

Integration of rare earth elements (REE) into a novel ICP-MS method for environmental analysis

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Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ TQe ICP-MS using a single measurement mode for rare earth elements in a variety of environmental and geological samples.

Introduction

Rare earth elements (REEs) are a group of 14 elements, (all metals) that tend to be found together in geological deposits. REEs represent useful chemical tracers and are often used as geochemical fingerprints in hydro geochemical processes to study ocean circulation, rock-water interactions, water physical mixing, etc.¹ In addition to this, REEs are valuable for modern industries and widely used in advanced technologies, such as medical diagnostics (magnetic resonance imaging, MRI), permanent magnets, rechargeable batteries, electric cars, and electronic products.^{2,3} However, despite their utility,



REEs pose significant risks to the environment if handled inappropriately as electronic or medical waste, etc. For example, increased concentrations of gadolinium (Gd) were reported recently in tap⁴ and river water collected close to medical facilities where it is used as a contrast agent in MRI or computerized tomography (CT).^{5,6} Other elements could accidentally leach out into the environment from consumer electronics or residues from industrial production of batteries disposed of incorrectly. Consequently, it is important to monitor REE levels in ground and surface waters, and therefore, most of the elements are mentioned in regulated methods for the analysis of drinking and surface waters, such as ISO method 17294, governing water analysis in the European Union.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most widely employed technique for the analysis of trace elements in environmental samples. Although the most common analytes, such as chromium, arsenic, selenium, cadmium, mercury, or lead, are well established in methods used by analytical testing laboratories, quantifying REEs in such samples still comes with challenges. These include the ultra-low concentrations of these elements in water samples (typically $\text{ng}\cdot\text{L}^{-1}$), variable chemical composition of samples, and spectral interferences. Besides their potential to cause interferences on key analytes by formation of doubly charged interferences (e.g., $^{150}\text{Nd}^{2+}$ on $^{75}\text{As}^+$),⁷ lighter members of this group of elements can contribute to and therefore create false positives on the resulting signal for the heavier homologs (e.g., formation of $^{156}\text{Gd}^{16}\text{O}^+$ on $^{172}\text{Yb}^+$).

This application note describes how interference free, low level analysis of rare earth elements can be integrated into a fast, sensitive, and robust ICP-MS method for the analysis of different water samples (e.g., drinking and surface waters). This analytical method was tested using water samples collected locally as well as applicable certified reference materials (CRMs).

Experimental

Experimental optimization of instrument parameters

An iCAP TQe ICP-MS was used for all measurements. The sample introduction system consisted of a Peltier cooled, baffled cyclonic spraychamber, PFA nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. To avoid unwanted matrix effects, the High Matrix skimmer cone insert was selected for this application. Table 1 gives an overview of the full configuration of the system. For automation of the sample introduction process, a Teledyne CETAC™ ASX-560 autosampler (Omaha, NE, USA) was used.

To remove potential interferences, the ICP-MS was operated in single mode (TQ- O_2) using the parameters presented in Table 1. Although kinetic energy discrimination (KED) using helium as an inert collision gas is often used to remove abundantly occurring polyatomic interferences, the use of a triple quadrupole mass analyzer in conjunction with oxygen as a reactive gas provides significant improvements:

- Polyatomic interferences are removed with equivalent or even higher efficiency, especially in the higher mass range (e.g., WO^+ interferences on mercury).
- Other types of interferences, such as doubly charged ions, are removed effectively in comparison to He-KED mode.

- In comparison to a method using different settings for some analytes, time savings can be realized at no expense of achievable detection limits.

In short, the TQ- O_2 mode removes spectral interferences in the following way: the collision reaction cell (CRC) is pressurized with oxygen as a reaction gas. For all analytes, Q1 is set to analyte mass (M^+), whereas Q3 is set to either the analyte mass as well (for elements unreactive or with low reactivity towards oxygen), or to MO^+ or even MO_2^+ (for analytes reactive to oxygen). Based on the mass filtration in the first quadrupole, potential side reactions with other ionic species are suppressed, and other elements, potentially occupying the intended product ion mass of MO^+ , are removed. This mode allows for complete interference removal and improved sensitivity.

Rare earth elements are well known to form doubly charged ions (M^{2+}) due to their moderate 2nd ionization potential, leading to interferences in the mass range between m/z 70 and 88, but they can also create interferences among themselves through the formation of oxides (MO^+). This is highlighted in Figure 1, showing how potential interferences on erbium (Er) caused by the presence of neodymium (Nd) and samarium (Sm) can be avoided.

