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

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1 **Abstract**

2 The present study is based on the use of a conventional quadrupole ICP-MS for determining directly
3 rare earth elements (REEs) in both fresh or slightly saline waters and digested sediments. The
4 development of a robust method using a collision reaction cell (different collision gases and fluxes
5 have been tested) and kinetic energy discrimination is proposed for the accurate quantification of
6 REEs without any mathematical corrections and preconcentration steps. The choice of He gas over H₂
7 and its flow in the collision reaction cell as well as the isotopes studied are thoroughly discussed with
8 the aim of reducing drastically interferences. The exhaustive list of interferences (argides, chlorides,
9 oxides, hydroxides, hydrides and doubly charged) have been investigated for the first time at
10 different concentration levels, relevant with those found in environmental matrices based on the
11 FORum of European Geological Surveys (FOREGS) database. The interference equivalent
12 concentrations (IECs) have been determined and summarized. Although the impact of barium
13 interferences onto europium and the impossibility to measure Sc have been pointed out, this
14 method has been validated for all the other REEs in aquatic environmental matrices by studying the
15 recoveries of spiked natural waters (5 commercial mineral waters with content of dry residue ranging
16 from 22 to 2513 mg L⁻¹ and a filtrated natural river water from Northern France) with relevant
17 concentrations of REEs. Standard reference materials (*i.e.* three waters (AQUA-1, SLRS-6 and SLEW-
18 3) and four sediments (BCR-667, HISS-1, Metranal-1 and PACS-3)) were also analysed to ensure the
19 robustness of the method.

20

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

22

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 investigating the scavenging of particulate matter and sedimentation processes [6,7]. In addition, REEs have become extremely important for high technology applications and processes due to their unique magnetic, phosphorescent, and catalytic properties [8,9]. Moreover, REEs are considered as “Technology Critical Elements” (TCEs) by several scientific organizations (*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 worldwide [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

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

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

11 Herein, a simple and direct method for the determination of REEs in aquatic environmental samples
12 (*i.e.* waters and digested sediments) is proposed without any mathematical corrections, using ICP-
13 QMS equipped with a standard introduction system and a collision reaction cell. Different gases and
14 their fluxes, kinetic energy discrimination (KED) voltages and isotopes have been tested to remove
15 spectral interferences. For the first time, the exhaustive list of potential interferents has been studied
16 at different environmental concentration levels based on FORum of European Geological Surveys
17 (FOREGS) database. The method has been validated by assessing the potential impact of remaining
18 interferents for the quantification of REEs, the recoveries of low REEs levels in spiked natural water
19 matrices and the accuracy of measurements for several certified water and sediment references.

20 2. Material and methods

21 2.1 Reagents

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

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

8 2.2 Determination of interference equivalent concentrations (IECs)

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

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

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

6 2.3 Matrix effect on recovery of spiked solutions

7 A second set of experiments was performed with different French commercial mineral waters (Mont
8 Roucous[®], Evian[®], Volvic[®], Saint Amand[®], Hépar[®]) as matrices. These waters were selected in order
9 to cover a wide range of hardness and amount of dry residues (ranging from 22 mg L⁻¹ for Mont
10 Roucous[®] to 2513 mg L⁻¹ for Hépar[®] (see Table S2, appendix). Waters were acidified at 2% (v/v) using
11 ultrapure HNO₃. In addition, a natural water sample from the Marque River (France) was used as a
12 matrix. Some of its main features have been previously described [37,38]. Briefly, the Marque River
13 flows in northern France close to the city of Lille. Its annual average flow is around 1 m³ s⁻¹ at the
14 sampling site located at Villeneuve d'Ascq. The river Marque is 32 km long, its watercourse receives 7
15 main effluents of wastewater treatment plants (WWTP), corresponding to approximately 150,000
16 inhabitant equivalent. Its status is bad according to the ranking of the Water Framework Directive
17 (WFD, 2000) due to an excess of nutrients, pesticides, industrial pollutants and a lack of oxygen.
18 Sampling was performed 200 meters upstream the Villeneuve d'Ascq wastewater treatment plant (N
19 50° 37' 48.4"; E 3° 11' 6.6"). The freshwater was collected in a 5 L high-density polyethylene (HDPE)
20 bottle previously cleaned with acid and rinsed with ultrapure water. Filtration of the whole collected
21 water was performed using polyethersulfone filter (0.45 µm of porosity) and water was poured in
22 another 5 L precleaned HDPE bottle. Filters were changed as little as possible to limit potential
23 contamination. No blank control or study of the effect of the filtration on the concentrations of REEs
24 was carried out as this step was mainly performed to remove particles that could clog the
25 introduction system of the ICP-MS. The filtrated sample was immediately acidified at 2% (v/v) using
26 ultrapure HNO₃ before analysis. All these waters were analysed in triplicate without and with spike of

