greater sensitivity is obtained, the potential for increased interference effects is also enhanced.

An ultrasonic nebulizer was used by Halicz *et al.*(48) for the direct determination of REE ions in fresh waters. Matrix effects (signal suppression) arising from high total dissolved solids in these waters could be compensated for by using Re as an internal standard. This enabled recoveries of between 85 and 120% to be obtained from analyte spike – recovery experiments. Method validation was also achieved through the analysis of the CRM SLRS-3. Although certified data are not available for these analytes in this material, comparison with previously published data indicated good agreement.

A microflow nebulization/desolvation sample introduction system was used to overcome spectroscopic interferences during the direct determination of REE ions in molten ice samples (33). Despite the use of the desolvation system, the presence of barium hydroxide and lanthanum oxide could affect the $^{155}\text{Gd}^+$ signal by a total of 20%, with 13% originating from $^{138}\text{Ba}^{16}\text{O}^+\text{H}^+$ and 7 % from $^{139}\text{La}^{16}\text{O}^+$. The effects of the other potentially interfering species, e.g. from $^{124}\text{Sn}^{16}\text{O}^+$ on $^{140}\text{Ce}^+$, was potentially negligible because of the very low concentrations of such species in molten ice samples. Very low LODs (0.01 pg g⁻¹ or less for all analytes except Gd) were obtained using this sample introduction system with sector field ICP-MS as a detector. As a means of method validation, the authors spiked concentrations of 0.62 pg g⁻¹ into fresh snow and obtained recoveries of between 95 and 105%. The levels found in the ice ranged from 0.004 (the lowest value for Tm) up to 60 (the highest value for Ce) pg g⁻¹ and so a spike concentration of 0.62 pg g⁻¹ was appropriate. This methodology preserved the sanctity of the samples of interest whilst proving accuracy of the analysis using a similar matrix. A similar paper also discussed the use of a micro-flow nebuliser and desolvation system to introduce molten ice samples (49). Detection limits were between 0.0004 (Lu) and 0.03 (Gd) pg g⁻¹. The authors commented that they suspected that the samples may have been contaminated with some of the lighter REE (La, Ce, Pr and Nd). Desolvating units with micro-flow nebulization systems were connected to a TOF-ICP-MS, an SF-ICP-MS and a quadrupole ICP-MS instrument so that a comparison of spectral interference and oxide-formation on the determination of REE ions could be made (31). Using these desolvating units, the signal intensities increased by a factor of ~10 when compared with analysis using a cross flow nebulizer for TOF-ICP-MS and quadrupole ICP-MS and by a factor of ~5 for SF-ICP-MS. In addition, there was a significant reduction in oxide formation. The Results obtained using TOF-ICP-MS for the analysis of the CRM SPS-SW1 were in

excellent agreement with certified values for all REE except La, Ce and Dy which yielded data between 115 and 121% of certified values. Results obtained using a quadrupole ICP-MS instrument for the same sample were better with data being 98.9 – 103.8% of certified values for all REE except Dy which was 170%. Analysis of the CRM SLRS-4 yielded data in good agreement between techniques and with those from a previous study. The instrumentation was applied to the analysis of Antarctic ice core samples. It was concluded that TOF-ICP-MS, used in conjunction with the desolvation system, could be an alternative to the quadrupole ICP-MS and SF-ICP-MS techniques even though SF-ICP-MS with a desolvation device was the most sensitive of the methods. Some isobaric interferences such as ^{142}Nd (^{142}Ce , 11.08%), ^{144}Nd (^{144}Sm , 3.1%) and ^{164}Dy (^{164}Er , 1.61%) and spectral interferences were successfully corrected during sample analysis. However, Ba concentrations exceeding $1\text{ }\mu\text{g L}^{-1}$ caused high background signals using the TOF-ICP-MS for mass ^{139}La and ^{140}Ce .

A comparison of a micro-concentric nebulizer (MCN) and a membrane-desolvation sample introduction system equipped with a different MCN, both used with a SF-ICP-MS instrument, was made (34). The introduction devices were compared in terms of sensitivities, LOD, REE- O^+ formation, matrix induced interferences, long term signal variations and recovery of REE from spiked sea water samples and a pristine water. Signal responses using the MCN / desolvation system combination were enhanced by factors of 4–10. The LODs for the two systems were comparable, although the $^{14}\text{Ce}^{16}\text{O}/^{140}\text{Ce}^+$ ratio was three orders of magnitude lower for the MCN / desolvation system than for the MCN alone. Signal suppressions in the presence of 100 mg L^{-1} Na varied from about 15 to 25% for light REE and about 5 to 10% for medium mass and heavy REE when using the MCN. A uniform signal depression of 15% was observed for all REE when the MCN/desolvation device was used. These problems could largely be overcome using an internal standard with the MCN/desolvation system, although more than one internal standard was required for the MCN alone. The MCN/desolvation system was used to analyse the CRM SLRS-4, Results were comparable to those reported in a previous study.

Other papers also used no sample preparation other than filtration and acidification. One was prepared by Campodonico *et al.* who determined numerous analytes including REE in river waters(50). The analysis was conducted using ICP-MS. The reference materials NIST 1643e and SLRS-5 were used for

validation purposes, but these were for the other ions rather than the REE. There was no method validation for the REE other than the occasional repeat analysis of a sample to determine whether the data were reproducible. A paper by Armand *et al.* Discussed the determination of La, Eu and Lu in stream waters (51). Although SLRS-4 and NIST 1643d were analysed, no validation of the REE data was made. The reader was directed to a paper published 10 years previously for LOQ values. Inguaggiato *et al.* also performed no protocols prior to REE determination in volcanic waters using ICP-MS (52). Again, the REE were amongst a suite of analytes determined and although several reference materials were analysed to validate the data, none were relevant to the REE. Further examples were presented by Lawrence *et al.*(53-56) who used ICP-MS to determine REE in different water types. In the first of these examples, the determination of Eu was troublesome because of the elevated Ba present in the samples and because of the salinity. In the second example (54) the accuracy of the data was demonstrated through the analysis of the certified material SLRS-4. The results were compared with those obtained in a comparison exercise and reported previously by Yeghicheyan *et al.* (57). The results were within 4% of those obtained previously with the exception of Tm, which was 12% higher.

Dissolved and nano-particulate / colloidal REE concentrations in glacial melt-waters were determined by Tepe and Bau(58). The dissolved fraction was determined directly using ICP-MS after filtration through a 0.2 µm filter and acidification. The colloidal fraction was obtained using filtration of 3300 mL of water through a 0.2 µm filter followed by ultra-filtration using a Millipore 10 kDa membrane unit. The analytes were again determined directly using ICP-MS. The REE concentrations found in these fractions from Greenland were compared with those from other sites including the Orinoco River (59), the Rhine (60-62), the Kalix River in Sweden (63) and the Mississippi River (64). Many of these papers had similarities in that most introduced the sample to the analytical instrument directly. Exceptions were the paper by Shiller(64) who used an organophosphate chelating resin to preconcentrate the analytes for some samples and at least one of the papers by Kulaksiz and Bau, who used the same preconcentration protocol developed by Shabani *et al.*(65). Another similarity is that few of them had any quality control protocols to ensure that the data being obtained were accurate. The exception was the paper by Shiller who used an

isotope dilution protocol for calibration and also analysed the standard reference materials PPREE1 and SCREE1, both obtainable from the US Geological Survey. Agreement was within 5% of the accepted values for most analytes and within 7% for all others except Gd in SCREE1 which was 16% lower. Ingri *et al.*(63) reported a high Yb level in the HCl blanks and that therefore, this analyte could not be determined in the samples. In addition, since no preconcentration protocol was conducted, the high mass REE remained below LOD. One further paper that reported the determination of REE in ground and seawaters was presented by Duncan and Shaw(66).

The analytical characteristics of these sample introduction systems for the REE determination in natural waters are compared in Table 1.

Potentiometric sensors have also been developed for the direct determination of some REE. In one example, sensors based on two neutral ionophores, N,N'-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-diamine and 3,3-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol modified PVC membrane sensors were used for Nd determination (67). A second example by the same research group used 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene)diphenol and N,N'-bis(pyridoxylideneiminato) ethylene as the ionophores on the PVC membrane to detect Pr ions (68). The second paper resorted to spiking waters with concentrations of 16, 100 and 500 $\mu\text{g L}^{-1}$ Pr. Although results were in good agreement with those obtained using atomic absorption, the concentration levels at which the Pr were spiked is clearly far too high for unpolluted natural waters. Other examples include 3-amino-5-mercapto-1,2,4-triazole (AMT)-modified screen-printed electrode, developed for La determination (21) and 1,5-di(cyanoethane)-2,4 : 7,8 : 13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene and 1,5-di(cyanoethane)-2,3,4-pyridine-7,8 : 13,14-dibenzo-1,3,5-triaza-9,12-dioxa cyclopentadeca-2,7,13-triene modified PVC membranes for Nd determination (69). Each of these applications used potentiometric determination of the analyte ions. Some of these applications reported very high LOD (10^{-7} mol L⁻¹) whereas others were at the 3×10^{-9} mol L⁻¹ level which, although low, is insufficiently low to determine REE in natural water samples. Despite this obvious shortcoming, the electrodes tended to have a long linear range, react

quickly to the analyte and are stable. Another drawback is that they are selective rather than specific. In the paper by Singh *et al.*, interferences from Co, La, Pr and Yb were observed. Since they have relatively poor sensitivity, they have been applied for the determination of the analyte ions in spiked samples.

Mention should also be made of the paper by Yeghicheyan *et al.* who reported the results of an inter-laboratory study of the certified material SLRS-5(70). During this study, the material was sent to numerous French laboratories which then used ICP-MS and/or SF-ICP-MS to analyse it. Results for the REE, Si and 21 other analytes were reported. The GEOTRACES program designed to compare inter-laboratory analyses of waters to ensure that meaningful data can be obtained from different sites has also paid attention to the determination of the REE. In one publication(71), Nd ratios and REE data from one particular seawater site were determined. Most of the 15 laboratories determining Nd ratios used an iron co-precipitation followed by an ion exchange clean-up prior to either TIMS or multi-collector ICP-MS detection. Others used a solid phase extraction using C18 columns. Six laboratories determined other REE. Agreement for the REE was within 15% for all except Ce. This was attributed to Ce being the most blank-sensitive of the elements. A similar study, also part of the GEOTRACES program was also reported(72).

3. Preconcentration Methods

In general, a preconcentration method should be fully validated, efficient, rapid, use a low volume, or ideally, no harmful organic solvents and not require a very large volume of sample. Ideally, it should also be readily transferable to other detection techniques and be applicable to as many of the analytes of interest as possible.

As with all analytical methods or techniques, the necessity for accuracy is paramount. Full validation using certified reference materials (CRMs) is the ideal scenario, but there is a paucity of these for REE in water. In the absence of CRMs, analyte spike - recovery experiments may be undertaken. Here, some

pragmatism must be exercised. It is usually necessary to use spikes of an appropriate concentration. For instance, when determining REEs at the ng L^{-1} levels in water, it is usually inappropriate to spike with $\mu\text{g L}^{-1}$ levels. This is especially true if ICP-MS is being used for detection. However, if the only detection technique available to the authors of a research paper is ICP-OES, then spiking at the $\mu\text{g L}^{-1}$ level may still give an indication whether or not the preconcentration method works. It would then be for other workers who adopt this preconcentration method for their work to determine whether or not it is suitable for use with ICP-MS detection.

Ideally, a preconcentration procedure should transfer all of the analyte from the original large volume of sample into a smaller volume ready for analysis. Therefore if the original sample is 10 mL in volume and this undergoes a procedure in which the volume immediately prior to analysis is 1 mL, the concentration of the analyte should be increased by a factor of 10. If a preconcentration factor of only 6 is obtained, then the method is not as efficient as it could be. However, if the preconcentration factor is always 6, the method still has some merit. However, if the preconcentration factor varies between sample matrix type, further work may be necessary to refine the method. Worse still, if the preconcentration factor varies at random, then the method is neither robust nor under experimental control.

The rapidity of a preconcentration method is also important for most workers. Consider two fully validated methods that yield the same preconcentration factor but where one takes 10 minutes and the other 3 hours per sample. For an analyst confronted with 200 samples to prepare in a working week, the choice of which method to adopt is obvious.

—The amount of sample required for a preconcentration method can also be an important consideration. If a method requires a litre of sample to be used to obtain the necessary preconcentration factor, then transportation of the samples back to the laboratory will be more troublesome than for a method where only 50 mL is necessary. Similarly, storage of the sample will also be more problematic for samples with very high volume.

These considerations will be discussed throughout the next few sections in an attempt to assist any reader starting in this area of research.

3.1 Solid Phase Extraction

Most of the preconcentration procedures used prior to the determination of the REE are based on solid phase extraction using different solid supports to adsorb REE ions from natural water samples. The solid phase extraction methods that have been described in the literature are discussed below for the different type of the solid supports.

a) Polymeric supports

Polymeric solid supports having different structure and functional groups have been used for the preconcentration of the REE ions from natural waters. The features of these methods are summarized in Table 2. Polymeric supports containing styrene-divinylbenzene(23) and trade products of styrene-divinylbenzene such as Amberlite XAD-16 (12), Amberlite XAD-4 (22, 24, 37, 73) and Chromosorb 106 (6) have been used as solid phase supports for the solid phase extraction of REE. Alternative polymeric supports, e.g. acrylic ester matrix polymers such as Amberlite XAD-7(74) or divinylbenzene–methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups (38) have also been used. Organic ligands that are able to complex REE have either been impregnated (12,74) into these polymers or immobilised using a chemical reaction (6, 22, 23,24, 37,73). Styrene-divinylbenzene copolymer beads chemically modified with alkyl phosphinic acid have also been used to preconcentrate REE ions from seawaters using an on-line system (2).

Divinylbenzene–methacrylate copolymeric resin containing polyaminopolycarboxylic acid groups basically, ethylenediaminetriacetic acid and iminodiacetic acid groups is sold as syringe-driven chelating columns (SDCCs). These have been used directly to preconcentrate REE without any modification of the surface of the support (38). Very high preconcentration factors were obtained by Waqar *et.al.* (23) and Gok *et al.* (12). Waqar *et al.* used a

fluorinated β -diketone – based resin. The chelating capacity ranged from 0.053 (Lu) to 0.071 (La) mmol g⁻¹. However, a very high volume of sample (e.g. 1000 mL) was passed through the column. The flow rate of sample was 6 mL min⁻¹ and so the kinetics must have been relatively rapid. However, since sample preparation for one sample replicate took nearly three hours, it was very time consuming. A similar problem was observed in the paper by Gok *et al.* (12). Here, preconcentration of the analytes (Ce, La and Y) took four hours. Detection was achieved using UV-Vis, leading to extremely high LODs (250 – 850 μ g L⁻¹) and only three analytes were determined. These factors limit the viability of the methods use. The lowest LODs were obtained by Vicente *et al.*, (74) who retained the analytes as the 8-hydroxyquinoline chelate on Amberlite XAD-7. Only 85% of the analytes were retained on the column, meaning that standards had to be put through the same process. The kinetics were extremely rapid, with sample flow rates of up to 12 mL min⁻¹ being possible without loss of retention. However, only some of the REE (Eu, Tb, Ho, Tm and Lu) were determined and the method took 12 min per sample replicate. No capacity values were given. The method proposed by Zereen *et al.*, (6) was an online procedure that had a very short analysis time and could be applied to the determination of 13 REE. The 4-(2-thiazolylazo) resorcinol immobilized Chromosorb 106 resin used by these authors was stable, i.e. there was no loss of retention for over 500 cycles of loading / elution. The authors noted though that it did swell after 300 uses, meaning that back pressure increased putting strain on the flow injection connections. The method developed yielded sub-ng L⁻¹ detection limits and was validated through the analysis of the seawater material CASS-4. Results were in good agreement with those obtained by other workers. Further validation was achieved using analyte spike – recovery experiments on estuarine and coastal seawater samples. The spike concentrations were appropriate for the samples and recovery values of between 91 and 105% were obtained. The sorption capacity of the resin ranged from 91.1 (Lu) to 108 (Nd) μ mol g⁻¹. Polyhydroxamic acid synthesized from acrylamide as the monomer and N, N'- methylene bis acrylamide as cross linker was used in a self-fabricated glass cartridge for the preconcentration of REE ions from seawater (4). To reach the LOD values given in Table 2, a high volume of sample (200 mL) had to be passed through the column. The kinetics were reportedly rapid. However, since loading of the sample took 200 min, the method was very time consuming. The resin had a high capacity, with 135 mg g⁻¹ for REE being quoted.