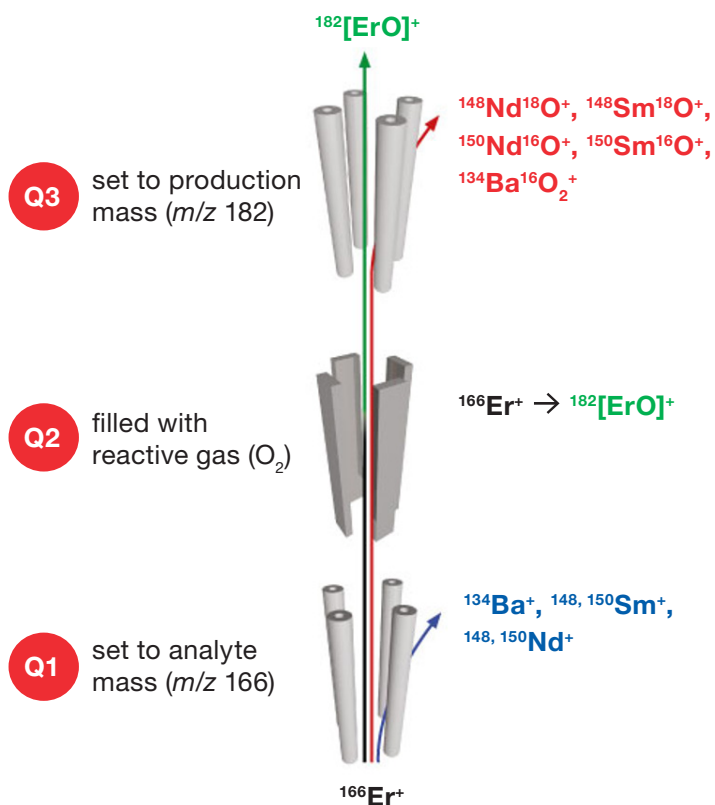


Figure 1. Schematic showing the use of TQ- O_2 mode and a mass shift reaction for interference free detection of erbium (Er)

Table 1. Instrument configuration and operating parameters

| Parameter | Value |
|---------------------|--|
| Nebulizer | Borosilicate glass micromist, 400 $\mu\text{L}\cdot\text{min}^{-1}$, pumped at 40 rpm |
| Pump tubing | Orange – green, 0.38 mm i.d. |
| Spraychamber | Quartz cyclonic, cooled at 2.7 °C |
| Injector | 2.5 mm i.d., quartz |
| Interface | Nickel sampler and nickel skimmer cone with High Matrix insert |
| Plasma power | 1,550 W |
| Nebulizer gas | 1.04 $\text{L}\cdot\text{min}^{-1}$ |
| QCell setting | TQ- O_2 |
| Gas flow | 100% O_2 , 0.34 $\text{mL}\cdot\text{min}^{-1}$ |
| CR bias | -6.3 V |
| Q3 bias | -12 V |
| Scan setting | 0.1 s dwell time, 5 sweeps, 3 main runs |
| Lens setting | Optimized using autotune |
| Sample uptake | 55 s |
| Wash time | 55 s |
| Total analysis time | 2 min 50 s |

Data acquisition and data processing

All parameters in the measurement mode were defined automatically using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The autosampler was controlled using the Qtegra ISDS Software as well using a dedicated software plug-in.

Quality control is critical in analysis, especially when running long batches containing different sample matrices. To ensure quality control, the internal standards were monitored, and continuing calibration checks (CCVs) were performed periodically throughout the analytical run. A full suite of quality control tests is included in the Qtegra ISDS Software and can be configured (with respect to applicable % limits, repetition rate, and actions on warning/failure) as required.

Sample preparation

Precleaned polypropylene bottles were used for the preparation of all blanks, calibration standards, and samples. The bottles were rinsed with ultrapure water (18.2 $\text{M}\Omega\cdot\text{cm}$) and left to dry in a laminar flow clean hood before use. Two CRMs were used: SLRS-5 (River water, National Institute of Standards and Technology) and BCR-2 (Basalt, Columbia River, United States Geological Survey). In addition, a total of eight individual water samples were collected from various locations in and around Bremen, Germany (see Table 2 for details) and analyzed for 35 elements. All water samples were acidified with 2% v/v HNO_3 (OPTIMA™ grade, Fisher Scientific) after collection. In addition, the samples were filtered through a 0.45 μm membrane to remove particles.

The BCR-2 CRM required autoclave digestion using a combination of HNO_3 , HClO_4 and HF prior to analysis. The total dilution factor incurred throughout the digestion process was 2,500.

All blanks, calibration standards, and quality control standards (QC) were prepared using 2% v/v HNO_3 and single element standards (SPEX CertiPrep, Metuchen, NJ, USA) to result in the concentration ranges listed in Table 3. In addition to major elements (typical concentration ranges in the $\text{mg}\cdot\text{L}^{-1}$ range) and common contaminants (expected concentrations in the $\mu\text{g}\cdot\text{L}^{-1}$ range). This allowed to establish instrumental detection limits for these analytes.

An internal standard solution, containing Ga, In, and Bi, all at 5 $\mu\text{g}\cdot\text{L}^{-1}$ in 2% v/v HNO_3 , was added on-line to all samples via a T-piece (mixing rate between internal standard and samples 1:1) before entering the nebulizer. The internal standards were selected to cover the entire mass range of the analytes selected to get the best possible correction for potentially occurring matrix effects or instrumental drift. The allocation of the different internal standards to the individual elements is highlighted in Table 4.

