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Direct determination of rare earth elements in natural water and digested sediment samples by inductively coupled plasma quadrupole mass spectrometry using collision cell

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Abstract

The present study is based on the use of a conventional quadrupole ICP-MS for determining directly rare earth elements (REEs) in both fresh or slightly saline waters and digested sediments. The development of a robust method using a collision reaction cell (different collision gases and fluxes have been tested) and kinetic energy discrimination is proposed for the accurate quantification of REEs without any mathematical corrections and preconcentration steps. The choice of He gas over H_2 and its flow in the collision reaction cell as well as the isotopes studied are thoroughly discussed with the aim of reducing drastically interferences. The exhaustive list of thereferences (argides, chlorides, oxides, hydroxides, hydrides and doubly charged) have been invertigated for the first time at different concentration levels, relevant with those found in entitionmental matrices based on the FORum of European Geological Surveys (FOREGS) datab. se. he interfering element concentrations have been determined and summarized. Although t're mpact of barium interferences onto europium and the impossibility to measure Sc have been on ted out, this method has been validated for all the other REEs in aquatic environmental matrices by studying the recoveries of spiked natural waters (5 commercially available mineral waters with dry residues ranging from 22 to 2513 mg L⁻¹ and a filtrated natural river water from Northern France) with relevant concentrations of REEs. Standard reference materials (i.e. three wrters (AQUA-1, SLRS-6 and SLEW-3) and four sediments (BCR-667, HISS-1, Metranal-1 and PA (S-3,) were also analysed to ensure the robustness of the method.

Keywords: Rare earth elements, ICP-QMS, collision reaction cell, certified water, certified sediment.

1. Introduction

Rare earth elements (REEs) comprise a group of 15 elements with atomic numbers ranging from 57 to 71 (La to Lu) called lanthanides. According to the International Union of Pure and Applied Chemistry (IUPAC), scandium and yttrium are also included in this categorization because of their similar chemical and physical properties (*i.e.* predominance of the trivalent oxidation state and similar ionic radii) [1]. These elements have low solubility and mobility in the terrestrial crust and their patterns of abundance allow the interpretation of natural geological and chemical processes [2,3]. Concerning natural waters and sediments, REEs can be used as tracers of water masses circulation [4,5]. They can also constitute a valuable probe for in estigating the scavenging of particulate matter and sedimentation processes [6,7]. In duitien, REEs have become extremely important for high technology applications and process es due to their unique magnetic, phosphorescent, and catalytic properties [8,9]. Moreover, REEs are considered as "Technology Critical Elements" (TCEs) by several scientific orb nizations (*e.g.* Action TD1407 NOTICE from the European COST network) [10].

The use of REEs has been accompanied by the emission of increasing quantities of several of these elements in the environment and their concentrations can affect their overall shale normalized geogenic patterns. This is particularly the case of gadolinium for which large positive anomalies, attributed to Gd-based contrast agents used in magnetic resonance imaging (MRI), can be regularly detected in rivers worldvinde [11-13]. REEs can therefore constitute good tracers for anthropogenic inputs but they are also considered as emerging pollutants [14,15].

The determination of REEs can be performed by several analytical techniques such as neutron activation analysis, X-ray fluorescence spectrometry, ultraviolet-visible spectrometry, electrochemistry, atomic absorption spectrometry, inductively-coupled plasma-optical emission spectrometry (ICP-OES) and the various forms of inductively-coupled plasma-mass spectrometry (ICP-MS, *i.e.* inductively-coupled plasma quadrupole mass spectrometer (ICP-QMS), sector field inductively-coupled plasma mass spectrometer (SF-ICP-MS), time-of-flight inductively-coupled

3

plasma mass spectrometer (TOF-ICP-MS)) [16,18]. Among these techniques, ICP-MS has become one of the most powerful technique for the determination of REEs due to its high sensitivity, selectivity, wide linear range and multi-element capability. However, the accurate determination of rare earth elements remains complex mainly due to their low concentrations in natural samples associated with possible interferences. Indeed, one of the main challenges to be addressed during their analyses by ICP-MS is to handle polyatomic interferences (e.g. oxides and hydroxides) which are mainly related to the presence of Ba and light-REEs (LREEs) in the samples. Several approaches have been considered to overcome such spectral interferences and to improve the detection limits. Solid phase extraction (SPE), and to a lesser extent liquid-liquid extraction (LLE) are often used as preconcentration and matrix separation steps [19]. Co-precipitation with a metal vdroxide (*e.g.* iron hydroxide) can also be employed [20]. Nevertheless, these procedures are often time consuming and may introduce contamination or produce a partial loss of the ana ytas Another disadvantage of these methods is that they cannot deal with all spectral interent nect such as the presence of LREEs impacting the determination of heavy-REEs (HREEs) through the residual presence of (hydr-)oxide LREEs interferences. Mathematical approacl es [21-23], or even measurement of doubly charged ions [24,25] have been envisaged to correct oxide and hydroxide interferences during ICP-MS analysis. However, mathematical corrections can lead to additional measurement uncertainties [26]. Other analytical strategies rely on sample introduction (e.g. ultrasonic nebulization, electrothermal vaporization, membrane resolvation, high matrix introduction and low flow micro-concentric nebulization) to improve sensitivity and/or to decrease the presence of interferences [18,20,27]. The majority of these specialized sample introduction systems do not always separate the analyte from the matrix and interferences could be therefore enhanced. Moreover, membrane-desolvation introduction systems do not tolerate high-salt matrix samples [27]. The use of high-resolution ICP-MS allows overcoming most of polyatomic interferences (the resolving power (R) required for the separation of the interfering oxide ions from lanthanides ranges typically from 7000 to 10,000) [28]. Nevertheless, the investment cost of such a device is a barrier for many laboratories and it can be

4

noticed that many authors still performed measurements of REEs at lower resolution in order to achieve a better sensitivity. Considering conventional ICP-QMS, collision/reaction cell technology also represents a good strategy to handle interferences in the determination of REEs. Dioxygen [29] and carbon dioxide [30] have been used as reaction gases to convert REEs ions to their oxide thus performing the determination at m/z +16. However, some elements (*e.g.* Eu, Gd, Yb and Lu) could not be measured by this O-atom addition approach and had to be determined in standard mode with mathematical corrections. In the same way, ammonia has been employed as reactive gas to overcome polyatomic interferences on Nd, Gd, Yb and Lu [31]. Du and Houk [32] and more recently Rousis and Thomaidis [33] investigated the use of He and H₂ as cell passes and concluded that both were efficient to reduce oxide and hydroxide interferences with a preference for H₂.