Method validation was achieved through analyte spike-recovery experiments where spikes similar to the natural concentrations in the waters were recovered with values between 80.8 % (Tb) and 108% (Yb). Commercially available and pre-packed Nobias PA1 resin (39) and a syringe driven chelating column (SDCCs) containing Nobias CHELATE-PB1M resin (75), both products of Hitachi High-Technologies, were used for the preconcentration of Nd only and REE ions, respectively, from seawater samples. According to Table 2, the latter resin cartridge system provided the lowest LOD values for REE ions in seawater using a 10 min preconcentration time. The latter paper's main focus was the development of an automated pH adjustment system that relied on spectrophotometric measurements. Therefore, an exhaustive study on retention capacity etc. was not undertaken. It was noted though that the use of the automated system reduced contamination significantly when compared with the use of glass or polymer electrodes to monitor pH. Method validation for REE determination was achieved through analyte spike – recovery experiments where ng L⁻¹ levels of REE had recoveries of close to 100%.

The commercially available Chelex 100 resin is a styrene divinylbenzene copolymer containing paired iminodiacetate ions which act as chelating groups in binding polyvalent metal ions. Guéguen *et al.* (76) used Chelex 100 to preconcentrate La, Ce, Nd and Yb as well as some trace elements (Cd, Cu, Pb, Zn, Sc) from saline water. In their work, Chelamine resin was first used to separate the major elements from the trace analytes which were retained on the resin and then the effluent from Chelamine were then concentrated on Chelex to isolate the REE. Chelex-100 has been used for the preconcentration and separation of REE from different river waters, sea waters, ground water using batch systems (77-79) and mini-column system either with off-line or on-line preconcentration (16,80-83). Even though very low LODs were obtained by Sawatari *et al.* (77), this method, lasting at least 2 hours, was based on a batch extraction system from 1 L of the seawater sample. One notable problem with Chelex-100 is that it shrinks and swells with changing pH. This can lead to voids in mini-columns and / or increases in back-pressure. The method proposed by Kayasth and Swain (16) was also very time consuming because it involved several steps including boiling of the sample, a precipitation procedure for alkaline earth elements and finally a mini-column procedure using Chelex-100 and boiling of the eluents. Chelex-100, Toyopearl AF Chelate-650 (another commercially available iminodiacetate-based resin) and C18 cartridges loaded with

ethylhexylphosphates were compared for their efficiency to separate REE and, in particular, the magnetic resonance imaging contrast agent Gd-diethylenetriaminepentaacetate (Gd-DTPA) from the water matrix (84). The aim was to monitor the introduction of Gd-DTPA in a river. Although both of the commercial resins were preconcentrated the REE ions in river waters successfully, neither of them was appropriate to preconcentrate the Gd-DTPA complex; especially at the pH required to preconcentrate the ions. The LOD values given by Kim *et al.* (83), Zhu *et al.* (82), and Yabutani *et al.* (78) are also very low. The paper by Kim *et al.* (83) discussed the effects of humic acid substances on the determination of REE. Significant fractionation of heavy REE compared with lighter REE was observed. The paper by Zhu *et al.* (82) also used Chelex-100 to retain the REE. Analytes were preconcentrated off-line, eluted, and then an internal standard added prior to analysis. Recoveries for 14 REE were better than 90%. Some certified seawater samples (CASS-3, CASS-4 and NASS-5) as well as some non-certified seawater samples were analysed. The data were corrected for the recovery values. Detection limits were calculated from the instrumental detection limits and then multiplied by the preconcentration factor. Yabutani *et al.* (78) described a batch method in which 250 mL of buffered seawater was mixed with Chelex-100 resin for 2 hours. The resin was then filtered, washed with buffer solution to remove alkaline earth elements and the analytes eluted with acid ready for analysis using ICP-MS. Rare earth elements and numerous other analytes were determined with LODs being sub-ng L⁻¹. The preconcentration factor was 40. No certified materials and no analyte spike – recovery experiments were conducted during this study.

Some other commercially available resins have iminodiacetate functionality. These include Dionex MetPac CC-I (85-87), MetaSEP ME-2 (88), Toyopearl AF Chelate 650M (29), Muromac A-1 (89-91) and NOBIAS CHELATE PB1M (92). In addition, two commercially available units designed for the preconcentration of analytes, the seaFAST system (93) and the CETAC DSX-100 system (94) have been used for the preconcentration of REE from natural waters. All of these methods with the exception of those proposed by Hall, *et al.* (85), Liu *et al.* (87) and Kuhn and Kriews (94) were on-line methods. The method proposed by Hall, *et al.* (85) used an automated preconcentration system employing the Metpac CC-1 chelating resin, but the measurements of the eluents containing REE were performed off-line. According to the paper, the resin had a capacity of 0.45 meq and a selectivity that went: REE > Hg >> Cu >>

$\text{UO}_2 > \text{Ni} > \text{Pb} > \text{Zn} > \text{Co} > \text{Cd} > \text{Fe} \gg \text{Mn} > \text{Ba} > \text{Ca} \gg \text{Sr} > \text{Mg} \gg \text{Na}$. Method validation was achieved through analyte spike – recovery experiments with concentrations of 50 and 500 ng L⁻¹ being 92 – 96% recovered. The CETAC DSX-100 unit is an automated working system incorporating a closed chemical cycle which preconcentrates analytes and removes matrix components using a suspended particulate reagent (SPR). This comprises polymeric beads possessing chelating iminodiacetic functional groups, in a cartridge (94). The novelty of this paper is that the whole resin sample (diameter 0.2 µm) was introduced to the ICP through pneumatic nebulisation. A preconcentration factor of between 40 and 48 was obtained. As well as the REE (La, Ce, Eu, Gd, Yb, and Lu), other elements (Mn, Fe, Ni, Co, Cu, Zn, Cd, and Pb) were also determined. Method validation relied on these other elements being determined in the CRMs NASS-4 and CASS-3. The obvious drawback of the method is that the resin is destroyed during the analysis. Another example used NOBIAS CHELATE PB1M chelating resin (92) in a syringe driven device that could be used both on-line and off-line. This was one of the the fastest methods, taking 3 min for one sample. In addition, the column could automatically be changed enabling a faster throughput of samples with minimal operator input. This paper also reports evaluation of the resin InterSep ME-1. Precision values were similar for both resins leading to the authors concluding that both were suitable for REE preconcentration. No selectivity or capacity data were given for the resins. The method was validated through the analysis of NMIJ CRM 7201-a (a river water), with data in excellent agreement with certified values. The commercially available seaFAST system (93) utilizes a chelating resin with iminodiacetate and ethylenediaminetriacetic acid functional groups. The automated system provided more precise data than many other studies. The data were validated in three different ways, including the use of standard additions calibration, isotope dilution and the analysis of CRMs. The isotope dilution data for Nd agreed to within 15% of those obtained using the preconcentration system for 65 of the 69 samples analysed.

A paper by Munemoto *et al.* described the determination of REE in ground waters(95). A chelating resin disk (3 M Empore) was used to preconcentrate the REE 20-fold prior to ICP-MS determination. Recoveries of $102 \pm 4\%$ were established for all analytes, although the spike concentrations were not given. A column of pre-cleaned Chelex-100 was used by Abbott *et al.*(96) to extract REE from seawater and porewaters. Washing with buffer prior

to analyte elution with 3 M HNO₃ enabled a sample clean-up, including removal of potentially problematic Ba. Sample (10 mL) was analysed and the elution volume of acid was 12 mL. Therefore, there was no preconcentration. An in-house material ensured consistency of data, but no CRM was analysed and no analyte spike - recovery experiments were undertaken.

Ion exchange resins have also been used for the preconcentration of REE. The effectiveness of the cation exchange resins Dowex 50W X12 (97), Sep Pak Light-CM cartridges (98), Amberlite CG-120, Amberlite IR-120, Rexyn 101 and Dowex 50W X18 (99) to preconcentrate REE have been demonstrated in the literature. The method developed by Kubova *et al.* (97) using Dowex 50W X12 was not an easy or straightforward one. Sample (5 L) was passed at a flow rate of 4-5 mL min⁻¹ through a column packed with Dowex 50W X12. The method then involved a series of washings and evaporation stages that took several days to complete. The authors noted that contamination from the laboratory environment is unlikely. However, because of the huge volume of reagents used, problems associated with contamination cannot be completely disregarded. The cost of high purity reagents could also potentially be significant. Although several samples could be prepared simultaneously, the procedure is clearly not applicable to routine analysis. However, it did provide the lowest LOD values of those that used ICP-OES detection. The results for REE in nine mineral water samples obtained using ICP-OES were compared with those obtained using a similar cation exchange column followed by spectrophotometric detection. Results were in reasonable agreement. The sorption efficiencies of the ion-exchangers (Amberlite CG-120, Amberlite IR-120, Rexyn 101, Dowex 50W X18), various zeolites (clinoptilolite, mordenite, zeolite Y, zeolite Beta) as well as the chelating resins (Muromac, Chelex 100 and Amberlite IRC-718) for REE have been investigated and compared using batch system experiments. From the sorption experiments, the clinoptilolite, zeolite Y and Chelex 100 were suitable for the preconcentration of REE from natural waters (99). Some of the media did not retain the REE quantitatively at pH values of natural waters. Examples include the Muromac and the Amberlite IRC-718 at pH 6-7, where retention efficiency decreased to only 50 – 60%. The cation exchange resins Amberlite IR120 and Rexyn 101 showed similar trends. Many of the media had extremely rapid adsorption kinetics, with REE from 20 mL of sample solution being retained in less than one minute. The amount of medium

required to obtain full retention varied, with 0.01 g of clinoptilolite being sufficient, whereas others, e.g. Zeolite Y required 0.1 g. The big drawback with the clinoptilolite was that it contained some REE naturally. This meant that it could not be used for ultra-trace work ($< 0.02 \text{ mg L}^{-1}$), thus limiting its overall viability. Rousseau *et al.*(28) proposed three different separation protocols, one suitable for freshwater and two others suitable for coastal and open ocean seawaters. The AG50W-X8 (Dowex) cationic resin was used to preconcentrate REE ions from fresh water samples using an off-line chromatographic technique that also separated Ba from the analytes, hence diminishing the possibility of interferences. The second protocol contained two steps. The REE ions were first separated from the seawater matrix by co-precipitation with $\text{Fe}(\text{OH})_3$. The precipitate was then dissolved and the Fe separated from the REE using AG1-X8 anion exchange resin. Finally, after drying and re-dissolving the eluate containing the REE, traces of Ba and other impurities were removed using 2 mL of 2 M HCl and an AG50W-X8 column. The third protocol used Hitachi Nobias PA1 resin to preconcentrate the REE ions and this was followed by an AG50W-X8 cationic column for the separation of Ba from the eluates of the Nobias PA1 resin. The authors concluded that this third protocol enabled a better Ba removal and a faster sample preparation compared with the second protocol containing $\text{Fe}(\text{OH})_3$ co-precipitation (28). This paper used isotope dilution to validate the matrix elimination / preconcentration methodology. In addition, the CRMs SLRS-4, SLRS-5 and CASS-4 were also analysed with results for SLRS-4 and SLRS-5 being in excellent agreement with data from previous studies. The isotope dilution method has the advantage of good accuracy, but it comes at the cost of high price. Another disadvantage is that not all of the REE have more than one isotope.

A series of papers by Chevis *et al.* determined REE in sub-marine groundwaters following preconcentration using the cation exchange resin AG 50 W-X8 (100-102). After the analytes had been retained on the column, it was washed with small aliquots of 1.75 M HCl and 2 M HNO_3 to remove retained Fe and Ba. The REE were then eluted and evaporated to dryness on a hotplate. The residue was then taken up in 10 mL of 1% HNO_3 prior to analysis using a high resolution ICP-MS instrument. Many of the analytes were determined using both low and either medium or high resolution to ensure that there were no

interferences. Precision was always better than 5% RSD and generally better than 2%. No mention was made of data validation using reference materials for most of the papers, but one did compare their data for the material SLEW-3 with those obtained by Lawrence and Kamber in 2007(36).

Chitosan (CS) polymers have natural aminopolysaccharides as their functional group. The products of an *N*-deacetylated chitin have become important natural polymers because of their higher chelating ability compared with other natural polymers (103). This review paper by Varma *et al.* discussed the use of chitosan for retaining analytes and also the preparation methods used to derivatize it. The review contains 106 references and covers the earlier work in the area. Chitosan functionalised with different organic moieties has been applied to preconcentrate REE from water samples. Examples include iminodiacetate (104), serine diacetic acid (105), 2-amino-5-hydroxy benzoic acid (106), N-(2-hydroxyethyl)glycine (107) and ethylenediamine-N,N,N'-triacetate (108) groups. All of these methods used on-line preconcentration, so the time required for analysis of one sample is low, approximately 6 min. The LOD values of these methods are seemingly high, but this is because most used ICP-OES as a detection system. The exception was the method given by Lee, *et al.*(104), who obtained lower LOD values because they used ICP-MS detection (Table 2). The paper by Lee reports the determination of numerous analytes in addition to the REE. The recovery of the metals from the column were variable, with some not being retained (e.g. Rb and Sr) and others being retained very strongly; to the extent where they were not eluted efficiently. Recovery of the REE from the column were quantitative (96 – 104%) and with good precision (at worst, 5%). Hakim *et al.* used a fully automated system to retain seven REE and other analytes on a column prior to elution of the analytes into an ICP-OES instrument (105). The analytes' peak shapes improved through reversal of the flow during elution. Sensitivity enhancement factors ranged from 33 to 74 for the other elements, but the REE enhancements were greater, ranging from 73 to 120. Method validation was achieved through the analysis of a certified material (SLRS-4). However, the authors had to rely on the other elements as a measure of accuracy, since REE are not certified in this material. An interference study was reported in another paper, where a matrix similar to that expected to be found in a fresh water was added to the analytes(106). At the concomitant concentration levels studied, there were no interference effects. However, an interference study for a seawater matrix was not examined. The

third paper (107) measured the capacity of the resin that had been prepared using Cu as the test analyte. A value of 0.49 mmol g^{-1} of resin was calculated. The fourth paper (108) was similar to the third with the addition of analyte spike - recovery experiments. Spikes for the REE were at the $0.05 \text{ } \mu\text{g L}^{-1}$ level, which were appropriate for their samples. Recoveries for the REE were 91 – 109%.

A commercially available di(2-ethylhexyl) phosphoric acid resin (D2EHPA resin) (109) was used for the preconcentration of La, Ce and Nd from natural waters using an on-line preconcentration method in the presence of the complexing agent EDTA. The LODs obtained using this method were insufficiently low ($1.09 - 3.31 \text{ } \mu\text{g L}^{-1}$) to measure the REE ions in natural waters. This is because a microwave plasma torch-AES instrument was used as a detector rather than ICP-MS. The authors therefore resorted to using analyte spike - recovery experiments in which $500 \text{ } \mu\text{g L}^{-1}$ of the REE was spiked into waters. Recoveries were close to 100% and precision of measurement was 2.27 – 4.08%. Although the recovery values were good, the spiking concentration was clearly too high; even for MPT-AES detection. The authors did optimize the variables for the preconcentration adequately though. 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P-507) resin as the stationary phase was used for the preconcentration and separation of REE from matrix elements in ground water (110). This application used ICP-MS as a means of detection. Commercially available MetaSEP® ME-2 resin has been used to preconcentrate all of the REE ions from 32 rainfall events collected in suburban Tokyo using an off-line column preconcentration method (111). The LOD values obtained using this method combined with ICP-MS detection were very low (all sub ng L^{-1} , with some being as low as 0.001 ng L^{-1}), but the analysis time was about 75 min for one sample. A preconcentration factor of 30 was achieved. Method validation was achieved through the analysis of the CRM SLRS-4, with data being comparable to those from other workers. This matrix elimination method decreased the BaO and SrH polyatomic interferences to $< 0.2\%$. However, the rare earth oxide interferences were still significant. Commercially available Ln® Resin columns have been used during an off-line preconcentration method for the determination of REE ions in iron-rich waters (112). The sample loading flow rate was only 1 mL min^{-1} and, since 1000 mL of sample was used, a total of 1000 mins was required for the preconcentration step per sample replicate. The REE were then eluted, evaporated to dryness and the residue taken up in 10

mL of 2% HNO₃, providing an overall preconcentration factor of 100. This final solution was then introduced to an ICP-MS instrument through an ultrasonic nebuliser. The evaporation and measurement steps therefore added extra time to an already very large sample preparation time. The LODs for this method were impressive; ranging from 0.05 to 0.1 ng L⁻¹. The authors had to take the precaution of purifying all reagents by sub-boiling distillation prior to use. The method was validated through the analysis of the certified materials PPREE 1 and SCREE 1, supplied by the U.S. Geological Survey. Experimental data were in excellent agreement with certified values for all analytes. Despite the analytical success, there were one or two problems associated with the protocol. As well as the obvious very high time consumption per replicate limiting the number of samples that can be analysed per unit time, the columns were only capable of single use because the extracting group was removed during the process. Despite the high preconcentration factor achieved, the LOD for Tm was still insufficiently low for it to be determined precisely.