Further details of the measurement modes, acquisition parameters, and internal standards used for each element are summarized in Table 4. To analyze all elements using a single mode, the default settings of the Reaction Finder Method Development Assistant were modified accordingly.

Table 2. Overview of the samples analyzed, including location

| Item | Place | Category | Note | |
|------|-----------------|-----------------|-----------------|--|
| 1 | SLRS-5 | Ottawa | River | CRM |
| 2 | Drinking water | Bremen | Tap water | – |
| 3 | Achterdieksee | Bremen (north) | Lake | Sampling location is close to a major highway |
| 4 | Creek (no name) | Weyhe | Stream | Sampling area is rural |
| 5 | Weser River | Bremen (middle) | River | Main river, sampling location close to a harbor |
| 6 | Creek (no name) | Bremen (south) | Stream | Industrial area |
| 7 | Sodenmattsee | Bremen (west) | Lake | Sampling location is close to an area with heavy traffic |
| 8 | Sebaldsbrück | Bremen (east) | Lake | Sampling location is close to a major highway |
| 9 | Tweelbäkersee | Oldenburg | Lake | Sampling location is close to a major highway |
| 10 | BCR-2 | Portland, OR | Basalt sediment | CRM |

Table 3. R² and IDL data for 35 elements in 2% HNO₃

| Analyte and mass | Concentration range in calibration solutions [$\mu\text{g}\cdot\text{L}^{-1}$] | Coefficient of determination (R ²) | Instrumental detection limit (IDL) [$\mu\text{g}\cdot\text{L}^{-1}$] |
|---|--|--|--|
| ⁹ Be | 1–20 | 0.997 | 0.006 |
| ²³ Na | 5,000–100,000 | 0.999 | 13.3 |
| ²⁴ Mg | 5,000–100,000 | 0.999 | 3 |
| ²⁷ Al | 1–20 | 0.999 | 0.3 |
| ³⁹ K | 5,000–100,000 | 0.999 | 2.1 |
| ⁴⁴ Ca as ⁴⁴ Ca. ¹⁶ O at <i>m/z</i> 60 | 5,000–100,000 | >0.999 | 12.9 |
| ⁵¹ V as ⁵¹ V. ¹⁶ O at <i>m/z</i> 67 | 1–20 | 0.999 | 0.002 |
| ⁵² Cr as ⁵² Cr. ¹⁶ O at <i>m/z</i> 68 | 1–20 | 0.999 | 0.012 |
| ⁵⁵ Mn | 1–20 | 0.999 | 0.005 |
| ⁵⁷ Fe | 5,000–100,000 | 0.999 | 0.57 |
| ⁶⁰ Ni | 1–20 | 0.999 | 0.024 |
| ⁶³ Cu | 1–100 | >0.999 | 0.3 |
| ⁶⁶ Zn | 1–20 | 0.999 | 0.048 |
| ⁷⁵ As as ⁷⁵ As. ¹⁶ O at <i>m/z</i> 91 | 1–20 | 0.999 | 0.0038 |
| ⁸⁰ Se as ⁸⁰ Se. ¹⁶ O at <i>m/z</i> 96 | 1–20 | >0.999 | 0.0041 |
| ⁸⁹ Y as ⁸⁹ Y. ¹⁶ O at <i>m/z</i> 105 | 0.01–1 | >0.999 | 0.0009 |
| ⁹⁸ Mo as ⁹⁸ Mo. ¹⁶ O at <i>m/z</i> 114 | 1–20 | >0.999 | 0.0082 |
| ¹⁰⁷ Ag | 1–20 | 0.999 | 0.002 |
| ¹¹¹ Cd | 1–20 | 0.999 | 0.0016 |
| ¹²¹ Sb | 1–20 | >0.999 | 0.0016 |
| ¹³⁹ La as ¹³⁹ La. ¹⁶ O at <i>m/z</i> 155 | 0.01–1 | 0.999 | 0.0002 |
| ¹⁴⁰ Ce as ¹⁴⁰ Ce. ¹⁶ O at <i>m/z</i> 156 | 0.01–1 | >0.999 | 0.0004 |
| ¹⁴¹ Pr as ¹⁴¹ Pr. ¹⁶ O at <i>m/z</i> 157 | 0.01–1 | >0.999 | 0.0002 |
| ¹⁴⁶ Nd as ¹⁴⁶ Nd. ¹⁶ O at <i>m/z</i> 162 | 0.01–1 | 0.999 | 0.0006 |
| ¹⁴⁹ Sm as ¹⁴⁹ Sm. ¹⁶ O at <i>m/z</i> 165 | 0.01–1 | >0.999 | 0.0005 |
| ¹⁵³ Eu | 0.01–1 | >0.999 | 0.0001 |
| ¹⁵⁷ Gd as ¹⁵⁷ Gd. ¹⁶ O at <i>m/z</i> 173 | 0.01–1 | >0.999 | 0.0005 |
| ¹⁵⁹ Tb as ¹⁵⁹ Tb. ¹⁶ O at <i>m/z</i> 175 | 0.01–1 | 0.999 | 0.0002 |