1 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,
2 Nd). These concentrations were chosen based on SLRS-6 and FOREGS values REEs ratio.
3 Concentrations of some major elements which could interfere with REEs (Ba, Ca, Si, Sr) were also
4 determined.

5 2.4 Protocols for water reference materials analyses

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

12 2.5 Protocol for sediment reference materials analyses

13 Four reference materials have been used to validate the analytical method in sediment matrices:
14 BCR-667 (estuarine sediment reference material from European Commission - Joint Research
15 Centre), Metranal-1 (river sediment certified by the METROCHEM group), as well as PACS-3 and HISS-
16 1 (marine sediments certified by NRC-CNRC). Total mineralization was performed with 0.2 g of
17 sediment using a mixture of high purity nitric and hydrofluoric acids followed by an *aqua regia* attack
18 according to the protocol of Boughriet *et al.* [39]. Prior quantification of REEs, digestates were
19 filtered (0.45 µm, cellulose acetate) then diluted 1000-fold using 2% (v/v) HNO₃ to obtain a
20 concentration of REEs in the ng L⁻¹ range. Blank samples (*n* = 6) were systematically performed
21 following the same digestion and filtration procedures. Blank concentrations of REEs obtained were
22 negligible and did not impact the concentrations found in sediments. Concentrations of REEs in the
23 residue were not studied as the latter was not taking into account for REEs quantification in the
24 certified materials.

1 2.6 Elemental analyses
 2 Major elements (*i.e.* interfering elements Ba, Ca, Si and Sr) were quantified using an inductively
 3 coupled plasma optical emission spectrometer (ICP-OES 5110 VDV, Agilent Technologies) calibrated
 4 using standard solutions. The concentrations of REEs were determined using an inductively coupled
 5 plasma single quadrupole mass spectrometer (ICP-MS 7900, Agilent Technologies) equipped with a
 6 standard introduction system [borosilicate MicroMist concentric nebulizer (0.4 mL min⁻¹), quartz
 7 double pass spray chamber cooled at 2°C, quartz torch (2.5 mm ID) and nickel cones]. X-lenses were
 8 selected as ion optic configuration. High purity He and H₂ (> 99.999%) were used as collision/reaction
 9 gases in the octopole reaction system (ORS) to study polyatomic interferences suppression. Kinetic
 10 energy discrimination (KED) was also applied. Six different modes were used during this study. Ion
 11 lens parameters were optimized daily. Main parameters of the device and percentage of oxides and
 12 doubly charged formation are summarized in Table 1. To correct possible additional matrix effects
 13 and signal drift, ⁷⁴Ge (for Sc and Y), ¹¹⁵In (for Y and La - Eu), ¹⁸⁵Re (for La - Lu) and ²⁰⁵Tl (for Gd - Lu)
 14 were used as internal standards (ISTDs) with online addition of 50 µg L⁻¹ stock solution in 2% (v/v)
 15 HNO₃. The concentration of ISTDs, after dilution in the samples, were around 3.4 µg L⁻¹. ISTDs fitting
 16 the best with SLRS-6 reference material concentrations were used and chosen according to the
 17 experiment.