An interesting method of sample collection was reported by Petersen *et al.* (113). These workers used the commercial Chemcatcher device, which is a passive sampler to collect REE from estuarine waters. The device comprised a 3M Empore chelating disk and a cellulose acetate disk as the diffusion-limiting layer. The authors first used a flow through system to determine the effects of temperature and turbulence on the retention of the analytes, finding that turbulence had the greater affect. The device was then placed in a harbor for 4 weeks, then removed from the sea, the analytes eluted from the chelating disk and determined using ICP-MS. Although the sampling was clearly a very prolonged affair, it is possible to have several such devices placed in several areas simultaneously and hence, once they have been returned to the laboratory, the actual sample preparation protocol is reduced significantly. In addition, the transport of a small series of filters is clearly more straightforward than that of several dozen water samples all of which may be 100 mL – 1 L in volume. The passive sampler also enables sampling at regular intervals without the need for an operator being sent into the field several times a week.

b) Silica based supports

Different methods using silica based supports have been proposed to preconcentrate REE from natural water samples. The analytical properties of these are compared in Table 3. Most of these methods were developed to preconcentrate and separate only some of the REE ions, rather than the whole suite. This is probably because of the difficulty finding a chelating agent to complex all REE using the same experimental conditions. A solid phase extraction medium capable of preconcentrating REE was obtained by modifying silica gel with the chelating agent 8-hydroxyquinoline (114). Also used was the commercial RE-Spec column. The method involved the spiking of water samples with an altered isotope REE mixture, then the preconcentration protocol and finally measurement using ID-ICP-MS. This method was not a simple, straightforward application because it contained the extra step of heating the samples at 80 °C for 48 h prior to the column preconcentration to ensure thorough equilibration of the altered isotope spike. The 8-hydroxyquinoline-based medium was placed in a large column and then 1 L of sample passed through. This took approximately 3.5 hours. Recovery of the spiked REE ions varied between sample type with 81 - 84% being recovered from groundwater and 90 - 93% (with the exception of La at 52%) from seawater. The amount of Ba in seawater samples was decreased by a factor of 300-400 though, thereby decreasing potential polyatomic interferences. A similar protocol was adopted by Halicz *et al.* who used silica bonded 8-hydroxyquinoline to separate REE from highly saline samples (115). Despite only 3 mL of sample being used, LODs were sub-ng L⁻¹. The fully automated system achieved the preconcentration in less than 10 minutes per replicate. Method validation was achieved using the CRM NASS-2 and then comparing the data obtained with those obtained by Shabani *et al.* (65). The method was applied to samples from the Dead Sea. The only anomalous result was for Eu, which was attributed to the BaO polyatomic interference. The system was efficient at removal of Ba (< 0.5% remaining), but it is present in such high concentration in the Dead Sea that interference was still significant. In another method, the preconcentration was based on the adsorption of 1-Phenyl-3-Methyl-4-Benzoylpyrazol-5-one complexes of Eu, La, Y and Yb ions on silica gel (116). A maximum volume of 100 mL of sample could be passed through the column before analyte breakthrough occurred. The preconcentration procedure lasted 50 mins per sample replicate and yielded an enrichment factor of 100. The method was applied to the preconcentration of only three REE from lake water and synthetic seawater. Nanoporous silica (SBA-15) has been

physically functionalized using N`-[(2-hydroxy phenyl) methylene] benzohydrazide (BBH) (117) and 2-(2-nitrobenzylideneamino) guanidine (118) and both of these supports have been used for the preconcentration of REE ions. Both of the last two applications were batch solid phase extraction systems yielding very high preconcentration factors. The method proposed by Berijani *et al.*(117) provided a preconcentration factor of 400, obtained from extracting 2 L of sample using 50 mg of the medium, filtering and then eluting the analyte using 5 mL of nitric acid. However, there were a few faults with the paper. Only Dy was tested as the analyte rather than a suite of REE. As a means of method validation, analyte spike – recovery experiments were conducted. Even though the LOD was reported to be 0.05 $\mu\text{g L}^{-1}$, no Dy was found in tap water samples. In addition, the authors used a spike concentration of 4 or 6 $\mu\text{g L}^{-1}$. This is clearly at least one order of magnitude too high. Other drawbacks include the huge sample volume required and the time taken for the preconcentration. However, an interfering ion study was undertaken, which demonstrated that many ions in 1000-fold excess caused no significant interferences. The capacity of the medium was 47 mg g^{-1} . The paper by Kavosi *et al.*(118) described the retention of Dy, Eu, Nd, Sm and Yb. Spike concentrations of 3 $\mu\text{g L}^{-1}$ were used for well waters which were again far too high. However, the preconcentration factor achieved was far lower and hence the LODs obtained using ICP-OES detection were at the $\mu\text{g L}^{-1}$ level. Another drawback of the system was that the medium retained its retention capacity for only two cycles of retention / elution with the capacity decreasing further every subsequent cycle. An interference study indicated that a mixture of concomitants decreased recovery of the analytes to between 87 and 88.9 %. The medium had a capacity of between 25.6 and 31 mg g^{-1} for the analytes determined.

C18 cartridges have been used for the preconcentration and separation of REE ions from water samples. Either the REE ions are complexed with organic chelating ligands and the complexes are then adsorbed on the C18 medium, or, the organic ligand is chemically attached to the C18 medium as a first step and then the sample containing REE is passed through the medium when the REE become retained. Surface modification of C18 by the adsorption of bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and 2-ethylhexyl dihydrogen phosphate (H2MEHP) (65); ethylhexylphosphates (84) and 1-(2-pyridylazo) 2-naphthol (PAN) (119) have been accomplished and these modified C18 materials then used for the preconcentration of REE ions. The paper by Shabani *et al.*

(65) preconcentrated between one and five L of seawater at a flow rate of 20 mL min^{-1} , therefore requiring a time of between 50 and 250 mins. However, since an 8 channel peristaltic pump was used, several samples could be prepared simultaneously. Precision was excellent (typically 0.5 to 2%) and recovery of analytes spiked into demineralised water, synthetic seawater and natural seawater were $> 98\%$ for all analytes except La, which, although good for the demineralised water was only $\sim 89\%$ in the seawaters. Method validation was achieved through alternative techniques, including the use of Chelex-100 with NAA detection and solvent extraction followed by ICP-MS detection. Bahramifar and Yamini (119) used an automated method to preconcentrate Ce, Dy, La, Sm and Y (plus U). The method developed took approximately 6 mins per sample, enabling a sampling rate of about 10 per hour. An interference study indicated that none of the major ions investigated caused deviation of any more than 10% in the signal for $10 \mu\text{g L}^{-1}$ of the REE. The presence of 50 mg L^{-1} Ni appeared to cause greatest deviation, but even then, 87 % recovery for Ce was achieved. Impressive enrichment factors of between 275 and 332 were achieved. Spikes of $1 \mu\text{g L}^{-1}$ REE were recovered between 96 and 106% for the REE.

An example of the loading of the complexes of REE ions on C18 was presented by Vizioli *et al.* who preconcentrated Gd and La as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complexes in the presence of non-ionic micelles of polyethylene glycol tert-octylphenyl ether (Triton X-100) (18). This protocol enabled sample clean-up and concentration enhancement with minimum sample handling. Subsequent elution of the Gd and La complexes using ethanol enabled capillary zone electrophoresis separation and UV-Vis detection. Very high preconcentration values were obtained ($\times 1000$) yielding LODs of 20 and 80 pg L^{-1} for La and Gd, respectively. The preconcentration method was surprisingly quick (< 10 mins), however, the CZE separation took approximately 25 mins. Analyte spike – recovery experiments where 80 and 120 pg L^{-1} of La and 250 and 350 pg L^{-1} Gd were added, yielded recoveries of between 96.6 and 102.5 % and 101.2 and 104 % for La and Gd respectively. The preconcentration method was non-specific and so when tap water samples were analysed, several signals of unknown origin were observed. However, the powerful separation capabilities of CZE enabled these potential interferences to be separated from the analyte signals. The paper by Hennebrüder *et al.* reported the determination of Gd (as well as a few other REE) using SPE followed by ICP-MS

detection (84). This paper used commercial as well as media made in-house, and was discussed previously in the section covering iminodiacetate functional groups. The use of the modified C18 media was a modification of the method proposed by Shabani *et al.* in 1992(65). The analytes were removed from the cartridge using 6 M HCl, but since this causes interferences during ICP-MS detection, it had to be evaporated to dryness and the residue taken up in 1 M HNO₃. This was a time consuming process but yielded an enrichment factor of 40. The recovery factor of the analyte ions from spiked water samples ranged from 77 to 87%, although when Gd was introduced as the magnetic imaging contrast agent Gd-HTTHA, the recovery decreased to 70%. Such low recoveries are clearly not desirable, but are usable as long as the precision is good.

Another dispersive solid phase extraction approach was developed using mesoporous silica functionalized as a strong cationic exchanger (SCX) to enrich and separate a group of REE from a saline matrix (44). The silica particles were then destroyed using nitric and hydrofluoric acids prior to analyte introduction to ICP-MS. The method therefore had the drawbacks of hydrofluoric acid being used and that the silica particles were only single use. In addition, they also retained some of the matrix elements which caused interference effects. The authors overcame this problem by diluting the samples 1+9. The method developed was therefore more of a matrix removal process than a preconcentration. Despite this, LODs of between 0.1 and 0.9 ng L⁻¹ were obtained.

c) Other Solid Supports

Nanomaterials such as multi-walled carbon nanotubes (120), the fullerene derivative poly(β -styryl)-(1,2-methanofullerene-C60)-61-formo hydroxamic acid (121) and magnetic core-shell silica nanoparticles, functionalized with cinchonidine (CD-Fe₃O₄@SiO₂) (122) have been used to preconcentrate REE ions from water samples. In the last example, a magnetic solid phase extraction procedure was applied with ultrasonic mixing of the sample and magnetic core-shell silica nanoparticles in a batch system. This was followed by separation of the analyte (Eu)-loaded nanoparticles using a magnetic bar and elution of the REE ions using ultrasonic mixing of the nanoparticle loaded REEs and acid solution (1.5 mL of 1 M HNO₃). Detection was achieved using ICP-OES, yielding a LOD of 0.04 μ g L⁻¹. The other two methods were also off-line preconcentration methods. Unfortunately, these methods are time-consuming and need a high

volume of sample to reach the LODs and preconcentration factors given in Table 4. The paper by Liang *et al.*(120) reported an enrichment of 50 and extraordinarily low LODs of between 3 and 57 ng L⁻¹, considering ICP-OES was used as the detection method. The medium could be re-used a minimum of 50 times with no loss of efficiency. The adsorption capacity for the REEs were 8.30 mg g⁻¹ for La, 9.43 mg g⁻¹ for Eu, 9.93 mg g⁻¹ for Gd, 7.23 mg g⁻¹ for Ho, 9.70 mg g⁻¹ for Sm, 8.0 mg g⁻¹ for Tb and 8.57 mg g⁻¹ for Yb. An interference study in which 100 µg L⁻¹ solutions of REE were mixed with concomitants indicated that Fe³⁺ was most likely to cause interference, but only above a concentration of 100 mg L⁻¹. It would have been preferable to have used a lower concentration of REE, i.e. closer to the concentration found in samples, to obtain a better understanding of interference effects. Recovery of 20 µg L⁻¹ spikes in seawater were 94.4% (Ho) to 101.5 % (Tm). Spikes of 10 µg L⁻¹ into lake water yielded equally impressive recoveries. It should be noted though that since the natural levels of REE in the seawater were all < 1 µg L⁻¹ and, given that LODs were at the ng L⁻¹ level, spike concentrations at least one order of magnitude lower would have been more appropriate. Agrawal (121) used the fullerene derivative poly(β-styryl)-(1,2-methanofullerene-C60)-61-formo hydroxamic acid to preconcentrate several REE prior to ICP-MS determination. The sorption capacity of the medium ranged from 1.25 mmol g⁻¹ (for Gd) to 2.15 mmol g⁻¹ (for Ce). Unfortunately, the optimal pH for sorption varied significantly between different REE, e.g. pH 6.4 for Ce up to pH 10.5 for Gd. Similarly, different eluents were required to obtain complete elution. Therefore, the method developed was incapable of determining the REE simultaneously, even though ICP-MS was used as a detector. Another drawback was that 1000 mL of sample was used with a flow rate through the column of 1 mL min⁻¹.

Two composites, Fe₃O₄@SiO₂@polyaniline–graphene oxide composite (123) and Graphene oxide–TiO₂ (124) were used to preconcentrate all of the REE ions and La, Ce, Eu, Dy and Yb, respectively, from water samples. The method by Su *et al.* was based on a magnetic solid phase extraction procedure similar to the protocol by Berijani *et al.*(122), discussed in Table 4. The authors hypothesised that the hydroxide, epoxide, carboxyl and carbonyl groups of the graphene oxide chelated with the REE. Once chelated onto the composite, the material was collected using an external magnetic force, and then the REE eluted using 0.5 mL of 0.5 M nitric acid prior to ICP-MS determination. After optimization, the process yielded extremely low LOD, with values ranging from 0.04 to 1.49

ng L⁻¹. A concomitant ion study was also undertaken that demonstrated that the only realistic interference that existed was Na. The common ions found in waters were tolerable to several thousand mg L⁻¹ (Ca, Mg, etc), but the maximum tolerable limit for Na was only 5000 mg L⁻¹. There is therefore a possibility that seawater may potentially lead to interferences. The authors also measured the capacity of their adsorption medium, finding that capacity ranged from 7.7 mg g⁻¹ for Sm up to 16.3 mg g⁻¹ for Gd. The protocol was applied to the analysis of plant materials and water samples. A certified tea sample was used for method validation. For the water samples, analyte spike-recovery experiments were used with spike concentrations relevant to the natural concentrations; i.e. between 5 and 50 ng L⁻¹ being used. The material could be re-used at least 30 times before a degradation in performance was observed. The method by Zhang *et al.*(124) used a column of graphene oxide–TiO₂ composite in an on-line flow-injection preconcentration method and ICP-OES detection. The analysis time was about 3.5 min per replicate to achieve a 10 fold preconcentration factor. Detection limits were approximately 0.2 µg L⁻¹ and recoveries from spiking experiments ranged from 82.4 to 115.5%. An interference study showed that Na, Mg, Ca as well as anions such as Cl could be tolerated to levels at which they may be found in seawater. Other ions, e.g. Al, had a much lower tolerable limit. However a level of 10 mg L⁻¹ was tolerable and this is far in excess of anything likely to be in most waters. The medium was also reasonably robust, since it could be re-used at least 90 times. Breakthrough capacity values were 3.8, 2.9, 2.8, 2.7 and 3.2 mg g⁻¹ for La, Ce, Eu, Dy and Yb, respectively. Titanium dioxide nanotubes were used by Chen *et al.* (125) as a solid support for the preconcentration and determination of Nd, Tb, and Ho in environmental water samples. Using an optimized micro-column preconcentration method coupled with ICP-MS, a preconcentration factor of 100 was obtained yielding, LODs of 0.093, 0.018 and 0.025 ng L⁻¹ for Nd, Tb and Ho, respectively. A similar paper by the same research group (126) extended the protocol to include other REE ions. Again, validation for the water samples was achieved using analyte spike - recovery experiments with the natural levels at the sub-µg L⁻¹ level being spiked with analytes also at 0.5 – 2 µg L⁻¹. Recoveries were 95.5 – 103%. In this second paper, the adsorption capacity values calculated from the breakthrough curves were 12.3, 10.1, 13.2, 11.5, 13.5 and 14.7 mg g⁻¹ for La, Ce, Eu, Gd, Lu and Yb, respectively. A limited interference study indicated that a 20,000 fold excess of Na and K could be tolerated when determining 2 µg L⁻¹ REE. This

would seem to indicate that seawater could potentially cause problems. The medium was reasonably stable, since it could be re-used at least 50 times before significant degradation was observed.