Table 3 (cont'd). R² and IDL data for 35 elements in 2% HNO₃

| Analyte and mass | Concentration range in calibration solutions [$\mu\text{g}\cdot\text{L}^{-1}$] | Coefficient of determination (R ²) | Instrumental detection limit (IDL) [$\mu\text{g}\cdot\text{L}^{-1}$] |
|---|--|--|--|
| ¹⁶³ Dy as ¹⁶³ Dy. ¹⁶ O at m/z 179 | 0.01–1 | >0.999 | 0.0002 |
| ¹⁶⁵ Ho as ¹⁶⁵ Ho. ¹⁶ O at m/z 181 | 0.01–1 | >0.999 | 0.0001 |
| ¹⁶⁶ Er as ¹⁶⁶ Er. ¹⁶ O at m/z 182 | 0.01–1 | 0.999 | 0.0001 |
| ¹⁶⁹ Tm as ¹⁶⁹ Tm. ¹⁶ O at m/z 185 | 0.01–1 | >0.999 | 0.0001 |
| ¹⁷² Yb | 0.01–1 | >0.999 | 0.0003 |
| ¹⁷⁵ Lu as ¹⁷⁵ Lu. ¹⁶ O at m/z 191 | 0.01–1 | >0.999 | 0.0001 |
| ²³⁸ U as ²³⁸ U. ¹⁶ O ₂ at m/z 270 | 0.01–1 | 0.999 | 0.0003 |

Result and discussion

Sensitivity, linearity, and limit of detection

Although for some elements, other modes such as kinetic energy discrimination might be able to provide at least equivalent interference removal and, in some cases, also slightly improved detection limits, the use of a single mode for all elements was preferred to reduce the analysis time per sample by omitting a gas switching cycle in the CRC. Especially when using valve-based systems for discrete sampling, a time saving of 10 seconds (corresponding to a typical flush/fill cycle in a CRC) makes up for a significant amount of the turnover time per sample.

Achieving high sensitivity is important especially when analyzing REEs in aqueous samples, where these elements are often present in ultra-trace amounts. The absolute sensitivity is significantly enhanced when using TQ-O₂ mode although both TQ-O₂ and He-KED mode have the capability of achieving detection limits in the sub ng·L⁻¹ range. However, in comparison, the TQ-O₂ mode performed significantly better (Figure 2).

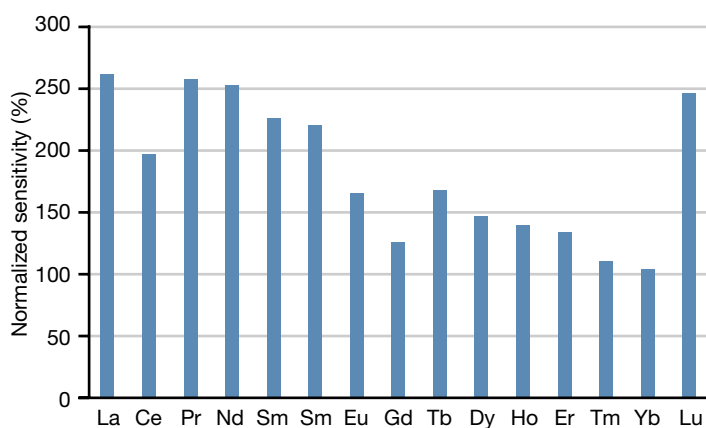


Figure 2. Comparison of the sensitivity in TQ-O₂ mode and He-KED mode for all REEs. The sensitivity in TQ-O₂ mode is normalized relative to the sensitivity observed in He-KED mode.

Table 3 summarizes the obtained instrumental detection limits together with the coefficient of determination (R²) for all elements analyzed in this study. The IDLs were calculated using three times the standard deviation of ten replicate measurements of the calibration blank. Although there are no regulatory limits specified yet for REEs in environmental samples, the IDLs obtained were significantly below the measured concentrations in the unknown samples collected for this study.

Table 4. Internal standards used for each element with corresponding target isotopes, Q1, and Q3

| Analyte and mass | Q1 resolution | Q3 resolution | Internal standard |
|---|---------------|---------------|-------------------|
| ⁹ Be | High | Normal | ⁷¹ Ga |
| ²³ Na | High | High | ⁷¹ Ga |
| ²⁴ Mg | High | High | ⁷¹ Ga |
| ²⁷ Al | High | Normal | ⁷¹ Ga |
| ³⁹ K | High | High | ⁷¹ Ga |
| ⁴⁴ Ca as ⁴⁴ Ca. ¹⁶ O at m/z 60 | High | High | ⁷¹ Ga |
| ⁵¹ V as ⁵¹ V. ¹⁶ O at m/z 67 | iMS | Normal | ⁷¹ Ga |
| ⁵² Cr as ⁵² Cr. ¹⁶ O at m/z 68 | iMS | Normal | ⁷¹ Ga |
| ⁵⁵ Mn | iMS | Normal | ⁷¹ Ga |
| ⁵⁷ Fe | High | High | ⁷¹ Ga |
| ⁶⁰ Ni | iMS | Normal | ⁷¹ Ga |
| ⁶³ Cu | iMS | Normal | ⁷¹ Ga |
| ⁶⁶ Zn | iMS | Normal | ⁷¹ Ga |
| ⁷⁵ As as ⁷⁵ As. ¹⁶ O at m/z 91 | iMS | Normal | ¹¹⁵ In |
| ⁸⁰ Se as ⁸⁰ Se. ¹⁶ O at m/z 96 | iMS | Normal | ¹¹⁵ In |
| ⁸⁹ Y as ⁸⁹ Y. ¹⁶ O at m/z 105 | iMS | Normal | ¹¹⁵ In |