18 **Table 1** ICP-MS and collision cell conditions

19 *Shaded modes indicate the modes 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

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

Collision reaction cell conditions					
No gas		He		H ₂	
0 mL min ⁻¹ KED 5 V Oct bias -8 V	4.5 mL min ⁻¹ KED 5 V Oct bias -18 V	5 mL min ⁻¹ KED 5 V Oct bias -18 V	5 mL min ⁻¹ KED 7 V Oct bias -18 V	10 mL min ⁻¹ KED 7 V Oct bias -100 V	6 mL min ⁻¹ KED 5 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⁺ /Ce ⁺ (%)					
1.5-2.6	2.0-2.8	2.1-2.9	2.2-3.0	2.5-2.9	0.4-0.7

1 3. Results and discussions

2 3.1 Development of the method

3 3.1.1 Determination of the collision/reaction cell gas

4 The preliminary step of this study was to select the most suitable gas to handle spectral interferences
5 during the analysis of REEs. In the light of the information found in the literature [32,33] and the
6 results obtained, helium appeared to be the most promising gas for suppressing interferences in
7 water and sediment matrices. For the 24 isotopes initially tested, the use of He always allowed
8 reduction of the interference in comparison with the no gas mode. By contrast, the use of H₂ showed
9 limitations. Indeed, for 18 isotopes out of the 24 tested, H₂ induced stronger interferences than the
10 no gas mode. This can be explained by the fact that some elements are directly interfered by MH⁺ or
11 MOH⁺ ionic species (*e.g.* ^{45}Sc , ^{139}La , ^{147}Sm , ^{175}Lu versus $^{44}\text{CaH}^+$, $^{138}\text{BaH}^+$, $^{130}\text{Ba}^{16}\text{OH}^+$ and $^{158}\text{Gd}^{16}\text{OH}^+$
12 respectively). The impact of REEs-hydride interferences on the determination of targeted REEs was
13 not significant in our case due to the low concentration of REEs employed [33,40]. It should be
14 however noted that the use of H₂ significantly reduced the amount of doubly charged $^{90}\text{Zr}^{2+}$
15 interference onto ^{45}Sc . Removal of doubly charged species by H₂ has already been observed for other
16 elements [41,42]. Such removal may be explained either by $^{90}\text{ZrH}^+$ formation [41,43] (although it
17 should be limited [44]), or charge exchange [41]. By contrast, all tested He modes were found to