Bentonite modified with N-(2-hydroxyethyl) ethylenediamine was proposed for the adsorption of Sm ions using both batch and column separation methods (127). A large volume of sample, 150 mL, was passed through the column enabling a preconcentration factor of 75 to be obtained. Despite this, even though ICP-OES was used as a means of detection, a disappointing LOD of $0.6 \mu\text{g L}^{-1}$ was obtained. In addition, the method took about 150 min per replicate. Validation was achieved using analyte spike-recovery experiments, where a wastewater sample containing $0.71 \mu\text{g L}^{-1}$ Sm was spiked with the rather high concentrations of 5 and $10 \mu\text{g L}^{-1}$. Another drawback of the protocol was that the resin showed signs of degradation (in terms of decreased recovery) after as few as 6 repeat analyses. An interference study demonstrated that Na could be tolerated to only 2000 mg L^{-1} . The capacity for the Sm was 17.7 mg g^{-1} . Activated carbon has also been used for the preconcentration of REE ions from water samples using a batch system (127). This method comprised 4 h of shaking the sample (2 L) with activated carbon plus filtration and desorption steps. A preconcentration factor of 400 was achieved yielding LODs of approx. 0.3 ng L^{-1} . This early paper is an excellent example of optimization protocols, with pH, mass of sorbent, type and volume of eluent and contact time all being studied.

5,7-dichloroquinoline-8-ol functionalized naphthalene in a column was used for the preconcentration of Nd, Eu and Lu ions (129). Subsequent dissolution of the functionalised naphthalene material loaded with these ions was achieved by passing DMF through the column. This enabled the REE to be determined using FAAS. The method therefore required filling the column with this material for each sample followed by dissolution of the REE loaded functionalised naphthalene material. The procedure was therefore not quick or easy. It also required a high volume of sample for the analytes to be preconcentrated sufficiently. Although a preconcentration factor of 200 was achieved, LODs were still at the $\mu\text{g L}^{-1}$ level. A paper by Sohrin *et al.* (130) discussed the use of 8-hydroxyquinoline immobilized onto fluorinated metal alkoxide glass for the preconcentration of a suite of elements including 14 REE

prior to detection using high resolution ICP-MS. A modest 10-fold preconcentration was achieved, but sensitivity was further enhanced through the use of an ultrasonic nebuliser to introduce the eluted analytes to the instrument. The retention medium was structurally rigid, with no shrinking or swelling observed. It had a capacity of 17-19 mg g⁻¹ and was stable for at least 50 uses. A Batch system for the preconcentration of La, Ce, Nd, Sm, Eu, Gd, Tb and Dy from waste waters using magnesium oxide powder was proposed (17). After drying the powders, these elements were determined using neutron activation analysis, although the authors did note that they would also be suitable for determination using ICP-MS.

Bis(2-ethyl-hexyl)hydrogen phosphate impregnated porous PTFE filter tubes were proposed as a sorbent extraction system for the determination of REE (131). A large volume of water (100 – 1000 mL) was passed through the tube at a flow rate of between 4 and 8 mL min⁻¹. Analytes were eluted using 5 mL of 10 M HCl at a flow rate of 1 mL min⁻¹. The analytes were then determined using ICP-MS. Recovery experiments were performed from spiked natural dried sea salt solution and were mainly quantitative with the exception for La, which was only 54%. The LOD values of the REE ions and adsorption capacities were not presented, making comparison with other methods difficult.

A poly (acrylamino-phosphonic dithiocarbamate) chelating fiber (132) was proposed for the preconcentration of REE from seawaters using an off-line SPE method. The fibre was placed within a column and 1000 mL of seawater, adjusted to pH 5, was passed through at a flow rate of 7 mL min⁻¹. After rinsing, the REE were removed from the fibre using 5 mL of 0.01 M ammonium citrate. A preconcentration factor of 200 was therefore achieved in a time period of approximately 2.5 hours. Analyte spike-recovery experiments in which ng L⁻¹ levels of REE were spiked into the samples showed excellent recovery. The authors also compared their data with those from other research groups, with concentrations of REE in seawater being broadly in agreement. The capacity of the fibre was tested in batch mode and gave values for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu of 0.705, 0.206, 0.216, 0.219, 0.220, 0.217, 0.215, 0.202, 0.202, 0.194, 0.190, 0.181, 0.183, 0.183, and 0.178 mmol g⁻¹, respectively. An interference study demonstrated that the major cations present in seawater did not cause interferences. Ultra-trace determination of REE using flow injection and an on-line SPE method was developed which used

maleic acid grafted polytetrafluoroethylene fibres (133). The preconcentration procedure was similar to that described by Zhang *et al.*, above, with a similar sample flow rate. However, the protocol was undertaken on-line, enabling a more rapid determination of analytes. Preconcentration factors of between 69 and 97 were achieved using a time of only 120 s. This enabled the removal of polyatomic interferences arising from Ba and also yielded LODs between 1 and 20 pg L⁻¹. The LODs were impressive and were among the lowest compared with those from other methods presented in Table 4. In addition, since the preconcentration time was so low, 22 replicates could be analysed per hour. The procedure was applied to waters and sediment samples, with validation achieved using CRM for the sediments and analyte spike-recovery for the waters. Spike levels of 2 ng L⁻¹ for seawater and 10 ng L⁻¹ for river water resulted in recoveries of between 90 and 106 %. Cellulose-immobilized ethylenediaminetriacetic acid (EDTrA) was proposed for the matrix removal and preconcentration of REE from seawaters using an off-line preconcentration method (134). These authors determined a total of 23 analytes including the REE and used over an hour to obtain a preconcentration factor of 100. The main focus of this report was to find a medium that was applicable to as many analytes as possible rather than to REE alone. Despite this, analyte spike - recovery experiments using 0.1 µg L⁻¹ yielded quantitative recovery. Unfortunately, the capacity of the material was not determined. However, the CRMs SLEW-1, CASS-2 and CASS-4 were analysed giving data in good agreement with certified values for the non-REE analytes. A flow injection, on-line sorption system was developed that used a PTFE knotted reactor which had been pre-coated with the chelating reagent 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (30). The REE ions in the samples were adsorbed by chelation reaction with the reagent on the walls of the reactor. After elution and sample introduction using an ultrasonic nebuliser, detection was achieved using TOF-ICP-MS. This method gave low LODs (3 – 40 pg L⁻¹) in a very short experimental time of less than 4 min per sample. Preconcentration factors of 15 – 22 were achieved, with the ultrasonic nebulisation contributing further to the high sensitivity. Method validation was through analyte spike - recovery experiments of the CRMs SLEW-2, SLRS-3, CASS-3 and NIST 1643d. Recoveries of 0.025 and 0.05 µg L⁻¹ were 89.1 – 118%.

Transcarpathian clinoptilolite activated at 350 °C was used as a retention medium to preconcentrate Tb by Vasylechko *et al.* (135). Spiked tap water samples were preconcentrated on a column of the material prior to elution and subsequent spectrophotometric determination of the Tb using arsenazo III reagent. The detection limit was 0.75 µg L⁻¹ and the linear range spanned 2.5 – 200 µg L⁻¹. These levels are clearly far too high to measure the Tb in unpolluted natural samples. The authors resorted to analyte spike - recovery experiments for method validation and obtained values of between 93.3 and 102 %. Although an interference study was undertaken, it is interesting to note that it concentrated on Ca, K, Mg, Na and anions such as sulfate, bicarbonate, nitrate and chloride rather than other REE. In addition, the concentration of Tb used during these interference tests was 1 mg L⁻¹, which is an unrealistic concentration and is also five times more than the linear range of their technique. Despite the clear drawbacks of this method, a high enrichment factor of 130 was achieved.

The analytical properties of these other supports used for the preconcentration of REE from natural water samples are compared in Table 4.

3.2 Liquid–liquid extraction

Only a few studies based on liquid-liquid extraction techniques for the separation and preconcentration of REE ions from natural waters have been published. Liquid-liquid extractions are often time consuming and laborious, with extractions often being repeated three times per sample replicate in an attempt to maximise extraction efficiency.

Different applications of liquid-liquid extraction of REE ions from natural waters using chelating agents have been proposed. The analytical properties of these methods are compared in Table 5. Liquid–liquid extraction of cerium(IV) and lanthanum(III) by complexing with N-phenyl-(1,2-methanofullerene C₆₀) 61-formohydroxamic acid (PMFFA) into chloroform was reported for the separation, preconcentration and simultaneous trace determination of these ions(136). The chloroform extracts were introduced directly to the plasma of an ICP-OES instrument, and the method was applied to the determination of Ce

and La in seawater and other water samples. However, this extraction procedure is not capable of simultaneous extraction of both elements since the extraction of Ce occurs at pH 9.5 whereas La ions require pH 8.5. Since multi-element extraction and analyses is not possible using this method, the time required and sample volume required is double. The effects of concomitant ions were tested, but the concentrations of the analytes used were $10 \mu\text{g mL}^{-1}$ rather than at realistic concentrations found in waters. In addition, only five-fold excesses of concomitants were tested and, interestingly, not many of the concomitants tested were REE. However, the concomitants that were added caused no significant interferences. Another drawback was the use of a chlorinated solvent. Results from ICP-OES were compared with those obtained spectrophotometrically, where the PMFFA complexes were measured directly. Good agreement was obtained.

The determination of ultra-trace amounts of Er based on the quenching of the fluorescence signal of Rhodamine 6G by the formation of ternary ion association complex of erbium, 5,7 diiodooxine and Rhodamine 6G was proposed (15). The ternary complex was extracted into xylene. This method suffered interference effects from Cu, Zn, Mn, Co, Ni, and as well as other rare earth ions. Therefore, the total concentration of all REE in seawater was determined using this method. The method is therefore clearly not selective and, since the total concentration of REE is determined using Er as a proxy, there is no way of telling which one (or more) is present. A typical three stage extraction of REE from seawater using HDEHP (phosphoric acid 2-ethylhexyl ester -mono and di ester mixture) in heptane, followed by back extraction into nitric acid prior to detection using ICP-MS was reported by Lawrence and Kamber(36). The paper reported levels of REE in the CRMs SLRS-4, SLEW-3, CASS-4 and NASS-5. The data for these samples were compared with those obtained by other workers. Particularly good agreement was found between these data and those by Willie and Sturgeon (29) and with Shaw *et al.*(40). Only a modest 13-fold enrichment was achieved, but the method did remove Ba efficiently, facilitating the determination of Eu. Pivaloyltrifluoroacetone (PTA) has been used to complex REE in natural waters and the REE-PTA chelates were then extracted into CCl_4 (7). Once extracted, $10 \mu\text{L}$ of the organic phase was analysed directly

using ETV-ICP-MS. The lack of a back extraction or evaporation of organic solvent in this method means that it is rapid. Under optimal conditions, LODs of 0.2 – 0.91 ng L⁻¹ were obtained and recoveries were 93 – 105%. The linear range spanned in excess of three orders of magnitude.

An ultrasound-assisted emulsification–micro-extraction (USAEME) technique combined with ICP-OES detection was applied to the simultaneous determination of trace levels of La and Ce in water samples (1). The method used 5,6,14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane (a dioxo-diazamacrocyclic) as chelating agent and tetrachloroethylene as the extraction solvent. Ultrasonic waves were used to disperse a very low volume (30 µL) of extraction solvent in the water sample (10 mL) along with the chelating agent. After ultrasonic mixing, the mixture was centrifuged and the sedimented organic phase collected from the bottom of the tube. After evaporation of the organic solvent at 80 °C, 1 mL of nitric acid (1 mol L⁻¹) was added and the resulting solution analysed. The whole process was optimised using a quarter fraction factorial design and central composite design. Only a 10-fold enrichment was obtained, but LODs of 0.012 for La and 0.61 µg L⁻¹ for Ce were obtained. The advantages of the method included its rapidity (< 10 mins), low cost, use of a very low volume of organic solvent and a linear range spanning four orders of magnitude. Another advantage was that a concomitant ion study indicated that there were no significant interferences. A very similar USAEME method coupled with ICP-OES detection was proposed for the simultaneous extraction and determination of Yb³⁺ and Ho³⁺ in water samples (137). This time the chelating agent was 1-(2-Pyridylazo)-2-naphthol. Tetrachloroethylene was still used as the extraction solvent. Detection limits were 0.364 and 0.252 µg L⁻¹ for Ho and Yb, respectively. Although the authors claimed the method was successful for the determination of these analytes in real water samples, their data shows that they were not detectable in tap or two river waters. The authors resorted to spiking the samples with 50 and 100 µg L⁻¹, which is at least an order of magnitude too high, but even then found recoveries of only 80.5 - 95%.

Synergistic extraction of REE from nitrate solutions using mixtures of dimethylheptyl methyl phosphate (P350) and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 in hexamethylene was performed (9). This was followed by their determination by injecting 10 µL of the organic phase into an ETV-ICP-MS

system. Compared with other liquid – liquid extraction techniques, this method provided the lowest LOD values. The method was applied to the determination of REE in soil samples and natural lake, sea and tap waters. Method validation for the waters involved analyte spike – recovery experiments in which ng L^{-1} levels of the analytes were added and then recovered at between 91 and 110%. Spike values ranged from 5 ng L^{-1} for Tm, Yb and Lu up to 100 ng L^{-1} for La and Ce. An interference study was conducted. Although most of the matrix elements present were extracted in the same way as the REE it was found that they were vaporized either during the char or clean stages rather than the atomization stage of the ETV program. This reduced interferences. Again, ETV sample introduction also decreased the formation of oxide-based interferences.

Liquid-liquid-liquid micro-extraction (LLLME) is a three phase micro-extraction technique comprising a donor solution, an organic phase and an acceptor solution. In this system, the analytes are extracted from the donor solution into the organic phase and back extracted simultaneously into the acceptor phase with the aid of stirring. Such a system has been developed for the determination of REE (138). In this method, 4-benzoyl-3-methyl-1-phenyl-5-pyrazolinone in benzene acted as extractant and a $4 \mu\text{L}$ drop of 4% (v/v) formic acid immersed into the organic layer was used as the back-extraction solution. After extraction, the acceptor phase was removed and the concentrations of REE determined using capillary electrophoresis with ultraviolet detection. This method should be applied with a great deal of care, since the micro-drop can easily be dislodged from the needle of the micro-syringe. Despite this problem, LODs of between 0.19 and $0.7 \mu\text{g L}^{-1}$ were obtained which were impressive given that UV absorbance was the means of detection.

A DLLME method using 2,6-pyridinedicarboxylic acid and Aliquat ® 336 (tricaprylmethylammonium chloride), was reported by Chandrasekaran *et al.* (43). This enhanced the hydrophobicity of the ion-association complexes, which were then extracted into chloroform and back extracted into nitric acid. The REE were then determined using ICP-MS equipped with a micro-nebuliser. The back extraction step and evaporation of chloroform made the method more complex and time-consuming. In addition, it decreased the preconcentration factor by a factor of three; resulting in an overall enrichment of 93 - 101-fold. An interference study demonstrated that a mixture of concomitants, each at 10 mg L^{-1} , decreased REE recovery significantly. This could partially be overcome

by increasing the concentration of the 2,6-pyridinedicarboxylic acid. A ligandless-dispersive liquid–liquid microextraction (LL-DLLME) and separation method for the preconcentration of REE was developed by Çelik *et al.* (5). This method was very simple and, because it does not need any complexing agent or any back extraction step, it is very rapid. Although successful in matrix removal, it provided only a modest analyte enrichment. However, the LODs produced were sufficiently low to determine the REE in river and sea waters. Method validation was accomplished by spiking with concentrations as low as $0.1 \mu\text{g L}^{-1}$, with most recoveries lying in the range 91 – 115%.