Table 4. (cont'd). Internal standards used for each element with corresponding target isotopes, Q1, and Q3

| Analyte and mass | Q1 resolution | Q3 resolution | Internal standard |
|--|---------------|---------------|-------------------|
| ⁹⁸ Mo as ⁹⁸ Mo. ¹⁶ O at <i>m/z</i> 114 | iMS | Normal | ¹¹⁵ In |
| ¹⁰⁷ Ag | iMS | Normal | ¹¹⁵ In |
| ¹¹¹ Cd | iMS | Normal | ¹¹⁵ In |
| ¹²¹ Sb | iMS | Normal | ¹¹⁵ In |
| ¹³⁹ La as ¹³⁹ La. ¹⁶ O at <i>m/z</i> 155 | iMS | Normal | ¹¹⁵ In |
| ¹⁴⁰ Ce as ¹⁴⁰ Ce. ¹⁶ O at <i>m/z</i> 156 | iMS | Normal | ¹¹⁵ In |
| ¹⁴¹ Pr as ¹⁴¹ Pr. ¹⁶ O at <i>m/z</i> 157 | iMS | Normal | ¹¹⁵ In |
| ¹⁴⁶ Nd as ¹⁴⁶ Nd. ¹⁶ O at <i>m/z</i> 162 | iMS | Normal | ¹¹⁵ In |
| ¹⁴⁹ Sm as ¹⁴⁹ Sm. ¹⁶ O at <i>m/z</i> 165 | iMS | Normal | ¹¹⁵ In |
| ¹⁵³ Eu | iMS | Normal | ¹¹⁵ In |
| ¹⁵⁷ Gd as ¹⁵⁷ Gd. ¹⁶ O at <i>m/z</i> 173 | iMS | Normal | ¹¹⁵ In |
| ¹⁵⁹ Tb as ¹⁵⁹ Tb. ¹⁶ O at <i>m/z</i> 175 | iMS | Normal | ¹¹⁵ In |
| ¹⁶³ Dy as ¹⁶³ Dy. ¹⁶ O at <i>m/z</i> 179 | iMS | Normal | ¹¹⁵ In |
| ¹⁶⁵ Ho as ¹⁶⁵ Ho. ¹⁶ O at <i>m/z</i> 181 | iMS | Normal | ²⁰⁹ Bi |
| ¹⁶⁶ Er as ¹⁶⁶ Er. ¹⁶ O at <i>m/z</i> 182 | iMS | Normal | ²⁰⁹ Bi |
| ¹⁶⁹ Tm as ¹⁶⁹ Tm. ¹⁶ O at <i>m/z</i> 185 | iMS | Normal | ²⁰⁹ Bi |
| ¹⁷² Yb | iMS | Normal | ²⁰⁹ Bi |
| ¹⁷⁵ Lu as ¹⁷⁵ Lu. ¹⁶ O at <i>m/z</i> 191 | iMS | Normal | ²⁰⁹ Bi |
| ²³⁸ U as ²³⁸ U. ¹⁶ O ₂ at <i>m/z</i> 270 | iMS | Normal | ²⁰⁹ Bi |

Interference removal

As mentioned previously, the different REEs may not only create interferences on key analytes under regulation, such as arsenic or selenium, but also interferences on other REEs can be expected and need to be resolved to avoid false positive results. False positive results can arise for the analysis of erbium in the presence of different concentrations of samarium, which can interfere if, for example, ¹⁵⁰Sm¹⁶O⁺ is not resolved from the common isotope for erbium analysis, ¹⁶⁶Er. TQ-O₂ mode showed excellent interference removal with no false positive being returned. A potential bias of up to 2.5 µg·L⁻¹ was observed for ¹⁶⁶Er in He-KED mode for concentrations of samarium between 10 µg·L⁻¹ and 1,000 µg·L⁻¹.

To highlight the ability of the iCAP TQe ICP-MS to remove all potential interferences caused in the presence of different rare earth elements, a river sediment CRM (BCR-2, United States Geological Survey) was analyzed. Although not a water sample, it is one of the few materials available certified for its content of REEs and contains between 0.5 µg·g⁻¹ (Tm, Lu) and >25 µg·g⁻¹ (e.g. La, Nd). Additionally, method detection limits (MDLs) for the REEs of choice were determined and results are summarized in Table 5. MDLs were calculated from the IDLs values determined experimentally (Table 4) but considering the dilution factor of 2,500 because of the digestion procedure. As can be seen from Table 5, good agreement between the experimental results and the certified/informative concentrations was obtained.