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

3 3.1.2 Selection of the isotopes

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

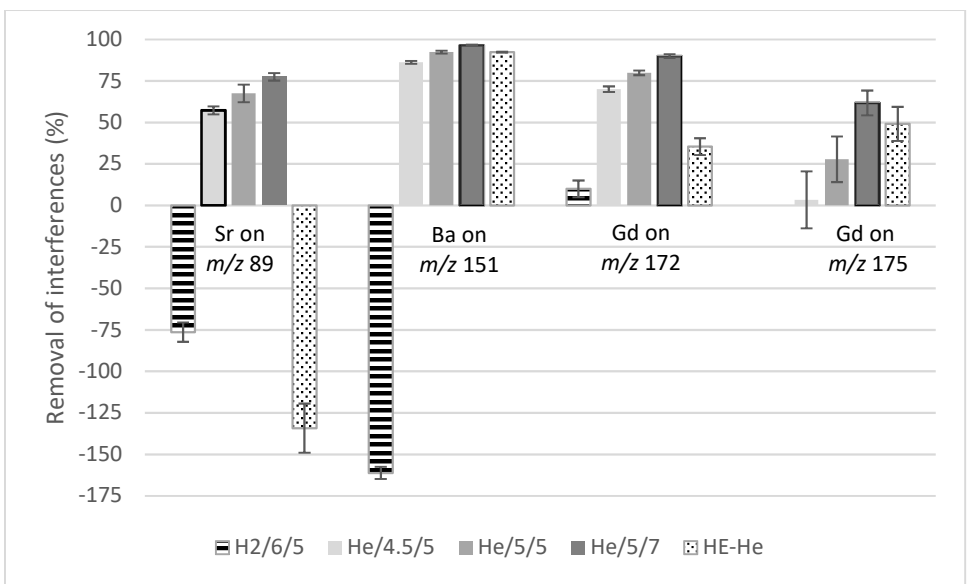
13 3.1.3 Choice of the He mode

14 In order to limit the duration of the analysis, only two modes of He were chosen. A first one was
15 selected for elements that were almost not interfered (*i.e.* ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{149}Sm ,
16 ^{165}Ho and ^{169}Tm). The “classical” He conditions proposed by the software were slightly modified as
17 follows: He set at 4.5 mL min^{-1} and KED at 5 V. For the other elements (*i.e.* ^{45}Sc , ^{151}Eu , ^{157}Gd , ^{159}Tb ,
18 ^{163}Dy , ^{166}Er , ^{167}Er , ^{172}Yb and ^{175}Lu), He flow rate was first increased at 5 mL min^{-1} with a KED
19 maintained at 5 V or increased to 7 V. However, these modes were still not robust enough for
20 removing polyatomic interferences such as gadolinium oxides and hydroxides on ytterbium isotopes.
21 Further tests were also performed by increasing He flow rate up to 6 mL min^{-1} while maintaining the
22 KED at 7 V. These latter conditions resulted in a drastic increase of the limits of detection (LOD), not
23 compatible with the aim of our study. The mode using He at 5 mL min^{-1} and KED set at 7 V was finally
24 chosen as the best compromise between reduction of IECs and sensitivity. Detection limits obtained
25 varied from 14 pg L^{-1} (Tm) to 179 pg L^{-1} (Y) (see Table S3 in appendix for more details on the method
26 performances).

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

4 As an example, the evolution of IECs on ¹⁷²Yb, for the different modes tested as a function of the
 5 concentration of gadolinium (generating ¹⁵⁶Gd¹⁶O⁺ and ¹⁵⁵Gd¹⁶OH⁺ interferences) has been assessed
 6 (see Fig. S1, appendix). It is interesting to notice that this evolution is linear whatever the gas used.

7 Considering MH⁺ interferences, the two selected modes allowed a reduction ranging from 57%
 8 (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
 9 and KED = 7 V) by comparison with the no gas mode. MAr⁺ and MCl⁺ interferences were completely
 10 handled whatever the mode employed. For MO⁺ and MOH⁺, percentages of removal varied from 80%
 11 for the lowest He mode (¹³⁰Ba¹⁶OH⁺ on ¹⁴⁷Sm) to 99.5% (²⁹Si¹⁶O⁺ and ²⁸Si¹⁶OH⁺ on ⁴⁵Sc) for the highest
 12 He mode. Finally, ¹⁵⁸Gd¹⁶OH⁺ was the most problematic interference with only 55% of removal on
 13 ¹⁷⁵Lu using He 5 mL min⁻¹ and KED = 7V mode. The removal of some interferences according different
 14 modes tested is shown in Fig. 1.



15
 16 **Fig. 1.** Examples of the removal or enhancement (%) of some major interferent elements on selected masses
 17 according to the nature of the gas and its flux used in comparison with no gas mode. *The mode framed in black*
 18 *for each interferent correspond to the selected mode. H₂ mode is not represented for Gd on m/z 175 for*

1 graphical scale reason (enhancement above 1000%). Positive values correspond to reductions of interferences
 2 while negative values represent enhancements. Error bars correspond to the standard deviation of the
 3 replicates (n=3).

4 3.2 IECs values for selected He modes and their impacts on the REEs quantifications
 5 Scandium could not be quantified accurately by the present approach in water samples by ICP-QMS
 6 device, even by using the highest He selected mode, because Ca and Si are two major elements that
 7 strongly interfere on ^{45}Sc in particular through the formation of $^{44}\text{CaH}^+$, $^{28}\text{Si}^{16}\text{OH}^+$ and $^{29}\text{Si}^{16}\text{O}^+$. With
 8 the median concentrations of Ca and Si provided by FOREGS, interferences account respectively for
 9 around 2 ng L^{-1} and for 6.7 ng L^{-1} of Sc, while concentrations of scandium in water are not expected to
 10 overpass few dozen of ng L^{-1} [48,49]. For sediment, Sc values should be higher and therefore more
 11 easily quantifiable. However, Si and Ca are once again major elements in sediment matrices,
 12 although Si should be eliminated during the mineralization step using hydrofluoric acid. In addition,
 13 zirconium (yielding doubly charged $^{90}\text{Zr}^{2+}$ interference) can be present in sediment at concentrations
 14 up to 1 g kg^{-1} . Accordingly, Sc was not analysed anymore in this study. However, ICP-OES or ICP-MS
 15 using O_2 as reactive gas [50] can be used as alternative methods to specifically quantify Sc.