Noack *et al.*(139) used multiple linear regression to optimise a method to preconcentrate REE and separate them from saline waters and brines. Analyte spike - recovery experiments were undertaken to validate the method. Since the sample preparation method yielded such a small preconcentration factor, the REE were not detectable in many (41%) of the unspiked samples. An attempt was made to overcome barium-based polyatomic interferences by acidification of the preconcentrated analytes with sulfuric acid to precipitate the Ba.

A solidified floating organic drop microextraction method was proposed for the preconcentration and determination of trace levels of La, Eu and Yb (32) and Dy and Y(140) using 1-(2-pyridylazo)-2-naphthol (PAN) as a chelator and as a modifier for ETV-ICP-MS. After the PAN-REE complexes had been extracted into 1-dodecanol by stirring, the sample vial was placed in an ice bath until the organic solvent was solidified. The solidified solvent was then transferred into a conical vial where it melted immediately at room temperature. The concentrations of REE ions in this extract were then measured using ETV-ICP-MS. Since such a small volume of extractant was used, the method could generate significant enrichment factors. Consequently, LODs were 0.019, 0.65, 2.1, 0.91 and 0.032 ng L^{-1} for Dy, Eu, La, Yb and Y respectively.

A two-step method based on dispersive SPE and DLLME was developed for the separation and preconcentration of 15 REE prior to ETV-ICP-MS detection (3). Chelex 100 was first used as the adsorbent during the D-SPE process to extract the REE from 25 mL of sample. The retained REE were then desorbed using HNO_3 . During this step, Tris and 1-phenyl-3-methyl-4-benzoylpyrazolone were added into the eluted solution. The REE complexes were

extracted and further preconcentrated into 15 μL of CCl_4 using DLLME and then 10 μL aliquots introduced to the ETV-ICP-MS system. This dual extraction technique exhibits high enrichment factors (between 234 and 566-fold) and is relatively simple. However, because it contains two extraction and one back extraction processes, it was relatively time-consuming. Since it has such high enrichment factors and uses ETV, it does have many of the lowest LOD values of the preconcentration methods given in Table 5 ($0.003 - 0.073 \text{ ng L}^{-1}$) and also minimizes potential interferences. The recovery of 5 and 20 ng L^{-1} spikes were erratic, ranging from 78 – 115%. A concomitant ion study demonstrated no significant interferences.

3.3 Co-precipitation and precipitation methods

Several co-precipitation methods using the manual batch mode of analysis have been proposed for the removal of the interfering matrices and preconcentration of the REE ions from natural waters. Co-precipitation methods in batch mode are often tedious, time-consuming and require a large sample volume. They also risk contamination of the precipitates. The analytical characteristics of these methods are compared in Table 6. A co-precipitation method using iron hydroxide was developed to preconcentrate REE in natural water samples prior to ICP-MS detection (10). In this method, iron hydroxide precipitate produced in the solution was used to enrich REE ions from solution and these precipitates were then collected in a syringe filter off-line. This filter was then connected into the on-line elution / ICP-MS measurement system. This method offered a 10-fold enrichment of analytes whilst removing alkali metals almost completely ($> 99\%$) and $> 80\%$ of Ca and Mg. Unfortunately, only 50% of Ba was removed and so the authors resorted to the use of a mixed-gas plasma to overcome polyatomic interferences. The CRM NMIJ 7201a was used as part of the validation process. This CRM is not certified for REE, but the authors compared the data obtained using the co-precipitation with those obtained using solid phase extraction. This process removed $> 95\%$ Ba and was therefore less prone to polyatomic interferences. Results from the two methods were in good agreement.

Several other co-precipitation methods were employed. Many of them analysed one or more of the CRMs NASS-5, CASS-4, SLEW-3 or SLRS-4. Results were compared with those from other studies. One method based on co-precipitation with iron hydroxide after the addition of a Tm spike was reported for the determination of trace elements including REE in seawater and other natural waters (25). The enrichment factor was only 33, but since sector field ICP-MS instrumentation was used for the measurement, sensitivity was still adequate. Co-precipitation of REE using $\text{Mg}(\text{OH})_2$ has been achieved by several workers (40, 27, 141). In the example by Shaw *et al.*, four enriched isotope spike additions (^{142}Ce , ^{145}Nd , ^{161}Dy and ^{171}Yb) were used to measure the concentrations of Ce, Nd, Dy and Yb directly using isotope dilution-ICP-MS. The spiked isotopes also served as internal standards for the remaining REE. This method reduced the Ba concentration in samples by more than 99.8%. The recovery of REE depended on the water type analysed, with saline waters recording recoveries of typically 70 – 80%, whereas fresh waters had poorer recovery (40 – 60%). The paper by Freslon *et al.* (27) was similar in design to that by Bayon *et al.*, above (25), but this time a spike of Tm was used for the magnesium rather than iron co-precipitation prior to the simultaneous determination of the REE using SF-ICP-MS. This method produced the lowest LOD values compared with other co-precipitation and precipitation methods presented in Table 6. However, co-precipitation recoveries varied between 72% (Tb) and 93% (Dy). The other magnesium co-precipitation method, proposed by Hsieh *et al.* (141), reported the use of laser ablation to create a dry plasma that reduced the signal intensities for all H-, O-, and OH- based molecular ions, thereby decreasing analyte hydride formation and polyatomic interferences. In particular, it helped prevent interferences arising from Ba and its oxides.

A preconcentration protocol using iron chloride and ammonia solution co-precipitation was used by Arendt *et al.* (142) to enrich REE and other analytes from seawater samples. The method had several severe drawbacks including the use of 10 L of sample and employed numerous clean-up columns to remove the Fe and other concomitants as well as separating the analytes. The whole process took several days. Isotope ratios for several elements (Nd, Hf, U etc) were determined using a combination of high resolution ICP-MS and TIMS. A similar paper to discuss REE preconcentration in seawater using iron co-precipitation was presented by Zheng *et al.* (143). Again, the precipitate was washed with dilute ammonia solution prior to separation of analytes from the

matrix using chromatographic columns. Finally, the sample was introduced to the ICP-MS instrument *via* an Aridus desolvation system. This increased sensitivity whilst simultaneously decreasing oxide and hydroxide-based interferences. The reference materials CASS-4 and NASS-5 as well as some GEOTRACES samples were analysed for method validation. Co-precipitation with gallium hydroxide was used for the preconcentration of 17 trace elements including La at pH 10 with detection using ICP-MS(144). For this one REE ion, the recovery was 97% and the LOD was 0.1 ng L^{-1} . A preconcentration factor of 10 was achieved. A higher preconcentration factor of 200 could be used when ICP-OES was used as a detector for the other analytes, but not when ICP-MS was used, because of severe matrix effects.

An on-line FI filterless precipitation–dissolution system was developed for the determination of trace REE using a knotted reactor (41). Sample was mixed with ammonia solution and the precipitate was collected on the inner wall of the reactor without filtration. This was followed by dissolution of the precipitate using acid solution and on-line ICP-MS detection. The method was cheap, rapid (< 6 mins) and yielded enrichment factors of between 56 (La) and 75 (Lu). Data from the analysis of SLRS-3 in this study were in reasonable agreement with those reported elsewhere.

A flotation method for the preconcentration of La and Y (plus Th) from spiked water samples was developed by Abdallah *et al.* (13). Eriochrome Cyanine R was used to form a water-insoluble precipitate with the La and Y which can be floated easily using oleic acid surfactant at ambient temperature. The scum layer was quantitatively collected, stripped with HCl solution and the analytes measured spectrophotometrically as arsenazo(III) complexes. Even though this flotation method is fast and produces very high preconcentration factors, the LODs were very high $0.5 \text{ } \mu\text{g mL}^{-1}$ which was a function of the detection technique. Since there was such poor sensitivity, the authors acknowledged that it had to be used with spiked water samples rather than natural ones. Both the La and Y were determined at 650 nm, whereas Th was determined at 540 nm.

3.4 Other preconcentration methods

Other methods of preconcentration, such as cloud point extraction (CPE), have been proposed for the preconcentration of REE from natural waters and for matrix removal. These methods are discussed below and their analytical characteristics are compared in Table 7.

A CPE method used to preconcentrate REE from mineral water, river water and reference water samples using ICP-OES detection was described by dos Santos Depoi *et al.* (42). Octylphenoxypolyethoxyethanol (Triton X-114) and 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) were used as surfactant and complexing agent, respectively. The optimization of the TTA and Triton X-114 concentration as well as the pH of the solution was undertaken by applying a three-factor Doehlert matrix design with seven, five, and three levels, respectively. Despite enrichment factors being only 9 – 14, exceptionally low LODs were obtained ($0.002 - 0.1 \mu\text{g L}^{-1}$). However, these were still insufficient to detect REE in mineral water samples. Spike concentrations of 0.5 or $1 \mu\text{g L}^{-1}$ were recovered at better than 91%. Analysis of the CRM SPS-SW1, simulated surface water yielded data in good agreement with reference values.

Different membrane types have been used to separate REE ions after immobilization of an organic ligand onto them. An 8-hydroxyquinoline immobilized polyacrylonitrile hollow fibre membrane was developed for the preconcentration of REE and simultaneous matrix separation from seawater samples (146). The membrane was placed in a glass column and then seawater (1500 mL) was pumped through at a rate of 10 mL min^{-1} . After rinsing with an aliquot of water, the REE were eluted with 5 mL of a mixture of 1 M HCl – 0.1 M HNO₃. A 300-fold enrichment was therefore achieved. The eluted analytes were determined using ICP-MS. The method clearly took several hours to complete and required a large volume of sample to obtain the LODs that spanned 0.21 to 2.7 ng L^{-1} . Validation was achieved using representative spike concentrations, with recoveries being 91 – 107%. An interference study in which the major cations of seawater were tested indicated no interferences. Precision was better than 5%. N'-[(2-hydroxyphenyl)methylene] benzohydrazide immobilised on a triacetylcellulose membrane (11) and N,N'-bis(dansylamidoethyl)-N,N'-bis(2-pyridylmethyl)propylenediamine (L) as a fluoroionophore immobilised in a plasticized PVC membrane was synthesised and applied to preconcentrate Dy and La ions, respectively, from spiked natural waters (14). The membranes developed for the determination of Dy ions were placed in a disposable plastic cuvette or in a cell and the signals measured before and after the

addition of sample solution containing analyte ion. They were tolerant to other REE and ions such as Pb up to a factor of 200 greater than the Dy concentration. Similarly, Mg, Ca, K and Na were tolerable to levels 2000 times the Dy concentration. The method had a linear range spanning 5×10^{-7} (LOD) to 8×10^{-6} M and was, therefore, inappropriate for real samples. After use, the optode could be re-generated using thiourea, but this typically caused a 3.5 % drift. The paper by Shamsipur (14) was based on fluorescence detection and therefore had some merit in that it had a very long linear range (covering five orders of magnitude) and had a reasonably low LOD (of 2×10^{-9} M La). However, this is still insufficiently low to be able to determine La in unpolluted water samples. The La selective membrane reportedly did not suffer from interferences from most common cations. However, the La concentration of 10^{-6} M used in the interference studies was several orders of magnitude higher than that found in natural waters. The response time was rapid (2 mins) and re-generation using 0.01 M EDTA for 5 mins enabled the La to be stripped from the optrode. The membrane was stable for several months without use and short term precision was 2.3% (n=5) for a La concentration of 5×10^{-8} M. This paper had significant advantages over another that determined La using an optrode (145). This had much higher LOD (1×10^{-7} M), a longer response time (5-6 mins) and, although the linear range was still long, it covered a much higher range (1.0×10^{-6} to 1.0×10^{-2} M).

The water-soluble polymer polyacrylic acid formed complexes with the REE and these were retained on the ultrafiltration membrane of centrifugal filter units (147). The collected complexes were then eluted using 2 x 5 mL of 3% nitric acid prior to ICP-MS detection. The method was applied to seawater samples with 300 μ L of the complex being added to 15 mL of water sample. The method was therefore mainly a matrix separation rather than a preconcentration. Despite this, LODs at the ng L⁻¹ level were obtained. Precision (n = 5) at 50 ng L⁻¹ ranged between 1.29 and 3.96%. Analyte spike – recovery experiments in which 0, 0.05, 0.1, 0.2, 0.5 and 1 μ g L⁻¹ were added to the sample resulted in recoveries of between 89.2 and 95.8 %.

A method for the preconcentration and determination of Ce(III) using a carbon paste electrode, chemically modified with N⁻[(2-hydroxyphenyl)methylidene]-2-furohydrazide was developed (20). The Ce was first accumulated from samples on the electrode at -200 mV for 350 s and then

anodic stripping voltammetry was used for the quantification. A reasonably low LOD of 0.8 nmol L^{-1} was obtained (approx. $0.1 \mu\text{g L}^{-1}$) and the linear range spanned $5 - 90 \text{ nmol L}^{-1}$. An interference study on 50 nmol L^{-1} Ce samples indicated that La could interfere above a concentration of $0.05 \mu\text{mol L}^{-1}$ and Sm above $0.12 \mu\text{mol L}^{-1}$. At best, the method could be called selective rather than specific.

A counter current chromatography (CCC) technique was developed for the enrichment of REE and Gd-complexes in surface waters prior to ICP-MS detection (45). The stationary phase was di-2-ethylhexylphosphoric acid dissolved in n-decane and the mobile phase was 0.01 M HNO_3 . A comparison with a SPE technique was made for the REE and a Gd complex (Gd-DTPA). The CCC met with mixed success. The lighter and middle range REE were recovered close to 100%, but the heavier Yb and Lu had far poorer recovery (57 and 73%, respectively). For these two analytes, the SPE protocol was more efficient (89 and 84%). The CCC technique was substantially quicker, requiring 25 min compared with 120 min to obtain the same preconcentration factor for SPE. However, SPE has the advantage over CCC in that several samples can be preconcentrated simultaneously.

3.5 A comparison of preconcentration methods

Several different preconcentration methodologies exist and each has their pros and cons. In general, any method that minimizes sample handling will also minimize the potential for contamination. In addition, the fewer the steps of a method, the better. This is because this lowers the chance of mis-labelling containers and hence confusing samples. This may seem an easy problem to avoid. Simply paying attention to detail could prevent this type of problem, but this is sometimes difficult when numerous samples are being prepared simultaneously. Another consideration is the number of reagents used. In general, the fewer and the more dilute the reagents required, the better. This again, will diminish the potential for contamination.

Solid phase extraction is one of the more common methods of preconcentration and may be used either off-line or on-line. On-line methods may have the advantage of being a closed system, i.e. on-line systems tend to be less prone to airborne contamination. Resins / adsorption media may simply be packed into

columns with porous plugs at either end enabling the medium to be trapped whilst the sample is flowed through it. The mini-columns are often slurry packed to prevent voids or channels, but may also be packed with dry particles. On-line systems also tend to use fewer containers, again decreasing the potential for contamination. The on-line methods tend to result in lower preconcentration factors than off-line methods. This is because 100 mL of sample passing through a column at a flow rate of 3 mL min^{-1} will take 33 minutes to become fully retained. This is not cost-effective when an ICP using 13 L min^{-1} argon is being used as a detector. Therefore, on-line methods tend to use lower sample volume, e.g. 10 – 25 mL, so that the preconcentration can be completed more rapidly. In addition, on-line methods usually only prepare one sample at a time. The other big advantage of on-line systems is that they may readily be automated. Automation provides several advantages over manual sampling. It enables the analyst to undertake other tasks whilst still analysing samples. It also decreases the possibility of human error during the preparation. Ideally, the same column system may be used several times, i.e. the retention and elution cycles do not adversely affect the stability of the medium. It is no practical use if the medium loses its functional groups and retention capability every time an eluent is used to elute the analytes since more time would be spent preparing the columns than analysing the samples. Other points to consider are the kinetics of the retention. If a medium has rapid exchange / adsorption kinetics, then the analytes may be retained more rapidly. This has the advantage of being able to pass a greater volume of sample through the medium in a shorter time; hence providing a lower LOD in the same time-frame or enabling a higher sample throughput. Batch methods may occur simply by mixing the retention medium with the liquid sample and then filtering. Under such circumstances, it is easy to mix 1 g of retention medium with 100 mL or even much higher volume of sample. After collection of the retention medium, elution can be achieved using a small volume of acid which is then introduced to the detection technique off-line. Assuming the elution volume is similar for the on- and off-line methods, it is clear that the off-line methods could have the higher preconcentration factor. Using an off-line batch system it is easy to prepare several samples simultaneously. However, the cost and space requirements for numerous sample filtration devices are other factors that should be considered.