Table 5. Quantitative results obtained for the CRM BCR-2 sample analyzed in TQ-O₂ mode. All REEs concentrations are reported as µg·g⁻¹.

| Analyte and mass | MDL | Measured (n=4) | CRM consensus values |
|---|--------|----------------|----------------------|
| ¹³⁹ La as ¹³⁹ La. ¹⁶ O at <i>m/z</i> 155 | 0.001 | 26 ± 0.5 | 25 ± 1 |
| ¹⁴⁰ Ce as ¹⁴⁰ Ce. ¹⁶ O at <i>m/z</i> 156 | 0.001 | 55 ± 1 | 53 ± 2 |
| ¹⁴¹ Pr as ¹⁴¹ Pr. ¹⁶ O at <i>m/z</i> 157 | 0.001 | 7.0 ± 0.2 | 6.8 ± 0.3 |
| ¹⁴⁶ Nd as ¹⁴⁶ Nd. ¹⁶ O at <i>m/z</i> 162 | 0.002 | 30 ± 1 | 28 ± 2 |
| ¹⁴⁹ Sm as ¹⁴⁹ Sm. ¹⁶ O at <i>m/z</i> 165 | 0.001 | 6.9 ± 0.5 | 6.7 ± 0.3 |
| ¹⁵³ Eu | 0.0003 | 2.1 ± 0.1 | 2.0 ± 0.1 |
| ¹⁵⁷ Gd as ¹⁵⁷ Gd. ¹⁶ O at <i>m/z</i> 173 | 0.001 | 7.1 ± 0.1 | 6.8 ± 0.3 |
| ¹⁵⁹ Tb as ¹⁵⁹ Tb. ¹⁶ O at <i>m/z</i> 175 | 0.001 | 1.10 ± 0.03 | 1.07 ± 0.04 |
| ¹⁶³ Dy as ¹⁶³ Dy. ¹⁶ O at <i>m/z</i> 179 | 0.001 | 7.1 ± 0.2 | – |
| ¹⁶⁵ Ho as ¹⁶⁵ Ho. ¹⁶ O at <i>m/z</i> 181 | 0.0003 | 1.45 ± 0.05 | 1.33 ± 0.06 |
| ¹⁶⁶ Er as ¹⁶⁶ Er. ¹⁶ O at <i>m/z</i> 182 | 0.0003 | 4.2 ± 0.3 | – |
| ¹⁶⁹ Tm as ¹⁶⁹ Tm. ¹⁶ O at <i>m/z</i> 185 | 0.0003 | 0.6 ± 0.1 | 0.54 |
| ¹⁷² Yb | 0.001 | 3.7 ± 0.2 | 3.5 ± 0.2 |
| ¹⁷⁵ Lu as ¹⁷⁵ Lu. ¹⁶ O at <i>m/z</i> 191 | 0.0003 | 0.55 ± 0.02 | 0.51 ± 0.02 |

Analysis of REEs in environmental samples

As part of this study, a river water reference material (SLRS-5) and eight different water samples were analyzed as technical replicates to assess the method performance. The results for the river water CRM were also found to be in excellent agreement with the reference values (Table 6). As the water samples were aspirated directly without any dilution, the MDL is effectively the same as the IDL. As can be seen, the different samples analyzed were significantly variable in their overall matrix content or composition, with

total concentrations of the most common alkaline and alkaline earth elements (Na, K, Mg, and Ca) between less than 20 mg·L⁻¹ (SLRS-5 CRM) to over 200 mg·L⁻¹ (Weser River). This again may cause a difference in the response of the plasma, so that internal standardization is key to avoid bias caused by potentially occurring matrix effects. No correlation of the combined concentration of the REEs with the concentration of other elements (such as alkaline/alkaline earth elements) could be found.

Table 6. Quantification results for different water samples. All concentrations are reported as µg·L⁻¹. Values annotated with * are known reference values (expected values).