Herein, a simple and direct method for the determination of REEs in aquatic environmental samples (*i.e.* waters and digested sediments) is proposed with any mathematical corrections, using ICP-QMS equipped with a standard introduction syndem and a collision reaction cell. Different gases and their fluxes, kinetic energy discrimination. (KED) voltages and isotopes have been tested to remove spectral interferences. For the first time, the exhaustive list of potential interferents has been studied at different environmental concentration levels based on FORum of European Geological Surveys (FOREGS) database. The metion has been validated by assessing the potential impact of remaining interferents for the quantimentation of REEs, the recoveries of low REEs levels in spiked natural water matrices and the accuracy of measurements for several certified water and sediment references.

2. Material and methods

2.1 Reagents

All solutions were prepared using ultrapure water (Milli-Q gradient, Millipore, $\rho = 18.2 \text{ M}\Omega$ cm). Mono-elemental standards used for interferences studies were purchased either from SCP Science (Courtaboeuf, France) or from Courtage Analyses Services (Mont-Saint-Aignan, France). The stock REEs multistandard solution used for calibration (100 mg L⁻¹ in 5% HNO₃) was obtained from SCP

Science. Nitric acid (67-69%, optima and trace metal grade) was purchased from Fisher Scientific (Illkirch, France). Trace metal grade hydrochloric acid (35-38%) and suprapure hydrofluoric acid (40%) were acquired from Merck (Darmstadt, Germany). Certified reference materials were purchased from the Canadian National Research Council (NRC-CNRC, Ottawa, Canada) for SLRS-6, AQUA-1, SLEW-3, HISS-1 and PACS-3), from Courtage Analyses Services for Metranal-1, and from the European Commission Joint Research Centre (JRC, Geel, Belgium) for BCR-667. All other chemicals used in this study were ACS reagent or analytical grade.

2.2 Determination of interference equivalent concentration: (IEC)

After determining the best parameters to quantify accurately REFs (v + cP-MS) (in particular the choice of isotopes), numerous interferences were thoroughly studied. The study of chloride interferences was performed by addition of HCl up to 34 mmol L⁻¹ (requivalent to 2 g L⁻¹ NaCl). For the other interferences (hydrides, oxides, hydroxides, argides and doubly charged), 2% (v/v) HNO₃ solutions were spiked with interfering elements standard solutions. The concentrations of the interferents in these solutions were chosen based on the COREGS database [34,35] in order to reflect the environmental matrices. Two levels of concentration were also considered: the first concentrations set corresponded to the median values to cover a representative view of European environment, while the second set was focused on the ninth decile in order to work on higher concentrations. It is to be noted that in the cale on the concentrations of interferents below 10 ng L⁻¹, the interferences were not studied as they were expected to be negligible.

As the FOREGS database contains concentrations of REEs both in water and sediment (see Table S1, appendix), we decided to consider the highest values between concentrations in water and sediment in a 1/100,000 ratio according to our analytical protocol for the analyses of REEs in sediments. For gadolinium, other values have been selected in order to take into account specific anthropogenic inputs: the lowest level corresponds to the ninth decile found in FOREGS database while the maximal concentration (2 µg L⁻¹) corresponds to a value that can be attained in wastewater treatment plant effluent, as Gd is widely used in contrast agent for magnetic resonance imaging [11,36].

For each concentration, analyses were performed in triplicate to assess a standard deviation value. The biased concentration induced by the interferent was determined by analysing solutions with a known level of interferent. In order to avoid interferences between the elements studied (*e.g.* light-REEs oxides on heavy-REEs), five different batches were performed: (*i*) Sc, Y; (*ii*) La, Ce, Pr, Nd, Sm; (*iii*) Eu, Gd; (*iv*) Tb, Dy, Ho, Er, Tm; and finally (*v*) Yb, Lu.

2.3 Matrix effect on recovery of spiked solutions

A second set of experiments was performed with different French commercial mineral waters (Mont Roucous®, Evian®, Volvic®, Saint Amand®, Hépar®) as matrices. These waters were selected in order to cover a wide range of hardness and amount of dry residues (anging from 22 mg L⁻¹ for Mont Roucous[®] to 2513 mg L⁻¹ for Hépar[®] (see Table S2, appendix). Waters were acidified at 2% (v/v) using ultrapure HNO₃. In addition, a natural water sample from the Marque River (France) was used as a matrix. Some of its main features have been previously described [37,38]. Briefly, the Marque River flows in northern France close to the city of U.e. Its annual average flow is around 1 m³ s⁻¹ at the sampling site located at Villeneuve d'Ascq. The river Marque is 32 km long, its watercourse receives 7 main effluents of wastewater treatmen. Jants (WWTP), corresponding to approximately 150,000 inhabitant equivalent. Its status , bao according to the ranking of the Water Framework Directive (WFD, 2000) due to an excess of nutrients, pesticides, industrial pollutants and a lack of oxygen. Sampling was performed 200 ineters upstream the Villeneuve d'Ascq wastewater treatment plant (N 50° 37' 48.4"; E 3° 11' 6.6"). The freshwater was collected in a 5 L high-density polyethylene (HDPE) bottle previously cleaned with acid and rinsed with ultrapure water. Filtration of the whole collected water was performed using polyethersulfone filter (0.45 µm of porosity) and water was poured in another 5 L precleaned HDPE bottle. Filters were changed as little as possible to limit potential contamination. No blank control or study of the effect of the filtration on the concentrations of REEs was performed as this step was mainly performed to remove particles that could clog the introduction system of the ICP-MS. The filtrated sample was immediately acidified at 2% (v/v) using ultrapure HNO₃ before analysis. All these waters were analysed in triplicate without and with spike of

1 ng L⁻¹ (Eu, Ho, Lu, Tb, Tm), 5 ng L⁻¹ (Dy, Er, Gd, Pr, Sc, Sm, Yb), 25 ng L⁻¹ for Y and 50 ng L⁻¹ (La, Ce, Nd). These concentrations were chosen based on SLRS-6 and FOREGS values REEs ratio. Concentrations of some major elements which could interfere with REEs (Ba, Ca, Si, Sr) were also determined.