16 With the aim to assess the robustness of the present method for the determination of other REEs in
 17 water or sediment, the maximal percentage of overestimation induced by the highest interference
 18 (ninth decile of interference) on median concentrations of REEs in freshwater was determined. Since
 19 Tm and Lu values were not indicated in the FOREGS database (median concentration $< 2 \text{ ng L}^{-1}$), the
 20 ratios obtained from SLRS-6 and BCR-667 were used. Both concentrations were set at 0.8 ng L^{-1} (see
 21 Table 2). Limiting concentration ratios were also determined. These ratios (*i.e.* the concentration of
 22 interferences by the concentration of rare earths) correspond to the value for which overestimations
 23 induced by the interferent reach 10%. Above this value, the method can be considered as inaccurate.

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

Isotopes of	Median	IECs (ng L^{-1}) determined	Overestimation on	Limiting
-------------	--------	--	-------------------	----------

interest	concentration (ng L ⁻¹) of targeted REE in water/sediment	using interferent ninth decile concentration in water/sediment	median values induced by IECs (%) Water/Sediment	ratio $\frac{C_{interferent}}{C_{REE}}$
⁸⁹ Y	64/257	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 Gd	10/50.6	0.58/0.8 (Ce) 0.47/0.5 (Pr)	5.8/1.7 4.7/1.1	1.5*10 ² 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

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

4 As described in Table 2, the method developed during this study offers a good accuracy of the
5 measurement by limiting interferences to less than 5% for all REEs with the exception of ¹⁵⁷Gd and
6 ¹⁵¹Eu in water, with respective potential overestimations of 5.8% and 7.2%. However, the
7 overestimations of Gd are unlikely to happen. Indeed, Ce and Pr are the main interferents of Gd. Yet,
8 REEs are known to have similar chemical properties [3,9] and so they are expected to be
9 encountered approximatively at the same ratio of natural concentrations. Considering Eu, the bias
10 observed has been reported for a long time [46,47] and can be attributed to barium oxide and
11 hydroxide interferences. Thus, to keep a recovery of Eu lower than 110%, it should be checked that
12 the Ba/Eu concentration ratio does not exceed 2.0*10⁴. To give an exhaustive overview on IECs found
13 for each isotope, a detailed table is displayed in the supporting information section (see Table S4,
14 appendix).

15 More generally in rivers strongly impacted by urban discharges and/or which mineral composition is
16 important, some elements may be at the origin of several REEs overestimations. In the case of the

1 Marque River, high quantities of Sr ($\sim 1.2 \text{ mg L}^{-1}$) and Ba ($\sim 35 \text{ }\mu\text{g L}^{-1}$) bound to the predominance of
2 limestone in the aquifer associated to the presence of Gd (up to $1,500 \text{ ng L}^{-1}$) originating from treated
3 wastewater effluents are observed. Thus, Y, La, Lu, Eu and Yb concentrations may be slightly
4 overestimated. Limiting ratios summarized in Table 2 help to determine if the method is still accurate
5 in such case. For instance, by calculating these ratios using data from Table S5 and S6 (appendix), we
6 find that Y and Eu are significantly impacted by interferences in the Marque River water sample
7 collected for this study ($\frac{C_{Sr}}{C_Y} = 3.9 \cdot 10^4$ and $\frac{C_{Ba}}{C_{Eu}} = 4.4 \cdot 10^4$ while limiting ratios for quantifying
8 accurately Y and Eu are settled respectively at $3.2 \cdot 10^4$ and $2.0 \cdot 10^4$). The interferences on La, Lu and
9 Yb are negligible.

10 3.3 Validation of the method

11 3.3.1 Effect of the matrix

12 One natural freshwater sample from the Marque River and five mineral waters with different
13 characteristics (*i.e.* hardness, amount of dissolved salts and levels of interferences such as Sr and Ba)
14 were used to study the matrix effects on our method. Acidified water aliquots were spiked in
15 triplicate with known amounts of REEs close to the median concentration in European freshwaters
16 (FOREGS values). Decrease of ISTDs signals has been observed particularly for Saint Amand® and
17 Hépar® waters, showing an influence of the matrix onto the ionization efficiency of the plasma. Thus,
18 recoveries calculated could validate the use of the selected ISTDs. The spike recoveries have been
19 determined (see Table S7, appendix). Values for the different waters without addition of REEs and
20 the concentrations of interfering major elements can be found in supporting information (see Tables
21 S5 and S6, appendix). The concentrations of REEs in the non-spiked samples are given as indicative
22 values.