| Analyte and mass | MLD for water samples | SLRS-5 Measured (n=8) | SLRS-5 CRM value | Concentration range in 8 water samples |
|---|-----------------------|-----------------------|------------------|--|
| ⁹ Be | 0.006 | 0.004 ± 0.005 | 0.005* | 0.003–0.07 |
| ²³ Na | 13.3 | 5,374 ± 98 | 5,380 ± 100 | 10,972–110,328 |
| ²⁴ Mg | 3 | 2,443 ± 110 | 2,540 ± 160 | 3,332–35,128 |
| ²⁷ Al | 0.3 | 50.1 ± 6.0 | 49.5 ± 5.0 | 0.002–0.2 |
| ³⁹ K | 2.1 | 822 ± 60 | 839 ± 36 | 2,216–19,681 |
| ⁴⁴ Ca as ⁴⁴ Ca. ¹⁶ O at m/z 60 | 12.9 | 10,060 ± 380 | 10,500 ± 400 | 18,100–48,082 |
| ⁵¹ V as ⁵¹ V. ¹⁶ O at m/z 67 | 0.002 | 0.291 ± 0.020 | 0.317 ± 0.033 | 0.36–0.92 |
| ⁵² Cr as ⁵² Cr. ¹⁶ O at m/z 68 | 0.012 | 0.199 ± 0.021 | 0.208 ± 0.023 | 0.09–0.46 |
| ⁵⁵ Mn | 0.005 | 4.21 ± 0.28 | 4.33 ± 0.18 | 0.16–519.8 |
| ⁵⁷ Fe | 0.57 | 93.5 ± 2.8 | 91.2 ± 5.8 | 50.1–1,051 |
| ⁶⁰ Ni | 0.024 | 0.495 ± 0.038 | 0.476 ± 0.064 | 0.82–1.93 |
| ⁶³ Cu | 0.3 | 18.7 ± 1.8 | 17.4 ± 1.3 | 0.77–127.02 |
| ⁶⁶ Zn | 0.048 | 0.89 ± 0.018 | 0.845 ± 0.095 | 3.8–163.3 |
| ⁷⁵ As as ⁷⁵ As. ¹⁶ O at m/z 91 | 0.0038 | 0.389 ± 0.03 | 0.413 ± 0.039 | 0.06–1.08 |
| ⁸⁰ Se as ⁸⁰ Se. ¹⁶ O at m/z 96 | 0.0041 | 0.09 ± 0.02 | - | 0.04–0.12 |
| ⁸⁹ Y as ⁸⁹ Y. ¹⁶ O at m/z 105 | 0.0009 | 0.11 ± 0.006 | - | 0.01–0.77 |
| ⁹⁸ Mo as ⁹⁸ Mo. ¹⁶ O at m/z 114 | 0.0082 | 0.5 ± 0.1 | 0.5* | 0.1–1.2 |
| ¹⁰⁷ Ag | 0.002 | 0.005 ± 0.001 | - | 0.004–0.019 |
| ¹¹¹ Cd | 0.0016 | 0.0069 ± 0.0012 | 0.0060 ± 0.0014 | 0.001–0.031 |
| ¹²¹ Sb | 0.0016 | 0.29 ± 0.02 | 0.3* | 0.029–0.31 |
| ¹³⁹ La as ¹³⁹ La. ¹⁶ O at m/z 155 | 0.0002 | 0.21 ± 0.01 | - | 0.003–0.575 |
| ¹⁴⁰ Ce as ¹⁴⁰ Ce. ¹⁶ O at m/z 156 | 0.0004 | 0.26 ± 0.01 | - | 0.002–1.288 |
| ¹⁴¹ Pr as ¹⁴¹ Pr. ¹⁶ O at m/z 157 | 0.0002 | 0.05 ± 0.003 | - | 0.001–0.176 |
| ¹⁴⁶ Nd as ¹⁴⁶ Nd. ¹⁶ O at m/z 162 | 0.0006 | 0.18 ± 0.01 | - | 0.003–0.768 |
| ¹⁴⁹ Sm as ¹⁴⁹ Sm. ¹⁶ O at m/z 165 | 0.0005 | 0.039 ± 0.004 | - | 0.007–0.171 |
| ¹⁵³ Eu | 0.0001 | 0.008 ± 0.001 | - | 0.002–0.042 |
| ¹⁵⁷ Gd as ¹⁵⁷ Gd. ¹⁶ O at m/z 173 | 0.0005 | 0.033 ± 0.004 | - | 0.008–0.162 |
| ¹⁵⁹ Tb as ¹⁵⁹ Tb. ¹⁶ O at m/z 175 | 0.0002 | 0.003 ± 0.0002 | - | 0.001–0.02 |
| ¹⁶³ Dy as ¹⁶³ Dy. ¹⁶ O at m/z 179 | 0.0002 | 0.018 ± 0.001 | - | 0.001–0.112 |
| ¹⁶⁵ Ho as ¹⁶⁵ Ho. ¹⁶ O at m/z 181 | 0.0001 | 0.0038 ± 0.0002 | - | 0.0004–0.025 |
| ¹⁶⁶ Er as ¹⁶⁶ Er. ¹⁶ O at m/z 182 | 0.0001 | 0.011 ± 0.001 | - | 0.001–0.074 |
| ¹⁶⁹ Tm as ¹⁶⁹ Tm. ¹⁶ O at m/z 185 | 0.0001 | 0.0016 ± 0.0001 | - | 0.0002–0.011 |
| ¹⁷² Yb | 0.0003 | 0.010 ± 0.001 | - | 0.001–0.074 |
| ¹⁷⁵ Lu as ¹⁷⁵ Lu. ¹⁶ O at m/z 191 | 0.0001 | 0.0017 ± 0.0009 | - | 0.0004–0.012 |
| ²³⁸ U as ²³⁸ U. ¹⁶ O ₂ at m/z 270 | 0.0003 | 0.100 ± 0.003 | 0.1* | 0.014–0.596 |

To fully confirm the absence of any drift or matrix effect as an influencing factor to the results, a spike recovery test for all REEs was performed in all water samples analyzed, including the river water CRM. To reflect the typically observed concentrations in natural waters, a concentration of $0.05 \mu\text{g}\cdot\text{L}^{-1}$ was added to each sample. The overall spike recovery observed across all samples was excellent with an average recovery between 90% and 112%.