2.4 Protocols for water reference materials analyses

In order to validate our method for the quantification of REEs in water, 3 reference materials certified by NRC-CNRC have been used: SLRS-6, AQUA-1 (freshwaters) and SLEW-3 (estuarine water, salinity = 15 Practical Salinity Unit (PSU)). Replicates for each wr cer have been analysed to obtain consistent data. For assessing the repeatability of measurements these replicates have been analysed over two days. Concerning SLEW-3, samples were diluted 5-fold prior ICP-QMS measurements to avoid the clogging of the cones by the saline matrix.

2.5 Protocol for sediment reference matchiels analyses

Four reference materials have been used c_1 alidate the analytical method in sediment matrices: BCR-667 (estuarine sediment reference material from European Commission - Joint Research Centre), Metranal-1 (river sediment certified by the METROCHEM group), as well as PACS-3 and HISS-1 (marine sediments certified b; NkC-CNRC). Total mineralization was performed with 0.2 g of sediment using a mixture of hb nurity nitric and hydrofluoric acids followed by an *aqua regia* attack according to the protocol of Boughriet *et al.* [39]. Prior quantification of REEs, digestates were filtered (0.45 µm, cellulose acetate) then diluted 1000-fold using 2% (v/v) HNO₃ to obtain a concentration of REEs in the ng L⁻¹ range. Blank samples (n = 6) were systematically performed following the same digestion and filtration procedures. Blank concentrations of REEs obtained were negligible and did not impact the concentrations found in sediments. Concentrations of REEs in the residue were not studied as the latter was not taking into account for REEs quantification in the certified materials.

2.6 Elemental analyses

Major elements (*i.e.* interfering elements Ba, Ca, Si and Sr) were quantified using an inductively coupled plasma optical emission spectrometer (ICP-OES 5110 VDV, Agilent Technologies) calibrated using standard solutions. The concentrations of REEs were determined using an inductively coupled plasma single quadrupole mass spectrometer (ICP-MS 7900, Agilent Technologies) equipped with a standard introduction system [borosilicate MicroMist concentric nebulizer (0.4 mL min⁻¹), quartz double pass spray chamber cooled at 2°C, quartz torch (2.5 mm ID) and nickel cones]. X-lenses were selected as ion optic configuration. High purity He and H₂ (> 99.999(5) were used as collision/reaction gases in the octopole reaction system (ORS) to study polyatomic inte ferences suppression. Kinetic energy discrimination (KED) was also applied. Six different modes were used during this study. Ion lens parameters were optimized daily. Main parameters of the device and percentage of oxides and doubly charged formation are summarized in Table 1 to correct possible additional matrix effects and signal drift, ⁷⁴Ge (for Sc and Y), ¹¹⁵In (for Y a, 1 La - Eu), ¹⁸⁵Re (for La - Lu) and ²⁰⁵Tl (for Gd - Lu) were used as internal standards (ISTDs) with unline addition of 50 μ g L⁻¹ stock solution in 2% (v/v) HNO₃. Concentrations of ISTDs, after dilution in the samples, were around 3.4 μ g L⁻¹. ISTDs fitting the best with SLRS-6 reference material concentrations were used and chosen according to the experiment.

Table 1 ICP-MS and collision (ell cunditions

Shaded modes indicate the mo 'es tested during the study but not selected for the final method.

ICP-QMS conditions				
RF Power:	1550 W			
RF Matching:	1.80 V			
Plasma Ar gas flow rate:	15 L min ⁻¹			
Auxiliary Ar gas flow rate:	0.8-1 L min ⁻¹			
Nebulizer gas flow rate:	1.05 L min ⁻¹			
Lens voltage:	Optimized daily			
Sample depth:	9 mm			
Sample intake flow rate:	0.4 mL min ⁻¹			
Spray chamber temperature:	2 °C			
Point per mass:	1			
Integration time:	2 s			
Dwell time:	8 ms			
Sweeps:	250			
Replicate:	3			

Collision reaction cell conditions							
No gas		H ₂					
0 mL min ⁻¹ KED 5 V	4.5 mL min ⁻¹ KED 5 V	5 mL min ⁻¹ KED 5 V	5 mL min ⁻¹ KED 7 V	10 mL min ⁻¹ KED 7 V	6 mL min ⁻¹ KED 5 V		
Oct bias -8 V	Oct bias -18 V	Oct bias -18 V	Oct bias -18 V	Oct bias -100 V	Oct bias -18 V		
		Oxide formation	rate CeO /Ce (%)				
1.4-2.4	0.4-0.5	0.25-0.35	0.1-0.2	0.5-0.7	1.0-2.0		
Doubly charged ion formation rate Ce ²⁺ /C= ¹ /%)							
1.5-2.6	2.0-2.8	2.1-2.9	2.2-3.0	2.5-2.9	0.4-0.7		

Monitored isotopes: ⁴⁵Sc, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁴⁹Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁷Er, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu

Results and discussions

3.1 Development of the method

3.1.1 Determination of the collision/reaction cell cas

The preliminary step of this study was to seler: the most suitable gas to handle spectral interferences during the analysis of REEs. In the light of the information found in the literature [32,33] and the results obtained, helium appeared to be the most promising gas for suppressing interferences in water and sediment matrices. For the 24 isotopes initially tested, the use of He always allowed reduction of the interference in monomiation with the no gas mode. By contrast, the use of H₂ showed limitations. Indeed, for 18 souppes out of the 24 tested, H₂ induced stronger interferences than the no gas mode. This can be explained by the fact that some elements are directly interfered by MH* or MOH* ionic species (*e.g.* ⁴⁵Sc, ¹³⁹La, ¹⁴⁷Sm, ¹⁷⁵Lu *versus* ⁴⁴CaH*, ¹³⁸BaH*, ¹³⁰Ba¹⁶OH* and ¹⁵⁸Gd¹⁶OH* respectively). The impact of REEs-hydride interferences on the determination of targeted REEs was not significant in our case due to the low concentration of REEs employed [33,40]. It should be however noted that the use of H₂ significantly reduced the amount of doubly charged ⁹⁰Zr²⁺ interference onto ⁴⁵Sc. Removal of doubly charged species by H₂ has already been observed for other elements [41,42]. Such removal may be explained either by ⁹⁰ZrH* formation [41,43] (although it should be limited [44]), or charge exchange [41]. By contrast, all tested He modes were found to

increase this interference confirming the inefficiency of He for limiting the formation of doubly charged ions [42,45]. However, this type of interference only concerned Sc.

3.1.2 Selection of the isotopes

Only isotopes of REEs with no isobaric interference were considered for this study. Considering the elements with several isotopes free of isobaric interferences, the selection was further processed by studying the impact of other spectral interferences and/or by selecting the most abundant. For example, based on the first criterion, the choice to keep ¹⁵¹Eu and ¹⁵⁷Gd was made because of the strong interference of barium oxide or hydroxide on ¹⁵³Eu and ¹⁵⁵Gd. ^chese choices are in agreement with some studies for Eu but not for Gd for which ¹⁵⁸Gd is sometimes preferred [46,47]. Considering samarium, both ¹⁴⁷Sm and ¹⁴⁹Sm were conserved due to their climitar abundance and the fact that BaOH interferences impacting these isotopes were easil, har dled using He. The list of the selected isotopes is presented in Table 1.

3.1.3 Choice of the He mode

In order to limit the duration of the analysis, only two modes of He were chosen. A first one was selected for elements that were almost in this terfered (*i.e.* ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁴⁹Sm, ¹⁶⁵Ho and ¹⁶⁹Tm). The "classical" He co. ditions proposed by the software were slightly modified as follows: He set at 4.5 mL min⁻¹ one YED at 5 V. For the other elements (*i.e.* ⁴⁵Sc, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁶Er, ¹⁶⁷Er, ¹⁷²Yb ar.a ¹⁷⁵Lu), He flow rate was first increased at 5 mL min⁻¹ with a KED maintained at 5 V or increased to 7 V. However, these modes were still not robust enough for removing polyatomic interferences such as gadolinium oxides and hydroxides on ytterbium isotopes. Further tests were also performed by increasing He flow rate up to 6 mL min⁻¹ while maintaining the KED at 7 V. These latter conditions resulted in a drastic increase of the limits of detection (LOD), not compatible with the aim of our study. The mode using He at 5 mL min⁻¹ and KED set at 7 V was finally chosen as the best compromise between reduction of IEC and sensitivity. Detection limits obtained varied from 4 pg L⁻¹ (Tm) to 123 pg L⁻¹ (Nd) (see Table S3 in appendix for more details on the method performances).

High energy He (HE-He) mode proposed by the software with He set at 10 mL min⁻¹, KED = 7 V and its specific ion path (Oct bias = -100 V) was also tested. However, this mode was less effective than the mode at 5 mL min⁻¹ of He and KED = 7 V for the removal of the interferences studied.

As an example, Fig. 1 shows the evolution of IEC on 172 Yb, for the different modes tested as a function of the gadolinium concentration (generating 156 Gd 16 O $^+$ and 155 Gd 16 OH $^+$ interferences). It is interesting to notice that this evolution is linear whatever the gas used.



Fig. 1. Evolution of IEC induced by 156 Gd 16 O $^+$ or 155 Gd 16 OH $^+$ on 172 Yb according to the concentration of gadolinium. *Legends should be read as follows: Gas used/flux (mL min* ${}^{-1}$)/KED (V). Curves ending with an arrow represent the selected modes.

Considering MH^{+} interferences, the two selected modes allowed a reduction ranging from 57% (⁸⁸SrH⁺ on ⁸⁹Y using He at 4.5 mL min⁻¹ and KED = 5 V) to 80% (⁴⁴CaH⁺ on ⁴⁵Sc using He at 5 mL min⁻¹ and KED = 7 V) by comparison with the no gas mode. MAr⁺ and MCl⁺ interferences were completely

handled whatever the mode employed. For MO⁺ and MOH⁺, percentages of removal varied from 80% for the lowest He mode ($^{130}Ba^{16}OH^+$ on ^{147}Sm) to 99.5% ($^{29}Si^{16}O^+$ and $^{28}Si^{16}OH^+$ on ^{45}Sc) for the highest He mode. Finally, $^{158}Gd^{16}OH^+$ was the most problematic interference with only 55% of removal on ^{175}Lu using He 5 mL min⁻¹ and KED = 7V mode. The removal of some interferences according different modes tested is shown in Fig. 2.



Fig. 2. Examples of the removal or enhancement c (%) of some major interferent elements on selected masses according to the nature of the gas and c flux used in comparison with no gas mode. The mode framed in black for each interferent correspond to the selected mode. H_2 mode is not represented for Gd on m/z 175 for graphical scale reason (enhancement above 1000%). Positive values correspond to reductions of interferences while negative values represent enhancements. Error bars correspond to the standard deviation of the replicates (n=3).