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

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

7 3.3.2 Comparison with certified materials (waters and sediments)

8 The results obtained for the certified reference waters are summarized in Table 3. Concerning AQUA-
 9 1 (potable water), preliminary values have been presented at the 2019 Goldschmidt Conference
 10 (Barcelona, Spain) [52] and the results found here were coherent with those provided by the
 11 laboratory intercomparison (including our laboratory). Our own values are not displayed here as a
 12 publication about AQUA-1 compilation measurements is not available yet. The recoveries obtained
 13 ranged from 95% to 105% excepting for Eu with a recovery of 83%. However, as explained previously,
 14 Ba interferences could skew the concentration of europium and some laboratories may overestimate
 15 the Eu level.

16 **Table 3** Comparison of the values found in this study with the values from the literature for SLRS-6 and SLEW-3
 17 certified waters

Elements	SLRS-6 (freshwater) (<i>n</i> = 20, values in ng L ⁻¹)		SLEW-3 (estuarine water) (<i>n</i> = 10, values in ng L ⁻¹)	
	This study	Literature values [53]	This study	Literature values [54-58]
Y	128 ± 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
Ho	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

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

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

$$8 \quad E_n = \frac{\bar{y} - \mu}{\sqrt{U_{Lab}^2 + U_{Lit}^2}} \text{ (Eqn 1)}$$

9 In this equation \bar{Y} is the mean of our study, μ represents the mean of found in the literature, U_{Lab} and
10 U_{Lit} correspond to the expanded uncertainties of our study and the intercomparison study. Critical
11 value was set at 1 because expanded uncertainties were used for the calculation. If $E_n < 1$, the values
12 found are coherent with those previously reported. Shapiro-Wilk normality tests were performed on
13 our data choosing p-value of 0.01. For SLRS-6 all the elements followed a normal distribution and
14 thus expanded uncertainties could be calculated as follows using Equation 2:

$$15 \quad U_{Lab} = k * \sigma_{Lab} \text{ (Eqn 2)}$$

16 with k corresponding to a level of confidence of 95% for values following a normal distribution (here
17 $k = 2$) and σ_{Lab} representing the standard deviation. All the E_n values ranged from 0.06 (Er) to 0.52
18 (Tb) showing compatibility of the obtained results with those of the intercomparison study.
19 Moreover, measurements were repeatable with standard deviation below 10% for all the elements.

20 Concerning the estuarine water SLEW-3, concentrations that can be found in literature are generally
21 given after preconcentration steps and removal of the matrix [54-58,61]. Here, the data reported are
22 given without any other modification of the sample than a 5-fold dilution for limiting total dissolved
23 solid content. Overall, values obtained were in adequacy with those found in literature with less than
24 10% of difference excepting for Eu and Lu which was below the detection limit. Y was analysed using
25 both low and high He modes since we suspected high potential interference of Sr. The concentration

1 of Y fell from 45 ng L⁻¹ using the low mode to 38 ng L⁻¹ using the high mode that could come from a
 2 residual ⁸⁸SrH⁺ interference with the low mode in such matrix. The concentration of Eu was slightly
 3 higher than expected. Ba interference may not explain the whole difference as interferences in
 4 SLEW-3 are expected to be around 0.1 ng L⁻¹ versus 0.2 ng L⁻¹ of overestimation (See Table 3 and
 5 Table S4 and S6 in appendix). Moreover, chloride interferences have been studied and are not
 6 expected to occur. This overestimation is yet not clear but is certainly related to matrix effect such as
 7 non-spectral interferences in saline matrix as explained by Rodushkin *et al.* [62]. Specific ICP setting
 8 configuration, matrix-matched calibration or the use of another ISTD (*e.g.* Lu) could be studied to
 9 resolve this inaccuracy. No statistical analysis was performed on the SLEW-3 water for the following
 10 reason: the average values displayed in Table 3 were found in articles where the number of
 11 replicates and the statistical distribution modes were not the same.

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

17 Concerning sediment matrices, results obtained for the four reference materials are summarized in
 18 Table 4.

19 **Table 4** Comparison of our values with the certified ones for the BCR-667, Metranal-1 and HISS-1 sediments
 20 and proposed indicative values for PACS-3 certified sediment.