An important consideration for a solid phase extraction method is the robustness of the retention medium. If it is fragile and is damaged after only a few sample loading / elution cycles, it is of less use than media that may be used reliably for hundreds of cycles. The reaction kinetics of the retention media used in both on-line and batch methods are also important because the more rapid the kinetics, the faster the sample throughput. One final consideration for SPE is that the retention medium should have as high a capacity as possible. If it is not completely selective for REE, a high capacity means that it will be able to collect some concomitants without immediate loss of the analytes.

Co-precipitation can lead to high preconcentration factors. On some occasions, e.g. the analysis of sea or estuarine water, the simple addition of ammonia solution can result in analyte being retained in the magnesium hydroxide precipitate formed. A simple filtration followed by dissolution using acid is often sufficient to prepare the sample completely. Other water types do not have sufficient magnesium present for this to occur efficiently, and hence other carriers, e.g. iron or gallium can be used. In any case, the reagents can be obtained in high purity, hence minimizing contamination. The procedures are often quite labour intensive, tedious and require a large number of filtration devices if numerous samples are to be prepared simultaneously. Once preconcentrated, the analytes are usually presented for detection in a dilute acid matrix, but with a high concentration of the carrier precipitate material. Care should therefore be taken that interferences are not going to be caused by this. If interference may be caused by the carrier, it may be necessary to perform another procedure that disposes of the carrier metal prior to the actual analyte determination.

Liquid-liquid extractions usually employ organic solvents. With the increasing drive for “green chemistry”, there is an attempt to use less of these. Traditional liquid-liquid extractions would typically mix sample with three aliquots of solvent and then combine these aliquots prior to analysis. Sometimes a back extraction can be performed, but this adds an extra step to the analysis and therefore adds to the possibility of contamination. It would certainly add to the time required for sample preparation. However, some of the most modern versions of liquid liquid extraction, e.g. those using solidified floating drops, micro-extractions etc., use an extremely low volume of organic material plus other relatively harmless solvents such as ethanol. The micro-methods tend to be quite

rapid and can produce very high preconcentration factors using a relatively small volume of sample. If the analytes are retained in a small volume of organic solvent, then this is not immediately compatible with many standard detection techniques because many ICPs lose stability when organics are introduced. The ultra-low volume of preconcentrated sample will also be incompatible with most standard sample introduction devices, that uptake sample at approximately 1 mL min⁻¹. However, if specialist introduction devices, e.g. flow injection or ETV, are coupled with ICP detection, it is possible for numerous analytes to be determined simultaneously. Another advantage of ETV sample introduction is that the analytes may be separated from the solvent prior to the determination stage. This will decrease potential interferences, such as the formation of oxides when using ICP-MS detection.

4 Conclusions

In this review, different preconcentration and matrix removal protocols as well as methods of direct determination of REE in water samples are compared with respect to their analytical characteristics such as LOD, analysis time, preconcentration factors, interferences etc. The LOD values of the preconcentration method can vary significantly depending on the detection method. Unfortunately, if a preconcentration method has been developed for use with ICP-OES detection, it does not necessarily follow that it is equally applicable to a more sensitive detection system. A worker new to the field may not simply adopt a method hoping that the data obtained will be accurate without performing suitable validation themselves.

It has been noted that there is a lack of suitable CRMs. This has often forced workers to use analyte spike – recovery experiments to validate their procedure. Often this has been done correctly, with spike levels suitable to what is there naturally or what is appropriate to their own detection system being used. Unfortunately, some studies were not validated properly.

Other workers have used a genuine CRM, even if it is not certified for REE and have then compared their data with those from other workers for the same materials. In many cases, agreement was good. The GEOTRACES program in which the data obtained from different laboratories were compared is also a step further forward in terms of quality. It is clear that there is an increasing need for the production of natural water CRMs that have certified values for REE.

It is to be expected that the rapid increase in the number of papers reporting the determination of REE in waters will continue as their use increases. It is also to be expected that methodologies used to preconcentrate them to measurable levels will also improve in terms of speed, sensitivity and in some cases, selectivity. The speed of the preconcentration technique is clearly one of the more important aspects that requires investigation. Many preconcentration methods can provide very large analyte enrichment factors, but if the method takes many hours or even days to complete, it is clearly not convenient. Usually associated with this is the volume of sample required for preconcentration. Transporting a litre of sample from each sampling site so that 300 mL can be pumped at a rate of 1 mL min⁻¹ through a preconcentrating medium is not convenient or a good use of laboratory time or space. However, if the same preconcentration factor can be achieved using only 10 mL of sample, then transport and storage of the samples is facilitated. Exchange media with very rapid exchange kinetics will enable a larger volume of sample to pass through per unit time whilst still retaining the analytes quantitatively. The most recent versions of liquid-liquid extraction also enable very high preconcentration factors to be obtained in short periods of time. However, they usually result in the analytes being in a small volume of organic solvent. Such small volumes of liquid are not readily compatible with most conventional sample introduction devices. Therefore, flow injection, ETV or some other specialist sample introduction device is necessary. Thusfar, these methods have been applied mainly to organic analytes. It is expected that they will also become more common for inorganic analytes.

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Table 1. Comparison of sample introduction system for the determination of REE ions.

Sample Introduction System	Detection Method	Analyte	LOD ng L ⁻¹	Interferences	Samples	Ref.
Ultrasonic nebulization	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.04 (La), 0.06 (Ce and Sm), 0.015 (Pr), 0.1 (Nd), 0.02(Eu), 0.04 (Dy and Gd), 0.01 (Ho, Lu and Tb), 0.03(Er and Yb), 0.005(Tm)	-	Spring water, river water	48
Microflow nebulization/desolvation (Aridus)	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.004 (Ce and La), 0.002 (Er, Pr, Tb and Yb), 0.01 (Nd and Sm), 0.003(Dy and Eu), 0.03 (Gd), 0.001(Ho, Lu and Tm),	¹³⁸ Ba ¹⁶ O ¹ H and ¹³⁹ La ¹⁶ O (¹⁵⁵ Gd)	Antarctic Ice	33
Microflow nebulization/desol	TOF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu,	0.6 (Ce and La), 0.5 (Eu, Pr), 0.8 (Nd), 0.9 (Sm), 0.7 (Dy, Er, Gd and Yb), 0.3	Ba (¹³⁹ La) and (¹⁴⁰ Ce), ¹⁴² Nd (¹⁴² Ce),	Antarctic Ice	31

vation (Aridus II)		Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	(Ho, Tb and Tm), 0.4 (Lu)	^{144}Nd (^{144}Sm), ^{164}Dy (^{164}Er)		
Microconcentric nebulizer (MCN)	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.06 (Er, Ho, La and Tb), 0.1 (Ce), 0.05 (Pr), 0.27 (Nd), 0.14 (Sm and Tm), 0.04(Eu), 0.15 (Gd), 0.17 (Dy), 0.14(Yb), 0.01 (Lu)	Na (15-25% signal suppressions for MREE+ and 5-10% signal suppressions for HREE+)	Surface and subsurface waters	34
Membrane- desolvation sample introduction system (Aridus)	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.2 (Ce, La and Lu), 0.18 (Pr), 0.3 (Gd and Nd), 0.15 (Sm), 0.17(Er, Eu and Yb), 0.07 (Tb), 0.09 (Dy), 0.11(Ho), 0.05 (Tm)	Na (15% signal suppressions for all REE+	Surface and subsurface waters	34
No specialist devices used	ICP-MS	La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu and			River waters	50

		other non-REE				
No specialist devices used	ICP-MS (and ICP-OES for other elements)	Eu, La, Lu and other non-REE			Stream waters	51
No specialist devices used	ICP-MS	Y La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Zr Hf			Volcanic waters	52

LOD = Limit of detection, ICP-MS = Inductively coupled plasma-mass spectrometry; ICP-OES = Inductively coupled plasma-optical emission spectrometry;

SF-ICP-MS = Sector field inductively coupled plasma-mass spectrometry; TOF-ICP-MS = Time of flight inductively coupled plasma – mass spectrometry

Table 2. Comparison of the solid phase extraction methods for the preconcentration of REE ions using polymeric supports.

Solid Support	Complexing or immobilizing agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time (min)	Samples	Ref.
Styrene divinyl benzene	Fluorinated β-diketone	ICP-OES	La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu		200	168 Batch method	Seawater	23
Amberlite XAD- 16	Octacarboxy methyl- C- methylcalix[4]resorcinare ne (OCMR).	UV-VIS	La, Ce and Y	830000 (La), 250000 (Ce), 660000 (Y)	125 (La), 83 (Ce) and 100 (Y)	250 Batch method	Seawater and well-water	12

Amberlite XAD-4	2,6-diacetylpyridine	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	4 (La), 8.7 (Ce), 7.6 (Pr), 7.4 (Nd), 9.2 (Sm), 7.0 (Eu), 5.6 (Gd and Tb), 4.2 (Dy), 7.3 (Ho), 6.4 (Er), 2.0 (Tm), 3.2 (Yb), 10.3 (Lu)	5	13 Batch method	Tap water and sea water	24
Amberlite XAD-4	8-hydroxy-2-quinolinecarboxaldehyde	ICP-OES	Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb, and Lu	420 (Pr), 250 (Sm), 20 (Eu), 100 (Dy and Gd), 160 (Tb), 50 (Ho), 80 (Tm), 10 (Yb), 11 (Lu)	12.5	28 Batch method	Tap water and sea water	22
Amberlite XAD-4	2,6-Pyridinedicarboxaldehyde	ICP-OES	Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb and Lu	120 (Ce), 150 (Nd), 130 (Sm), 11 (Eu), 58 (Gd), 93(Tb), 46 (Dy), 27 (Ho), 6 (Yb), 7 (Lu)	25	52 Batch method	Tap water and sea water	37

Amberlite XAD-4	6-(2-thienyl)- 2- pyridinecarb oxaldehyde	ICP-OES	Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	193 (Ce), 149 (Pr), 179 (Nd), 142 (Sm), 19 (Eu), 73 (Gd), 97 (Tb), 45 (Dy), 38 (Ho), 29 (Er), 54 (Tm), 6 (Yb), 11 (Lu)	25	52 Batch method	River water, tap water and sea water	73
Chromosorb 106	4-(2- thiazolylazo) resorcinol	ICP-MS	Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.31 (Ce), 0.06 (Pr), 0.10 (Nd), 0.11 (Sm), 0.06 (Eu), 0.21 (Gd), 0.07 (Tb), 0.22 (Dy), 0.18 (Ho), 0.19 (Er), 0.07 (Tm), 0.14 (Yb), 0.08 (Lu)	5	4.6 On-line method	Estuarine water and seawater	6
Styrene- divinylbenzene	Alkyl phosphinic acid	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho,	2.37 (La), 1.19 (Ce), 0.44 (Pr), 2.22 (Nd), 2.21 (Sm), 0.69 (Eu), 1.47 (Gd), 1.10 (Tb),	377.8-398	100 On-line method	Seawater	2

			Er, Tm, Yb and Lu	1.91 (Dy), 0.58 (Ho), 0.48 (Er), 0.93 (Tm), 2.20 (Yb), 0.08 (Lu)				
Amberlite XAD-7	Quinolin-8- ol	ICP-MS	Eu, Tb, Ho, Tm and Lu	0.016 (Eu), 0.0023 (Tb), 0.0017 (Ho), 0.0035 (Tm), 0.0015 (Lu)	5	19 On-line method	Seawater	74
Divinylbenzene– methacrylate copolymeric	Polyaminopo lycarboxylic acid	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.04 (La), 0.09 (Ce), 0.011 (Pr), 0.08 (Nd), 0.017 (Sm), 0.007 (Eu), 0.014 (Gd), 0.008 (Er and Tb), 0.013 (Dy), 0.005 (Ho and Tm), 0.009 (Lu and Yb)	9.6	6 On-line method	Seawater	38
Poly hydroxamic acid	-	ICP-MS	La, Ce, Pr, Nd,	0.16 (La and Nd), 0.18 (Ce and Tb), 0.14 (Pr	100	200 Batch	Seawater	4

			Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	and Tm), 0.15 (Sm), 0.21 (Eu), 0.19 (Gd), 0.16 (Dy), 0.17 (Ho and Yb), 0.19 (Er), 0.13 (Lu)		method		
Nobias PA1	-	TIMS	Nd isotopes	0.008 (for blank solution)	1166	480 Batch method	Seawater	39
NOBIAS CHELATE-PB1M	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.029 (La), 0.040 (Ce), 0.004 (Pr), 0.014 (Nd), 0.005 (Sm), 0.0008 (Eu), 0.0037 (Gd), 0.0007 (Tb), 0.0022 (Dy), 0.00009 (Ho), 0.0012 (Er), 0.00008 (Tm), 0.0018 (Yb),	125	10.4 On-line method	Seawater	75

				0.00022 (Lu)				
Chelex-100	-	ICP-MS	La, Ce, Nd, Yb	8 (La), 1 (Ce, Nd and Yb)	5	32	Fresh water, seawater	76
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.0051(La), 0.017 (Ce), 0.0027 (Pr), 0.019 (Nd), 0.034 (Sm), 0.012 (Eu and Yb), 0.013 (Gd), 0.0016 (Lu and Tb), 0.011 (Dy), 0.0012 (Ho), 0.0060 (Er), 0.0031 (Tm)	100	120 Batch method	Seawater	77
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb	0.01(La), 0.03 (Ce and Gd), 0.009 (Pr), 0.04 (Nd and Sm), 0.01 (Eu), 0.008 (Lu and Tb), 0.02 (Dy, Er and	40	120 Batch method	Seawater	78

			and Lu	Yb), 0.006 (Ho), 0.007 (Tm)				
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.04(La, Pr and Tb), 0.7 (Ce), 0.3 (Gd, Nd and Yb), 0.2 (Sm), 0.1 (Er and Eu), 0.2 (Dy), 0.03 (Ho and Tm), 0.05 (Lu)	33.3	120 Batch method	Seawater	79
Chelex-100	-	NAA	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	NA	20-40	260-460 Batch method	River water and Seawater	16
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd,	0.01(Ce, Eu, Ho and La), 0.06 (Nd), 0.03 (Sm and Yb), 0.04 (Er	100	54 Batch method	River water	81

			Tb, Dy, Ho, Er, Tm, Yb and Lu	and Gd), 0.006 (Lu, Pr and Tb), 0.02 (Dy), 0.009 (Tm)				
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.1(Ce, Eu and La), 0.07 (Ho and Pr), 0.3 (Dy, Nd and Yb), 0.5 (Sm), 0.4 (Gd), 0.08 (Tb and Tm), 0.2 (Er), 0.06 (Lu)	20	22 Batch method	Seawater	82
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.55(La), 0.08 (Ce), 0.14 (Pr), 0.18 (Nd), 0.23 (Sm), 0.07 (Eu and Ho), 0.42 (Gd), 0.03 (Tb), 0.15 (Dy), 0.12 (Er), 0.05 (Tm), 0.10 (Yb), 0.02 (Lu)	50-250	100-500	Seawater, groundwater	83
Chelex-100	-	ICP-MS	La,	100(La), 310 (Ce), 290	20	not	River water	84

			Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	(Pr), 130 (Nd), 110 (Sm), 470 (Eu), 190 (Gd), 260 (Tb), 90 (Dy), 300 (Ho), 200 (Er), 50 (Tm), 410 (Yb), 560(Lu)		given Batch method		
Chelex-100	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	4.2 pM La, 6.8 pM Ce, 0.8 pM Pr, 3.5 pM Nd, 0.5 pM Sm, 0.7 pM Eu, 0.3 pM Dy, Gd, 0.1 pM Ho, Tb and Yb, 0.2 pM Er, 0.05 pM Tm, and 0.3 pM Lu	1	Not given Batch method	Seawater and pore waters	96
Dionex @ MetPac CC-I	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd,	0.2 - 1 (Eu, Tb, Dy, Ho, Er, Tm, Yb Lu), 2 (La, Sm, Gd) 5 (Ce), 7	10	40 Batch method	Surface waters	85