3.2 IEC values for selected He modes and their impacts on the REEs quantifications Scandium could not be quantified accurately by the present approach in water samples by ICP-QMS device, even by using the highest He selected mode, because Ca and Si are two major elements that strongly interfere on ⁴⁵Sc in particular through the formation of ⁴⁴CaH⁺, ²⁸Si¹⁶OH⁺ and ²⁹Si¹⁶O⁺. With the median concentrations of Ca and Si provided by FOREGS, interferences account respectively for around 2 ng L⁻¹ and for 6.7 ng L⁻¹ of Sc, while concentrations of scandium in water are not expected to overpass few dozen of ng L⁻¹ [48,49]. For sediment, Sc values should be higher and therefore more

easily quantifiable. However, Si and Ca are once again major elements in sediment matrices, although Si should be eliminated during the mineralization step using hydrofluoric acid. In addition, zirconium (yielding doubly charged 90 Zr²⁺ interference) can be present in sediment at concentrations up to 1 g kg⁻¹. Accordingly, Sc was not analysed anymore in this study. However, ICP-OES or ICP-MS using O₂ as reactive gas [50] can be used as alternative methods to specifically quantify Sc.

With the aim to assess the robustness of the present method for the determination of other REEs in water or sediment, the maximal percentage of overestimation induced by the highest interference (ninth decile of interference) on median concentrations of REEs in firsthicater was determined. Since Tm and Lu values were not indicated in the FOREGS database (median concentration < 2 ng L⁻¹), the ratios obtained from SLRS-6 and BCR-667 were used. Both concentrations were set at 0.8 ng L⁻¹ (see Table 2). Limiting concentration ratios were also determined. These ratios (*i.e.* the concentration of interferents by the concentration of rare earths) co. esc, and to the value for which overestimations induced by the interferent reach 10%. Abov \cdot this value, the method can be considered as inaccurate.

 Table 2 Overestimations induced by maximal interferences in water and sediment onto the quantification of median concentration of REEs based on FORE C database and limiting ratios for the method.

Isotopes of interest	Median concentration (ng L ⁻¹) <i>c i</i> targeted f EE in water/sc timent	IEC (ng L ⁻¹) determined using interferent ninth decile concentration in water/sediment	Overestimation on median values induced by IEC (%) Water/Sediment	Limiting ratio <u>C_{interferent}</u> <u>C_{REE}</u>
⁸⁹ Y	64/27	1.42/0.009 (Sr)	2.3/0.004	3.2*10 ⁴
¹³⁹ La	34/325	0.31/0.03 (Ba)	0.9/0.008	2.3*10 ⁴
¹⁴⁰ Ce	55/666	0.10/0.12 (La)	0.2/0.02	4.6*10 ²
¹⁴¹ Pr	9/73.5	<0.02/<0.02	<0.3/<0.03	n/a
¹⁴⁶ Nd	40/282	<0.14/<0.14	<0.4/<0.05	n/a
¹⁴⁷ Sm	9/54	0.11/0.009 (Ba)	1.2/0.02	$6.6^{*}10^{4}$
¹⁴⁹ Sm	9/54	0.08/0.007 (Ba)	0.9/0.02	$9.1^{*}10^{4}$
¹⁵¹ Eu	5/10.1	0.35/0.03 (Ba)	7.0/0.3	2.0*10 ⁴
¹⁵⁷ Cd	10/50.6	0.58/0.8 (Ce)	5.8/1.7	$1.5^{*}10^{2}$
Gu		0.47/0.5 (Pr)	4.7/1.1	2.5*10 ¹
¹⁵⁹ Tb	2/7.9	<0.07/<0.07	<3.5/<0.9	n/a
¹⁶³ Dy	8/45.3	<0.2/<0.2	<2.5/<0.5	n/a
¹⁶⁵ Ho	2/9.2	<0.02/<0.02	<1.0/<0.3	n/a
¹⁶⁶ Er	6/26.7	<0.11/<0.10	<1.9/<0.5	n/a
¹⁶⁷ Er	6/26.7	<0.10/<0.10	<1.7/<0.4	n/a

¹⁶⁹ Tm	0.8/4	<0.02/<0.02	<2.5/<0.5	n/a
¹⁷² Yb	6/25.8	0.11/0.10 (Gd)	1.9/<0.4	$1.2*10^{2}$
¹⁷⁵ Lu	0.8/3.9	<0.06/<0.06	<7.5/<1.6	$1.3*10^{3}$

Elements responsible for the interferences are indicated in parenthesis. Sediment values of median concentrations of REEs and IEC induced have been divided by 100,000 as explained in section 2.2. n/a: not applicable

As described in Table 2, the method developed during this study offers a good accuracy of the measurement by limiting interferences to less than 5% for all REEs with the exception of ¹⁵⁷Gd and ¹⁵¹Eu in water, with respective potential overestimations of 5.8% and 7.2%. However, the overestimations of Gd are unlikely to happen. Indeed, Ce and Pr are the main interferents of Gd. Yet, REEs are known to have similar chemical properties [3,9] and so they are expected to be encountered approximatively at the same ratio of natural concentrations. Considering Eu, the bias observed has been reported for a long time [46,47] and can be attributed to barium oxide and hydroxide interferences. Thus, to keep a recovery of Eu 'ower than 110%, it should be checked that the Ba/Eu concentration ratio does not exceed 2.0*11⁴. To give an exhaustive overview on IEC found for each isotope, a detailed table is displated in the supporting information section (see Table S4, appendix).

More generally in rivers strongly im p_{a} teo by urban discharges and/or which mineral composition is important, some elements may be at the origin of several REEs overestimations. In the case of the Marque River, high quantities on 5r (~ 1.2 mg L⁻¹) and Ba (~ 35 µg L⁻¹) bound to the predominance of limestone in the aquifer as, ociated to the presence of Gd (up to 1,500 ng L⁻¹) originating from treated wastewater effluents are observed. Thus, Y, La, Lu, Eu and Yb concentrations may be slightly overestimated. Limiting ratios summarized in Table 2 help to determine if the method is still accurate in such case. For instance, by calculating these ratios using data from Table S5 and S6 (appendix), we find that Y and Eu are significantly impacted by interferences in the Marque River water sample collected for this study ($\frac{C_{Sr}}{C_Y} = 3.9*10^4$ and $\frac{C_{Ba}}{C_{Eu}} = 4.4*10^4$ while limiting ratios for quantifying accurately Y and Eu are settled respectively at $3.2*10^4$ and $2.0*10^4$). The interferences on La, Lu and Yb are negligible.