	BCR-667 (<i>n</i> = 5, values in mg kg ⁻¹)		Metranal-1 (<i>n</i> = 3, values in mg kg ⁻¹)		HISS-1 (<i>n</i> = 3, values in mg kg ⁻¹)		PACS-3 (<i>n</i> = 2, values in mg kg ⁻¹)
	This study	Certified values	This study	Literature values [63]	This study	Literature 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
Ho	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 ± 0.003	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 ± 0.05	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 ± 0.004	0.051 ± 0.002	0.22 ± 0.01

1 *Literature values correspond to the estimated mean of the references ± estimated standard deviation if there*
2 *are more than one published concentration. Study values correspond to the mean ± standard deviation.*

3 The European reference for the analysis of REEs (BCR-667) [30,67,68] was firstly used for checking
4 the accuracy of our method. Contrary to SLRS-6, comparisons with existing values were assessed
5 using recovery calculations. Indeed, due to the low number of replicates ($n = 5$), parametric test such
6 as Student's T-test could not be used. Values obtained were in conformity with the certified values
7 with recoveries ranging from 91% (La) to 100% (Pr, Sm). The other sediments (Metranal-1 [63] and
8 HISS-1 [64-66]) were secondly analysed and compared to values found in literature. Note that for
9 HISS-1 all the elements were not studied in some publications [64,66] and that some differences can
10 be observed for the concentrations obtained (explaining some high standard deviations among the
11 concentrations of LREEs). Overall, concentrations found were in good agreement with the compiled
12 values except for Pr which concentration has been determined by only one research group [65].
13 Finally, values for PACS-3 have, to the best of our knowledge, not been published yet. However,
14 values for PACS-1 [69] and PACS-2 [65,70-72] are really close to each other's and to our values
15 determined for PACS-3. Therefore, even if the number of replicates was not statistically robust,
16 values obtained in this study can be proposed as indicative values for the concentrations of REEs in
17 PACS-3 due to the good recoveries obtained for the concentrations of REEs in other sediments

1 analysed. Overall, this set of results clearly validate our method for the determination of all the REEs
2 in digested sedimentary samples.

3 **Conclusion**

4 This study proposes a direct method using classical ICP-QMS with standard introduction system for
5 quantifying REEs in freshwaters, estuarine waters and digested sediments. The method takes into
6 account and corrects accurately natural concentrations of the most common interferences (argides,
7 chlorides, hydrides, hydroxides, oxides and doubly charged) and can be transposed to many control
8 and research laboratories working on environmental samples. Helium gas was proved to be better
9 than H₂ for the removal of polyatomic interferences. Overestimation induced by interferences for
10 almost all REEs could be reduced below 4%, level that can be considered as acceptable. The method
11 has been validated by determining recoveries of REEs in different water-spiked matrices and by
12 analysing certified reference materials. Concentrations of REEs in PACS-3 have been assessed for the
13 first time in this study. As there is no preconcentration step, this method is limited to samples with
14 sufficient levels of REEs (*i.e.* above the LOQ) and thus may be not compatible for studies focused on
15 pristine environments. Besides, two elements remain tricky to quantify: Sc for which interferences
16 due to major anions (Ca, Si) cannot be completely solved, and Eu for which overestimation can reach
17 7.2% due to barium interferences. For some specific cases characterized by very low concentration of
18 REEs combined with high concentration of Sr (*e.g.* estuarine or marine water) and Gd (*e.g.* rivers fed
19 with high amount of wastewater treatment plant effluent), the present method also suffers from
20 some limitations. Indeed, $^{88}\text{SrH}^+$, $^{156}\text{Gd}^{16}\text{O}^+ / ^{155}\text{Gd}^{16}\text{OH}^+$ and $^{158}\text{Gd}^{16}\text{OH}^+$ can respectively skew the
21 quantification of ^{89}Y , ^{172}Yb and ^{175}Lu respectively. Generally, preconcentration of REEs and removal of
22 matrix are performed for these types of waters. The removal of Sr is never studied while Ba removal
23 is always commented as BaO and BaOH that are well known for being strong interferences on Eu.
24 However, the scope of this method has been set by calculating limiting ratios. Finally, even if this
25 method is dedicated to quantification of REEs with a simple quadrupole ICP-MS equipped with a

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

4

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10

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