			Tb, Dy, Ho, Er, Tm, Yb and Lu	(Nd), 0.6 (Pr)				
Dionex @ MetPac CC-I	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	38(La), 17 (Ce), 1 (Dy, Er, Eu, Gd, Ho, Pr, Tb and Tm), 2 (Nd), 1 (Sm), 18 (Yb)	10	18 On-line method	Seawater	86
Toyopearl AF Chelate 650M	-	TOF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.05(La), 0.04 (Ce and Pr), 0.29 (Nd), 0.06- 0.08 (Sm), 0.02-0.03 (Eu), 0.02-0.08 (Gd), 0.02 (Ho, Lu, Tb and Tm), 0.06-0.12 (Dy), 0.04-0.06 (Er), 0.09- 0.16 (Yb)	500	12 On-line method	Seawater	29

Muromac A-1	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.251 (La), 0.133 (Ce), 0.057 (Pr), 0.154 (Nd), 0.072 (Sm), 0.069 (Eu), 0.096 (Gd), 0.040 (Tb), 0.088 (Dy), 0.093 (Ho), 0.098 (Er), 0.084 (Tm), 0.135 (Yb), 0.068 (Lu)	11.6-15.6	10 On-line method	Seawater	89
NOBIAS CHELATE PB1M	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.14 (La) 0.15 (Ce) 0.022 (Pr), 0.041 (Nd), 0.021 (Sm), 0.019 (Er and Eu), 0.020 (Gd), 0.015 (Ho and Tb), 0.018 (Dy), 0.013 (Tm), 0.014 (Yb), 0.016 (Lu)	5	3 On-line method	River water, Lake water	92

NOBIAS CHELATE PA1	-	High resolution ICP- MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu	La = 0.65 pmol kg ⁻¹ Ce = 0.82, Ho and Pr = 0.04, Nd = 0.34, Sm = 0.08, Eu, Lu and Tm = 0.01, Gd = 0.05, Tb = 0.02, Dy = 0.13, Er = 0.12, Yb = 0.11	160 - 200	150 Batch method	Seawater	148
The chelating resin in the seaFAST system	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.302 (La), 0.142 (Ce), 0.012 (Pr), 0.036 (Nd), 0.010 (Sm), 0.009 (Eu, Tm and Yb), 0.017 (Gd), 0.002 (Tb), 0.015 (Dy), 0.0010 (Ho), 0.004 (Er). 0.007 (Lu)	15	15 On-line method	Seawater	93
The chelating	-	ICP-MS	La, Ce, Pr,	-	-	-	Hydrothermal	149

resin in the seaFAST system			Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu			On-line method	waters	
The chelating resin in the seaFAST system	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and Y	-	-	- On-line method	Pacific seawater	150
The chelating resin in the seaFAST system (Iron co-precipitation for Nd isotope ratio measurements)	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu			On-line method	Seawater	151

The chelating resin in the CETAC DSX-100	-	ICP-MS	La, Ce, Eu, Gd, Yb, Lu	2.95 (La), 6.15 (Ce), 0.06 (Eu), 0.25 (Gd), 0.19 (Yb), 0.04 (Lu)	40-48	60 Batch method	Certified Seawater samples	94
Dowex 50W X12	-	ICP-OES	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	1.3 (La), 5.1 (Ce), 2.8 (Pr), 2.9 (Nd), 3.1 (Sm), 0.5 (Eu), 1.6 (Gd), 1.9 (Tb), 1.0 (Dy), 0.6 (Ho), 1.2 (Er). 0.9 (Lu and Tm), 0.2 (Yb)	2	>2200 Batch method	Mineral waters	97
Sep Pak Light-CM cartridges	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.12 (La), 0.18 (Ce and Dy), 0.22 (Pr), 0.16 (Nd), 0.33 (Sm), 0.09 (Eu), 0.27 (Gd), 0.03 (Tb), 0.08 (Ho), 0.40 (Er). 0.15 (Tm), 0.37 (Yb), 0.04 (Lu)	100	338	Raw water, purified water and tap water	98

AG50W-X8 (Dowex) cationic resin	-	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	0.55-1.50	- Batch method	Certified reference River water	28
Fe oxide REE co- precipitation+ AG1-X8 + AG50W-X8 cationic column	-	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	16-50	>1440 Batch method	Certified reference Seawater	28
Nobias PA1 resin + AG50W-X8 cationic column	-	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	-	- Batch method	Certified reference Seawater and seawater	28
Chitosan	Iminodiaceta te	ICP-MS	La, Ce, Pr, Nd, Sm, Eu,	0.38 (La), 0.43(Ce), 0.12 (Ho and Pr), 1.1	50	- On-line	River waters, drinking	104

			Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	(Nd), 0.74 (Sm), 0.23 (Eu), 0.61 (Gd), 0.18(Tb), 0.34 (Dy), 0.29 (Er). 0.15 (Tm), 0.27 (Yb), 0.17 (Lu)		method	waters	
Chitosan	Serine diacetic acid	ICP-OES	Eu, Gd, Dy, Ho, Er, Yb, Lu	26 (Eu), 28 (Gd), 39 (Dy), 19 (Ho), 18 (Er), 5 (Yb), 3 (Lu)	73-120	6.5 On-line method	River waters	105
Chitosan	2-amino-5- hydroxy benzoic acid	ICP-OES	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	6 (La), 220(Ce), 15 (Pr), 20 (Nd), 8(Eu and Sm), 7 (Gd), 18(Er and Tb), 9 (Dy), 5 (Ho), 2 (Tm), 1 (Yb), 4 (Lu)	21.1-31.6	6 On-line method	River waters	106
Chitosan	N-(2- hydroxyethyl)glycine	ICP-OES	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy,	19 (La), 120 (Ce), 25 (Pr), 250 (Nd), 29(Sm), 10 (Eu), 28	83-102	6.3 On-line method	River waters	107

			Ho, Er, Tm, Yb and Lu	(Gd), 54(Tb), 20 (Dy), 100 (Er and Ho), 47 (Tm), 2 (Lu and Yb)				
Chitosan	ethylenediamine-N,N,N'-triacetate	ICP-OES	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	14 (La), 95 (Ce), 23 (Pr), 81 (Nd), 24(Sm), 8 (Eu), 22 (Gd), 50(Tb), 20 (Dy), 7 (Er and Ho), 47 (Tm), 2 (Lu and Yb)	87-120	6.3 On-line method	River waters	108
D2EHPA resin	EDTA	ICP-OES	La, Ce and Nd	1090 (La), 3310 (Ce), 2050 (Nd)	-	On-line method	Tap water, lake water and rain water	109
MetaSEP® ME-2	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.28 (La), 0.65 (Ce), 0.12 (Pr), 0.04 (Nd), 0.017(Sm), 0.0047 (Eu), 0.014 (Gd), 0.0032 (Tb), 0.011	30	75 Batch method	Rain water	111

				(Dy), 0.0017 (Ho), 0.007 (Er). 0.0027 (Tm), 0.015 (Yb), 0.005 (Lu)				
Ln® Resin	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,	0.05 (La, Ce, Pr, Tb, Ho and Tm) and 0.10 (Nd, Sm, Gd, Dy and Er)	100	1000 Batch method	Ground water, mineral water	112
3M Empore chelating disk	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	Not given	20	Not given Batch method	Groundwater	95

LOD = Limit of detection, ICP-MS = Inductively coupled plasma-mass spectrometry; ICP-OES = Inductively coupled plasma-optical emission spectrometry;

SF-ICP-MS = Sector field inductively coupled plasma-mass spectrometry; TOF-ICP-MS = Time of flight inductively coupled plasma – mass spectrometry;

TIMS = Thermal Ionization Mass spectrometry; NAA = Neutron Activation Analysis; EDTA = ethylenediaminetetraacetic acid

Table 3. Comparison of the solid phase extraction methods for the preconcentration of REE ions using silica based supports.

Solid Support	Complexing or immobilizing agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time (min)	Samples	Ref.
Silica gel	8-Hydroxyquinoline	ICP-MS	La, Ce, Nd, Sm, Eu, Dy, Er, Yb	0.56 (La), 0.49 (Ce), 0.33 (Eu and Nd), 0.35 (Sm), 0.29 (Dy), 0.26 (Er), 0.23 (Yb)	100	210	Seawater, spring water	114
Silica gel	1-Phenyl-3-Methyl-4-Benzoylpyrazol-5-one	ICP-OES	La, Eu and Yb	82 (La), 34 (Eu), 45 (Yb)	100	50	Lake water and synthetic seawater	116
SBA-15	N ⁻ [(2-hydroxy phenyl)	ICP-OES	Dy	50 (Dy)	400	5 Batch	Tap water, river water and	117

	methylene] benzohydrazide (BBH)					system	seawater	
SBA-15	2-(2-nitrobenzylideneamino) guanidine	ICP-OES	Dy, Eu, Nd, Sm, Yb	2900 (Dy), 1600 (Eu), 8400 (Nd), 3800 (Sm), 2500 (Yb)	100	15 Batch method	Well water, spring water	118
C18	Bis(2-ethylhexyl) Hydrogen Phosphate and 2-Ethylhexyl Dihydrogen Phosphate	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	200-1000	50-250 Batch method	Seawater	65
C18	Ethylhexylphosphates	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	13.33	Batch method	River water	84

C18	1-(2-pyridylazo) 2-naphtol (PAN)	ICP-OES	Ce, Dy, La, Sm, and Y	37 (Ce), 11 (Dy), 14 (La), 23 (Sm), 13(Y)	275-372	8-20 On- line method	Spring water, well water, tap water, seawater	119
C18	2-(5-bromo-2- pyridylazo)-5- diethylaminophen ol	CE-DAD	La, Gd	0.02 (La) , 0.08 (Gd)	1000	47 On- line method	Tap water	18
Dispersive solid phase extraction	meso-porous silica functionalized as a strong cationic exchanger (SCX)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd	0.4 (La and Nd), 0.9 (Ce), 0.1 (Gd and Pr), 0.5 (Sm), 0.2 (Eu)	Dilution by a factor of 2	19 Batch method	Oil formation waters	44

LOD = Limit of Detection; ICP-OES = inductively coupled plasma-optical emission spectrometry; ICP-MS = inductively coupled plasma – mass spectrometry; CE-DAD = Capillary electrophoresis – diode array detector

Table 4. Comparison of the solid phase extraction methods for the preconcentration of REE ions using other supports.

Solid Support	Complexing or immobilizing agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time (min)	Samples	Ref.
Multiwalled carbon nanotubes		ICP-OES	La, Sm, Eu, Gd, Tb, Yb, Ho	10 (La), 57 (Sm), 4 (Eu), 15 (Gd and Ho), 9 (Tb), 3(Yb)	50	50 Batch method	Lake water and synthetic seawater	120
1,2- methanofullerene- C60	Poly(b- styryl)- hydroxamic acid	ICP-MS	Ce, La, Pr, Nd, Sm, Gd	-	67	1000 Batch method	Seawater	121
Fe ₃ O ₄ @SiO ₂	Cinchonidine	ICP-OES	Eu	40 (Eu)	267	15 Batch method	Spiked tap, mineral and spring water samples	122

Fe ₃ O ₄ @SiO ₂ @pol yaniline–graphene oxide composite	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.16 (La), 0.21 (Ce and Dy), 0.69 (Pr), 1.49 (Nd), 0.18 (Sm), 0.07 (Eu), 0.54 (Gd), 0.05 (Ho), 0.07 (Er). 0.04 (Lu, Tb and Tm), 0.20 (Yb)	50	4 Batch method	Lake water, river water	123
Graphene oxide– TiO ₂ composite	-	ICP-OES	La, Ce, Eu, Dy and Yb	410 (La), 240 (Ce), 130 (Eu), 260 (Dy) and 210 (Yb)	10	3.5 On- line method	Lake water, river water, seawater	124
Bentonite	N-(2- hydroxyethyl) ethylenediam ine	ICP-OES	Sm	600 (Sm)	75	150 Batch method	Waste water sample	127
Activated Carbon	-	ICP-MS	La, Ce, Pr,	0.3	400	120	Ground water,	128

			Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu			Batch method	seawater	
Naphthalene	5,7- dichloroquin oline-8-ol	FAAS	Nd, Eu and Lu	40000 (Nd), 4000 (Eu), 30000 (Lu)	200	20	Seawater	129
Magnesium oxide powder	-	NAA	La, Ce, Nd, Sm, Eu, Gd, Tb, Dy	-	-	30 Batch method	Wastewater	17
Porous PTFE Filter Tube	Bis(2-Ethyl- Hexyl)Hydro gen Phosphate (HDEHP)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	20 (La, Ce, Pr, Nd) 200 (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu)	12.5 - 125 Batch method	Spiked natural sea salt (dried natural seawater) solution	131
Poly(acrylaminop hosphonic	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu,	2 (La), 1 (Ce, Gd, Nd and Sm), 0.9 (Pr),	200	143 Batch	Seawater	132

dithiocarbamate) Chelating Fiber			Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.7(Dy, Eu and Ho), 0.5(Tb and Yb), 0.2 (Er), 0.6(Tm), 0.3(Lu)		method		
Maleic Acid Grafted Polytetrafluoroeth ylene Fibers	-	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.009 (La), 0.020 (Ce), 0.003 (Pr), 0.016 (Nd), 0.014 (Sm), 0.013(Eu), 0.012(Gd), 0.002 (Tb and Tm), 0.004 (Dy and Yb), 0.001(Ho and Lu), 0.005 (Er)	69–97	2.75 On- line method	Seawater, river water	133
Cellulose- immobilized	EDTrA (ethylenedia minetriacetic acid)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	6 (La and Tm), 15 (Ce), 2 (Ho, Pr, Tb), 3 (Nd), 6(Sm), 35(Eu), 10(Gd), 12(Dy), 5 (Er, Lu and Yb)	100	77 Batch method	Seawater	134
Knotted reactor, PTFE	1-phenyl-3- methyl-4-	TOF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu,	0.67 (La), 0.032(Ce), 0.008 (Gd and Pr),	16-22	3.75 On-	Certified water samples	30

	benzoylpyrazol-5-one		Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.034 (Nd), 0.023 (Sm), 0.006 (Eu), 0.003(Tb), 0.015 (Dy), 0.005 (Ho and Tm), 0.012 (Er), 0.014 (Yb), 0.004 (Lu)		line method		
Transcarpathian clinoptilolite		Spectrophotometry	Tb	750	-	- Batch method	Spiked tap water	135

LOD = Limit of detection, ICP-MS = Inductively coupled plasma-mass spectrometry; ICP-OES = Inductively coupled plasma-optical emission spectrometry;

TOF-ICP-MS = Time of flight inductively coupled plasma – mass spectrometry; FAAS = flame atomic absorption spectrometry

Table 5. Comparison of the Liquid-liquid extraction methods for the preconcentration of REE ions.