3.3 Validation of the method

3.3.1 Effect of the matrix

One natural freshwater sample from the Marque River and five mineral waters with different characteristics (*i.e.* hardness, amount of dissolved salts and levels of interferents such as Sr and Ba) were used to study the matrix effects on our method. Acidified water aliquots were spiked in triplicate with known amounts of REEs close to the median concentration in European freshwaters (FOREGS values). Decrease of ISTDs signals has been observed particularly for Saint Amand® and Hépar® waters, showing an influence of the matrix onto the ionizatic * efficiency of the plasma. Thus, recoveries calculated could validate the use of the selected ISTDs. The spike recoveries obtained are displayed in Table 3 (values for the different waters without audition of REEs and concentrations of interfering major elements can be found in supporting in: "orm ition Tables S5 and S6, appendix). REEs concentrations in the non-spiked samples are given us undicative values.

Elements Spike (ng L ⁻¹)	Mont Roucous®	Volvis®	Evian®	Saint Amand®	Hépar [®]	Marque River
Y (25)	101 ± 8	1 (3 ± 2	101 ± 6	111 ± 9	103 ± 4	109 ± 3
La (50)	94 ± 4	25 ± 4	97 ± 2	99 ± 1	98 ± 6	98 ± 3
Ce (50)	97 ± 4	96 ± 3	100 ± 2	101 ± 1	98 ± 5	101 ± 5
Pr (5)	89 ± د	97 ± 2	98 ± 4	106 ± 2	96 ± 3	104 ± 4
Nd (50)	89 _ 8	94 ± 3	94 ± 3	95 ± 1	92 ± 4	94 ± 2
Sm (5)	۲ 4 ± 10	97 ± 4	96 ± 8	101 ± 2	89 ± 10	102 ± 4
Eu (1)	<u> გე + 13</u>	101 ± 10	109 ± 17	93 ± 21	120 ± 28	89 ± 14
Gd (5)	י יד ± 8	117 ± 3	124 ± 9	109 ± 13	114 ± 16	86 ± 9
Tb (1)	⊥ປ9 ± 4	109 ± 2	107 ± 8	104 ± 3	98 ± 6	86 ± 9
Dy (5)	91 ± 21	111 ± 3	99 ± 7	94 ± 2	101 ± 9	87 ± 6
Ho (1)	106 ± 4	112 ± 5	104 ± 4	103 ± 5	89 ± 10	93 ± 11
Er (5)	104 ± 7	110 ± 7	106 ± 8	99 ± 5	96 ± 3	95 ± 10
Tm (1)	105 ± 5	112 ± 2	105 ± 8	102 ± 3	89 ± 3	104 ± 7
Yb (5)	109 ± 12	105 ± 4	99 ± 7	99 ± 3	101 ± 18	84 ± 16
Lu (1)	102 ± 17	93 ± 7	100 ± 8	101 ± 4	99 ± 1	120 ± 16

Table 3 Recoveries obtained for spiked commercial o natural waters (n = 3)

Uncertainties correspond to the standard deviation of the replicates.

The method was found to be consistent to quantify REEs at such levels of concentration with recoveries ranging from 84% (for Yb) to 124% (for Gd). Most of recoveries obtained ranged from 90% to 110%. Marque River was the water matrix for which recoveries are most variable maybe due to its

complexity and the potential presence of colloids [51]. Moreover, most of relative standard deviations were under 10% which is tolerable. Elements with the highest standard deviations (*i.e.* Eu, Gd, Yb and Lu) were generally those found at the lowest concentrations and analysed using strong helium mode. The use of this mode resulted in a loss of sensitivity explaining higher variability, which explains the largest variation observed. From this experiment, the choice of the ISTDs used has been validated as recoveries obtained were satisfactory.

3.3.2 Comparison with certified materials (waters and sediments)

The results obtained for the certified reference waters are summarized in Table 4. Concerning AQUA-1 (potable water), preliminary values have been presented at the folge Goldschmidt Conference (Barcelona, Spain) [52] and the results found here were concrent with those provided by the laboratory intercomparison (including our laboratory). Chir own values are not displayed here as a publication about AQUA-1 compilation measurements is not available yet. The recoveries obtained ranged from 95% to 105% excepting for Eu with a repovery of 83%. However, as explained previously, Ba interferences could skew europium concentration and some laboratories may overestimate the Eu level.

 Table 4 Comparison of the values four
 in truis study with the values from the literature for SLRS-6 and SLEW-3

 certified waters

	J_75	-σ (freshwater)	SLEW-3 (estuarine water)		
	(n =).(D, values in ng L^{-1})	$(n = 10, values in ng L^{-1})$		
Elements	This s. dy	Literature values [53]	This study	Literature values [54-58]	
Y	12C <u>~</u> 3	128 ± 6	37.8 ± 2.0	39.8 ± 1.7	
La	250 ± 5	248.3 ± 12.1	8.31 ± 0.38	8.07 ± 0.36	
Ce	300 ± 5	292.7 ± 15.1	7.17 ± 0.55	7.10 ± 0.35	
Pr	58.6 ± 1.2	59.1 ± 1.8	1.48 ± 0.12	1.64 ± 0.08	
Nd	233 ± 4	227.8 ± 4.1	7.66 ± 0.64	8.22 ± 0.28	
Sm	39.1 ± 0.8	39.5 ± 1.5	7.44 ± 0.51	7.37 ± 0.31	
Eu	7.31 ± 0.32	7.26 ± 0.35	0.74 ± 0.07	0.55 ± 0.05	
Gd	31.8 ± 0.7	31.6 ± 2.5	3.27 ± 0.53	3.13 ± 0.05	
Tb	3.87 ± 0.15	4.07 ± 0.27	0.51 ± 0.08	0.46 ± 0.03	
Dy	21.2 ± 0.8	21.9 ± 1.1	3.44 ± 0.33	3.44 ± 0.13	
Но	4.25 ± 0.10	4.3 ± 0.3	0.93 ± 0.07	0.91 ± 0.02	
Er	12.3 ± 0.6	12.4 ± 0.7	3.07 ± 0.41	2.72 ± 0.14	
Tm	1.77 ± 0.11	1.79 ± 0.18	0.42 ± 0.04	0.35 ± 0.04	
Yb	11.1 ± 0.3	11.2 ± 0.7	1.82 ± 0.40	1.96 ± 0.11	
Lu	1.81 ± 0.15	1.91 ± 0.23	<0.90	0.31 ± 0.02	