Robustness

For reliable analysis in an essential testing laboratory, it is important that the results obtained are accurate and precise also in longer batches comprising different sample types. Commonly, quality control (QC) standards containing a known concentration of all analytes are analyzed periodically during a batch to monitor method performance.

To simulate a high-volume sample analysis, a larger sample batch was scheduled for analysis containing all water samples previously analyzed. Each sequence in the batch (consisting of 23 individual samples) was concluded with a quality control standard (continuing calibration verification, CCV, containing $0.05 \mu\text{g}\cdot\text{L}^{-1}$ of REEs) before restarting the next sequence. In summary, eight CCVs were analyzed in a batch containing 197 samples in approximately 10 hours. The relative standard deviation of all CCVs ($n=8$) in the batch did not exceed 3%. The response of the internal standards are shown in Figure 3. All internal standards showed excellent recovery (within approximately 70% to 110%) over the entire runtime of the batch, demonstrating robust analytical performance.

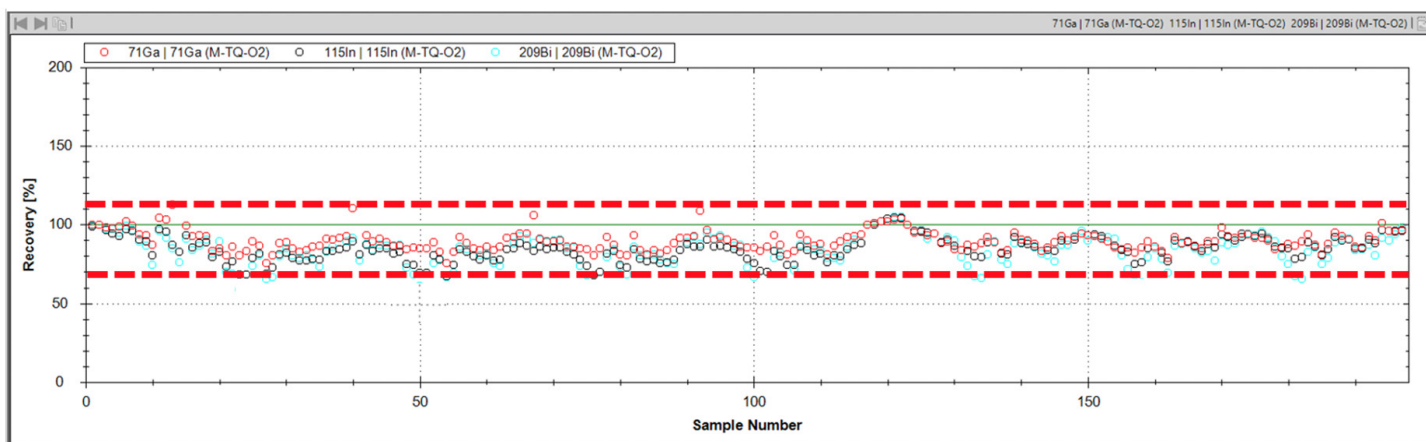


Figure 3. Response of the internal standards assessed over a period of ~10 hours of uninterrupted acquisition of 197 samples

Conclusion

The iCAP TQe ICP-MS was successfully employed to analyze 35 elements in different environmental samples (water samples and a previously digested sediment sample) following a simple sample preparation. This analytical method was rigorously tested, and the results obtained clearly demonstrated the following analytical advantages:

- The combination of a triple quadrupole mass analyzer with O₂ as the cell gas is effective for the removal of spectral interferences such as complicated isobaric and/or polyatomic interferences during the analysis of REEs.
- TQ-O₂ mode allows for high sensitivity analysis required for the accurate determination of the entire mass range (beryllium to uranium) with outstanding IDLs and linear response.
- The TQ-O₂ single measurement reduced the total analysis time to <3 min/sample (including uptake and wash time) for 35 elements (at both major and ultra-trace level). This sample turnover time can be reduced to <90 s by using a discrete sampling valve and will positively impact high sample throughput laboratories.
- The large linear dynamic range of up to 10 orders of magnitude allows for precise determination of multi elements at low and high concentrations without further sample concentration or dilution.
- Robust and stable analytical performance was demonstrated over 10 hours of continuous acquisition of 200 samples.

In summary, the iCAP-TQe ICP-MS system together with Qtegra ISDS Software allows for fast, sensitive, and robust determination of ultra-trace REEs in environment and geological samples, making it ideal for laboratories analyzing a high volume of samples per day.

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