Preconcentration Method	Complexing agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time min	Samples	Ref.
Liquid-liquid extraction	N-Phenyl-(1,2-methanofullerene C60)61-formohydroxamic Acid	ICP-OES	La and Ce	500	NA	4	Sea water	136
Liquid-liquid extraction	5,7 diiodooxine and Rhodamine 6G	MFS	Er	0.2	2.5	1	Sea water	15
Liquid-liquid extraction	HDEHP (phosphoric acid 2-ethylhexyl ester - mono and di ester mixture)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	-	8	12	Sea water	36
Liquid-liquid	pivaloyltrifluoroace	ETV-ICP-	La, Ce, Pr, Nd,	0.91(La), 0.85 (Ce),	7	5	River water and	7

extraction	tone (PTA)	MS	Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	0.69 (Pr), 0.62 (Nd), 0.48 (Sm), 0.60 (Eu), 0.56 (Gd), 0.68 (Tb), 0.52 (Dy), 0.21 (Ho), 0.26 (Er), 0.22 (Tm), 0.20 (Yb), 0.29 (Lu)			Lake water	
Liquid-liquid extraction	bis(2-ethylhexyl) phosphoric acid in heptane and back extraction into 6 M HCl	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu (+ In and Y)	-			Saline waters and brines	139
Optimized Ultrasound- Assisted Emulsification-	5,6,14,15-dibenzo- 1,4-dioxa-8,12- diazacyclopentadec ane	ICP-OES	La, Ce	12 (La), 610 (Ce)	10	11	Tap water and river water	1

Microextraction	(a dioxadiazamacrocyclic)							
Optimized Ultrasound-Assisted Emulsification-Microextraction	1-(2-Pyridylazo)-2-naphthol	ICP-OES	Yb, Ho	364(Ho), 252 (Yb)	10	5	Tap water and river water	137
Synergistic liquid liquid extraction	Dimethylheptyl methyl phosphate (P350) and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (PMBP)	ETV-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	0.07 (Eu and La), 0.09 (Ce), 0.05 (Er, Gd, Pr, Sm), 0.06 (Nd and Tb), 0.04 (Dy), 0.02 (Ho, Lu and Yb), 0.03 (Tm)	10	5	Lake water, seawater, tap water	9
Liquid-liquid-liquid extraction (LLLME)	4-benzoyl-3-methyl-1-phenyl-5-pyrazolinone	CE-UV	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho,	640 (La), 550 (Ce), 290 (Lu and Pr), 540 (Nd), 460	195 (La), 103 (Ce), 208 (Pr), 193 (Nd), 140	50	Lake water and tap water	19

	(PMBP)		Er, Tm, Yb, Lu	(Sm), 700 (Dy and Eu), 510 (Gd), 350 (Tb), 290 (Ho), 330 (Er), 300 (Tm), 430 (Yb)	(Sm), 147 (Eu), 200 (Gd), 113 (Tb), 95 (Dy), 115 (Ho), 114 (Er), 74 (Tm), 52 (Yb), 62 (Lu) and 164 (Y)			
Cloud point extraction (CPE)	1-(2-thenoyl)-3,3,3-trifluoroacetone	ICP OES	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	28 (La), 99 (Ce), 103 (Pr), 20 (Nd), 18 (Sm), 14 (Eu), 13 (Gd), 47 (Tb), 15 (Dy), 9 (Ho), 22 (Er), 3 (Tm), 2 (Lu and Yb)	14 (La, Pr), 12 (Gd, Lu), 11 (Nd, Yb), 10 (Ce, Dy,, Sm, Tm), 9 (Eu, Tb, Ho, Er)	35	Mineral water, river water and reference water	42
Dispersive liquid–liquid microextraction	2,6-pyridine dicarboxylic acid and Aliquat® 336	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho,	0.55 (La), 0.34 (Ce), 0.16 (Lu, Pr and Tm), 0.52	97	15	Groundwater	43

			Er, Tm, Yb and Lu	(Nd), 0.25 (Sm), 0.21 (Eu), 0.19 (Gd), 0.05 (Tb), 0.20 (Dy), 0.08 (Ho), 0.18 (Er), 0.24 (Yb),				
Dispersive liquid– liquid microextraction	None	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	7.04 (La), 26.60 (Ce), 1.77 (Pr), 5.95 (Nd), 9.77 (Sm), 4.40 (Eu), 5.51 (Gd), 1.08 (Tb), 3.53 (Dy), 0.76 (Ho), 3.77 (Er), 0.68 (Tm), 3.96 (Yb), 0.91 (Lu)	2	9	Tap water, river water and seawater	5
Solidified floating	1-(2-pyridylazo)-	ETV-ICP-	La, Eu, and Yb	2.1 (La), 0.65 (Eu),	500	30	Lake water,	32

organic drop microextraction	2-naphthol (PAN)	MS		0.91 (Yb)			river water	
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LOD = Limit of detection, ICP-MS = Inductively coupled plasma-mass spectrometry; ICP-OES = Inductively coupled plasma-optical emission spectrometry;

ETV-ICP-MS = Electrothermal Vaporization- inductively coupled plasma-mass spectrometry; CE-UV = Capillary electrophoresis – Ultra-violet;

MFS = Molecular Fluorescence spectrometry

Table 6. Comparison of the co-precipitation and precipitation methods for the preconcentration of REE ions.

Co-precipitating or precipitating agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time (min)	Samples	Ref.
Iron hydroxides	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.070 (La), 0.21 (Ce), 0.027 (Pr), 0.16 (Nd), 0.01 (Sm), 0.012 (Eu), 0.015 (Gd), 0.002 (Tb), 0.007 (Dy), 0.0025 (Ho), 0.005 (Er), 0.0006 (Tm), 0.0067 (Yb), 0.0007 (Lu)	10	1.5 (Precipitation time is not given)	River water	10
Iron hydroxides	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	-	180	Certified reference water materials	25

Iron hydroxides	ICP-MS or high resolution ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	-	-	-	Seawater	152
Iron hydroxides	ICP-MS and multi-collector ICP-MS for Nd isotope ratios	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and Nd isotope ratios	-	-	24 hour equilibration	Seawater	153
Iron hydroxides (C18 SepPak cartridges used for Nd ratios)	ICP-MS TIMS and multi-collector ICP-MS for Nd ratios	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and Nd isotope ratios	-	1250	3 day equilibration of ^{150}Nd and ^{172}Yb spikes.	Seawater	154

Iron hydroxides (C18 SepPak cartridges used for Nd ratios)	ICP-MS TIMS and multi-collector ICP-MS for Nd ratios	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and Nd isotope ratios	-	1250	-	Seawater	155
Iron hydroxides (C18 SepPak cartridges used for Nd ratios)	ICP-MS TIMS for Nd ratios	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and Nd isotope ratios	-	-	56	Seawater	156
Magnesium hydroxides	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.06 (La and Tm), 0.12(Ce), 0.08 (Pr and Yb), 0.18(Nd), 0.10(Sm), 0.03(Eu and Ho), 0.05(Gd), 0.04(Lu and Tb),	4	1440	Ground water, river water and seawater	40

			0.02(Dy), 0.11(Er)				
Magnesium hydroxides	SF-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.012(La), 0.020(Ce), 0.007(Pr), 0.029(Nd), 0.015(Sm), 0.006(Er and Eu), 0.016(Gd), 0.004(Tb), 0.005(Dy and Ho), 0.008(Yb), 0.001(Lu)		22	Reference seawater materials and seawater	27
Magnesium hydroxides	LA-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.03(Ce, La and Pr), 0.13(Nd), 0.11(Sm), 0.06(Er and Eu), 0.20(Gd), 0.03(Tb), 0.011(Dy), 0.04 (Ho and Lu), 0.05 (Tm),	32	15	Lake water, Synthetic seawater	141

			0.16(Yb)				
Gallium hydroxide	ICP-MS	La	1 (La)	10		Seawater	144
Ammonia	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	0.1(La), 0.12(Ce), 0.06(Pr), 0.27(Nd), 0.22(Sm), 0.05(Eu), 0.21(Gd), 0.11(Tb), 0.19(Dy), 0.15(Ho), 0.25(Er), 0.18(Tm), 0.17(Yb), 0.13(Lu)	55-75	5.33	Porewater samples	41
Flotation	Eriochrome Cyanine R complex formation followed by UV-VIS	La	500 000	200	5	Domestic water, river water	13

LOD = Limit of detection, ICP-MS = Inductively coupled plasma-mass spectrometry; SF-ICP-MS = Sector field inductively coupled plasma-mass spectrometry; TIMS = Thermal Ionization mass spectrometry; UV-Vis = Ultra-Violet-Visible; LA-ICP-MS = laser ablation- inductively coupled plasma-mass spectrometry

Table 7. Comparison of other preconcentration methods for the determination of REE ions in natural waters.

Preconcentration Method	Complexing or immobilizing agent	Detection Method	Analyte	LOD ng L ⁻¹	Preconcentration Factor	Time min	Samples	Ref.
Dispersive solid phase extraction (D-SPE) and Dispersive liquid-liquid	1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP)	ETV-ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y	0.040 (La), 0.048 (Ce), 0.038 (Pr), 0.073 (Nd), 0.006 (Sm), 0.004 (Eu and Tm), 0.026 (Gd), 0.003 (Er, Ho, Lu and	234, 321, 347, 341, 344, 352, 390, 475, 546, 537, 472, 557, 462, 566, and 387	24	Lake water, river water	3

microextraction				Tb), 0.014 (Dy), 0.008 (Yb)	for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y			
Membrane (polyacrylonitrile hollow fiber membrane)	8-hydroxyquinoline	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	2.7 (La), 1.6 (Ce), 0.91 (Pr), 1.7 (Nd), 1.8(Sm), 0.71(Eu), 1.1(Gd), 0.56(Tb), 0.73(Dy), 0.24(Ho), 0.21 (Er), 0.53(Tm), 0.31(Yb), 0.32(Lu)	300	150	Seawater	146
Membrane (triacetylcellulose membrane)	N`-[(2-hydroxyphenyl)methylene] benzohydrazide	UV-VIS	Dy	55880	-	1	Spiked tap water, river water, mineral water	11

Membrane (PVC-membrane)	N,N`-bis(dansylamidoethyl)-N,N`-bis(2-pyridylmethyl)propylene-diamine	MFS	La	277.8	-	2	Spiked tap water	14
Membrane filters (Millipore, Mixed Cellulose Esters)	Polyacrylic acid (PAA)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	1.3 (La), 0.8 (Ce, Eu), 9 (Pr), 2.1 (Nd), 2.3(Sm), 0.7(Gd and Ho), 1.1(Tb), 0.6(Dy), 0.9 (Er), 2.2(Tm), 1.5(Yb), 1.3(Lu) Given as LOQ	3	55	Coastal seawater	147
Electroanalytical (carbon paste electrode)	N`-[(2-hydroxyphenyl)methylidene]	Adsorptive stripping voltammetry	Ce	112.09	NG	6	Wastewater, polluted water	20

	ne]-2- furohydrazid e							
Countercurrent chromatography	Di-2- ethylhexilph osporic acid (D2EHPA)	ICP-MS	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Gd- DTPA	-	40	25	River waters	45

LOD = Limit of detection; ICP-MS = inductively coupled plasma-mass spectrometry; UV-Vis = Ultra-violet-Visible; ETV-ICP-MS = electrothermal vaporization-inductively coupled plasma – mass spectrometry; MFS = Molecular fluorescence spectrometry

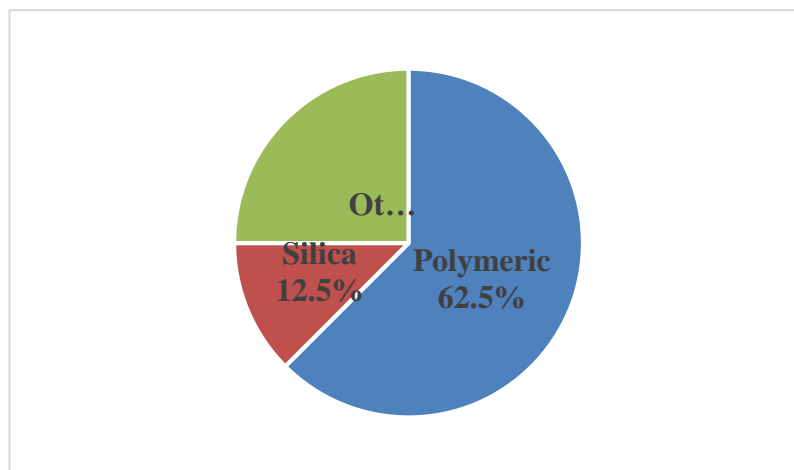
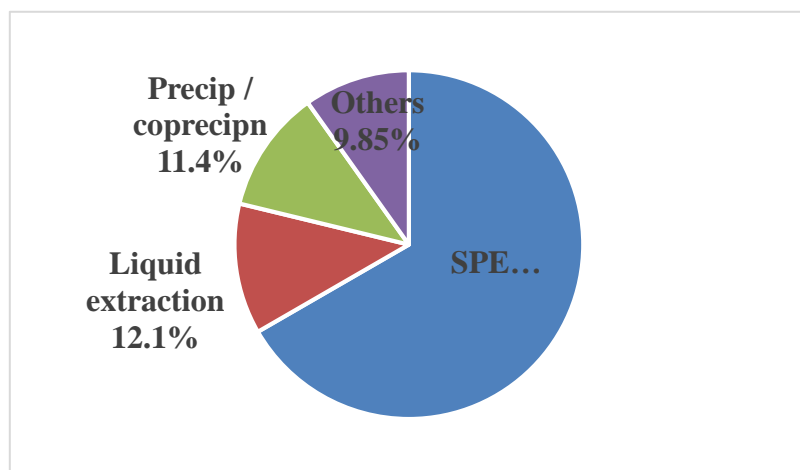
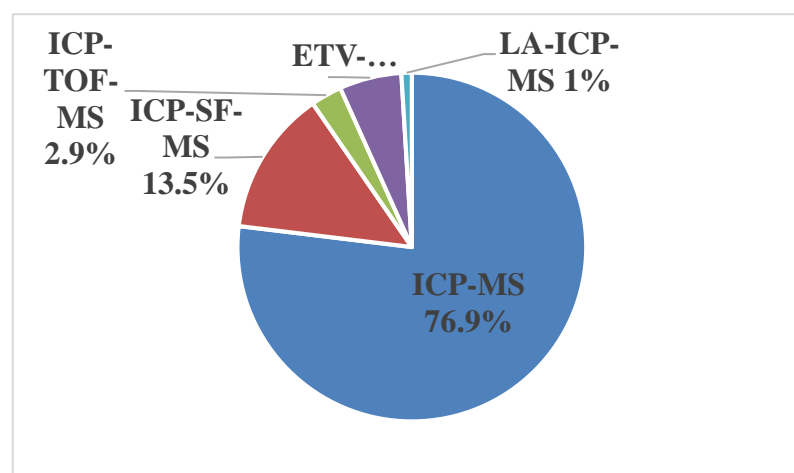
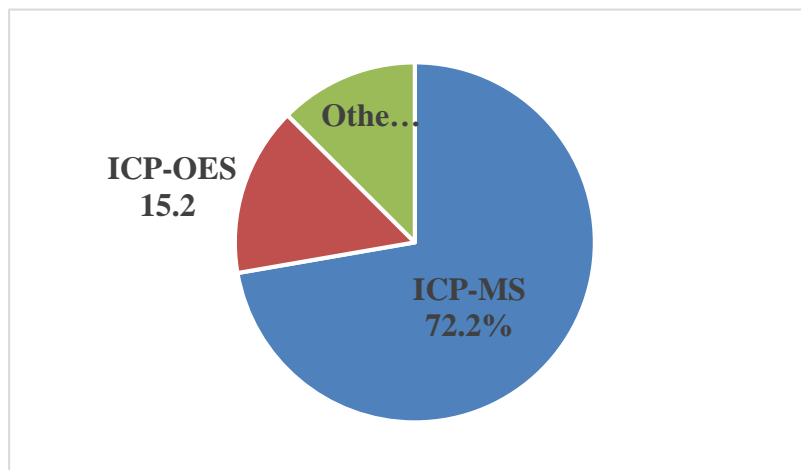


Fig. 1 The percentages of the published papers from the year 2000 that have determined rare earth elements in natural waters using the type of a) Instrumental techniques b) inductively coupled plasma mass spectrometry c) preconcentration methods d) solid supports in solid phase extraction

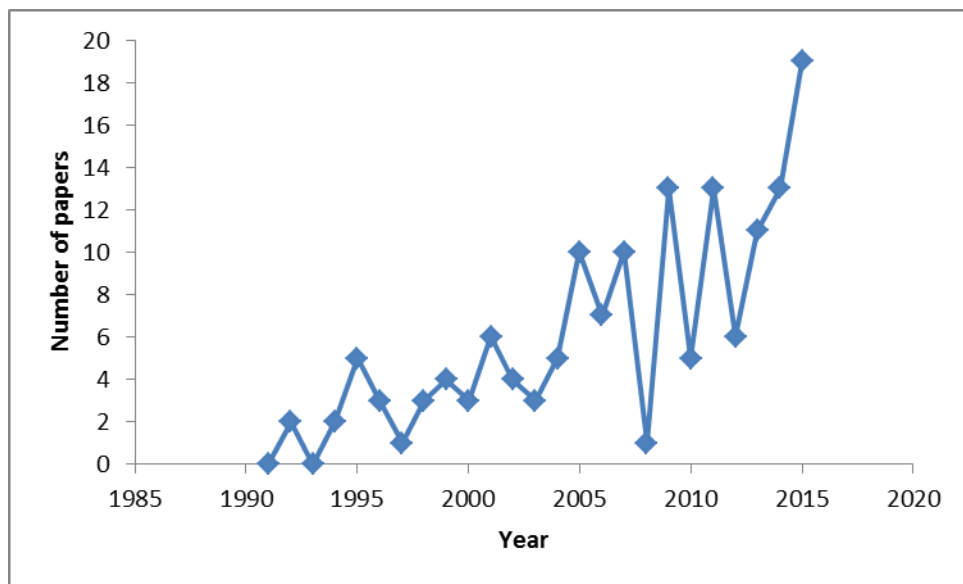


Figure 2. The numbers of the published manuscripts for the determination of REE in natural waters according to the publication year