Literature values correspond to the estimated mean of the references \pm estimated standard deviation if there are more than one published concentration. Note that Yeghicheyan et al.^[48] values correspond to mean \pm expanded uncertainties (U_{Lit}). Study values correspond to the mean \pm standard deviation.

Results obtained for SLRS-6 were in adequacy with those published by Yeghicheyan *et al.* [53] based on a nine-laboratory intercalibration. To determine the coherence of our results compared to those published in the literature, E_n number (ISO 13528) [59] were calculated using Equation 1 as described by Yeghicheyan *et al.* (2013) [60].

$$E_n=rac{ar{\mathrm{y}}-\mu}{\sqrt{U_{Lab}^2+U_{Lit}^2}}$$
 (Eqn 1)

In this equation \bar{y} is the mean of our study, μ represents the mean of found in the literature, U_{Lab} and U_{Lit} correspond to the expanded uncertainties of our study and the intercomparison study. Critical value was set at 1 because expanded uncertainties were used for the calculation. If $E_n < 1$, the values found are coherent with those previously reported. Sumption-Wilk normality tests were performed on our data choosing p-value of 0.01. For SLRs c all the elements followed a normal distribution and thus expanded uncertainties could be calculated as follows using Equation 2:

$$\upsilon_{Lab} = k * \sigma_{Lab}$$
 (Eqn 2)

with k corresponding to a level of confidence of 95% for values following a normal distribution (here k = 2) and σ_{Lab} representing the standard deviation. All the E_n values ranged from 0.06 (Er) to 0.52 (Tb) showing compatibility of the obtained results with those of the intercomparison study. Moreover, measurements were repeatable with standard deviation below 10% for all the elements.

Concerning the estuarine water SLEW-3, concentrations that can be found in literature are generally given after preconcentration steps and removal of the matrix [54-58,61]. Here, the data reported are given without any other modification of the sample than a 5-fold dilution for limiting total dissolved solid content. Overall, values obtained were in adequacy with those found in literature with less than 10% of difference excepting for Eu and Lu which was below the detection limit. Y was analysed using both low and high He modes since we suspected high potential interference of Sr. Y concentration

fell from 45 ng L⁻¹ using the low mode to 38 ng L⁻¹ using the high mode that could come from a residual ⁸⁸SrH⁺ interference with the low mode in such matrix. The concentration of Eu was slightly higher than expected. Ba interference may not explain the whole difference as interferences in SLEW-3 are expected to be around 0.1 ng L⁻¹ *versus* 0.2 ng L⁻¹ of overestimation (See Table 3 and Table S5 and S6 in appendix). Moreover, chloride interferences have been studied and are not expected to occur. This overestimation is yet not clear but is certainly related to matrix effect such as non-spectral interferences in saline matrix as explained by Rodushkin *et al.* [62]. Specific ICP setting configuration, matrix-matched calibration or the use of another ISLEW-3 water for the following reason: the average values displayed in Table 4 were formed on the Same.

In conclusion for SLEW-3 water, analyses carried or d.d not allow to fully validate our method in saline matrices due to: (*i*) high standad deviations for Gd and Yb; (*ii*) limits of detection/quantification too high for Lu and (*iii*) overestimation of Eu. However, results remain quite robust for a direct analysis strategy of Y. La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm in such saline matrix using classical introduction system and plasma configuration.

Concerning sediment matrices, results obtained for the four reference materials are summarized in Table 5.

 Table 5 Comparison of our values with the certified ones for the BCR-667, Metranal-1 and HISS-1 sediments

 and proposed indicative values for PACS-3 certified sediment.

		667					PACS-3
	BCR (n = 5, value	-667 s in mg kg ⁻¹)	$(n = 3, values in mg kg^{-1})$ $(n = 3, values in mg kg^{-1})$		HISS-1 (n = 3, values in mg kg ⁻¹)		(n = 2, values in mg kg⁻¹)
	This study	Certified	This	Literature	This study	Literature	
	This study	values	study	values [63]	This study	values [64-66]	This study
Y	19.1 ± 1.3	16.7-25.3	22.1 ± 0.5	17.5 ± 0.8	3.07 ± 0.15	3.00 ± 0.01	14.2 ± 0.2
La	25.3 ± 2.0	27.8 ± 1.0	32.5 ± 1.1	36.3 ± 1.1	4.14 ± 0.36	3.6 ± 0.6	14.9 ± 0.4

Ce	53.3 ± 3.5	56.7 ± 2.5	65.9 ± 2.3	71.6 ± 3.6	8.70 ± 0.70	8.9 ± 0.5	33.1 ± 0.3
Pr	6.12 ± 0.29	6.1 ± 0.5	7.42 ± 0.26	7.69 ± 0.24	0.94 ± 0.06	0.79 ± 0.01	3.98 ± 0.05
Nd	23.5 ± 1.4	25.0 ± 1.4	28.5 ± 1.1	32.0 ± 0.9	3.59 ± 0.23	3.6 ± 0.6	16.3 ± 0.1
Sm	4.68 ± 0.18	4.66 ± 0.20	5.36 ± 0.23	5.61 ± 0.20	0.63 ± 0.02	0.70 ± 0.02	3.44 ± 0.04
Eu	0.96 ± 0.06	1.00 ± 0.05	1.05 ± 0.03	1.16 ± 0.1	0.14 ± 0.02	0.195 ± 0.008	0.90 ± 0.01
Gd	4.25 ± 0.21	4.41 ± 0.12	4.61 ± 0.20	4.72 ± 0.22	0.54 ± 0.05	0.54 ± 0.04	3.14 ± 0.03
Tb	0.65 ± 0.05	0.68 ± 0.02	0.67 ± 0.02	0.75 ± 0.05	0.082 ± 0.005	0.11 ± 0.03	0.48 ± 0.02
Dy	3.91 ± 0.21	4.01 ± 0.14	3.93 ± 0.17	3.66 ± 0.18	0.51 ± 0.03	0.51 ± 0.11	2.96 ± 0.02
Но	0.78 ± 0.03	0.80 ± 0.06	0.79 ± 0.03	0.68 ± 0.03	0.10 ± 0.01	0.12 ± 0.01	0.60 ± 0.01
Er	2.25 ± 0.10	2.35 ± 0.15	2.18 ± 0.04	1.92 ± 0.13	0.32 ± 0.03	0.32 ± 0.05	1.68 ± 0.04
Tm	0.32 ± 0.01	0.33 ± 0.03	0.32 ± 0.02	0.30 ± 0.03	0.044 ± 0. ` '3	0.06 ± 0.02	0.24 ± 0.01
Yb	2.07 ± 0.10	2.20 ± 0.09	2.01 ± 0.06	1.78 ± 0.11	0.34 ± J.05	0.42 ± 0.08	1.54 ± 0.04
Lu	0.31 ± 0.02	0.33 ± 0.02	0.30 ± 0.02	0.27 ± 0.03	0.045 <u>-</u> ∩.∪∪4	0.051 ± 0.002	0.22 ± 0.01

Literature values correspond to the estimated mean of the references \pm estimated standard deviation if there are more than one published concentration. Study values corres sons' to the mean \pm standard deviation.

The European reference for the analysis of REEs (BCR-667) [50,67,68] was firstly used for checking the accuracy of our method. Contrary to SLRS-C comparisons with existing values were assessed using recovery calculations. Indeed, due to the new number of replicates (*n* = 5), parametric test such as Student's T-test could not be used. Values obtained were in conformity with the certified values with recoveries ranging from 91% ('...) to 100% (Pr, Sm). The other sediments (Metranal-1 [63] and HISS-1 [64-66]) were secondly and 'vsed and compared to values found in literature. Note that for HISS-1 all the elements were not occudied in some publications [64,66] and that some differences can be observed for the concentrations obtained (explaining some high standard deviations among the LREEs concentrations). Overall, concentrations found were in good agreement with the compiled value except for Pr which concentration has been determined by only one research group [65]. Finally, values for PACS-1 [69] and PACS-2 [65,70-72] are really close to each other's and to our values determined for PACS-1 [69] and PACS-2 [65,70-72] are really close to each other's and to our values determined for PACS-3. Therefore, even if the number of replicates was not statistically robust, values obtained in this study can be proposed as indicative REEs concentration in PACS-3 due to the good recoveries obtained for the concentrations of REEs in other sediments analysed. Overall, this

set of results clearly validate our method for the determination of all the REEs in digested sedimentary samples.

Conclusion

This study proposes a direct method using classical ICP-QMS with standard introduction system for quantifying REEs in freshwaters, estuarine waters and digested sediments. The method takes into account and corrects accurately natural concentrations of the most common interferences (argides, chlorides, hydroxides, oxides and doubly charged) and can be transposed to many control and research laboratories working on environmental samples. Holiun gas was proved to be better than H₂ for the removal of polyatomic interferences. Overes ima ion induced by interferences for almost all REEs could be reduced below 4%, level that can be considered as acceptable. The method has been validated by determining recoveries of REEs in different water-spiked matrices and by analysing certified reference materials. Concentretions of REEs in PACS-3 have been assessed for the first time in this study. As there is no precondentration step, this method is limited to samples with sufficient levels of REEs (*i.e.* above the LOQ, and thus may be not compatible for studies focused on pristine environments. Besides, two clonents remain tricky to quantify: Sc for which interferences due to major anions (Ca, Si) cannot be completely solved, and Eu for which overestimation can reach 7.2% due to barium interferences. For some specific cases characterized by very low concentration of REEs combined with high concentration of Sr (e.g. estuarine or marine water) and Gd (e.g. rivers fed with high amount of wastewater treatment plant effluent), the present method also suffers from some limitations. Indeed, ⁸⁸SrH⁺, ¹⁵⁶Gd¹⁶O⁺/¹⁵⁵Gd¹⁶OH⁺ and ¹⁵⁸Gd¹⁶OH⁺ can respectively skew the quantification of ⁸⁹Y, ¹⁷²Yb and ¹⁷⁵Lu respectively. Generally, preconcentration of REEs and removal of matrix are performed for these types of waters. The removal of Sr is never studied while Ba removal is always commented as BaO and BaOH that are well known for being strong interferences on Eu. However, the scope of this method has been set by calculating limiting ratios. Finally, even if this method is dedicated to quantification of REEs with a simple quadrupole ICP-MS equipped with a

collision reaction cell without any preconcentration step or modification of the introduction system, it should be interesting to test the performance of this method coupled with a desolvating system. The latter should allow to further reduce the IEC and to enhance the sensitivity of this method.

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Appendix A. Supplementary data and Supplementary duca to this article can be found online at doi:...

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31

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32

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2

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Highlights

- A direct method of quantification of REEs in water and digested sediment is proposed.
- The method does not require mathematical corrections and preconcentration steps.
- Flow of He gas and Kinetic Energy Discrimination (KED) voltages have been optimized.
- The method allows accurate quantification of REEs in environmental conditions.
- The method was validated using spiking experiments and certified reference materials.



■ H2/6/5 ■ He/4.5/5 ■ He/5/5 ■ He/5/7 ⊡ HE-He

Figure 1