

Direct Analysis of Ultratrace Rare Earth Elements in Environmental Waters by ICP-QQQ

Measure emerging pollutants in river water using the Agilent 8900 ICP-QQQ in MS/MS mass-shift mode



Authors

Naoki Sugiyama
Agilent Technologies, Inc.

Introduction

The Rare Earth Elements (REEs)—also known as the lanthanides—range from lanthanum to lutetium. Scandium and yttrium are also commonly considered to be REEs. REEs are used in a wide range of applications from the glass industry, phosphors, permanent magnets, and lasers to clean energy, defense technologies, and batteries (1–3). With their increasing importance in high tech applications, there is growing concern about the migration of REEs into the environment during mining, processing, use, discarding, or recycling. More evidence is required to understand the effects of REEs on the environment, ecosystems, and from dietary intake. Depending on the findings that emerge from the research, regulations may be introduced to limit the disposal of REEs into water courses. In support of both research and routine monitoring purposes, quick, reliable, and sensitive analytical methods are needed to measure these emerging pollutants at low concentrations in a range of sample-types.

While ICP-MS is suited to the measurement of REEs at trace levels, the direct measurement of REEs in waste and natural waters remains challenging for two main reasons. Typically, the natural background concentration of the REEs is very low in environmental waters, often at or below the detection capabilities of conventional single quadrupole ICP-MS. Also, the analysis may be hindered by spectral interferences such as BaO⁺ on Eu⁺, BaH⁺ on La⁺, or low mass REE-oxide ions overlapping high mass REEs. A chelating resin can be used to preconcentrate the REEs and separate them from Ba, which is usually present at a much higher concentration. But this approach must be optimized for each sample matrix, requiring time, skill, and resources that may not be available in routine labs.

Triple quadrupole ICP-MS (ICP-QQQ) is a simpler, faster, direct method for the analysis of REEs in environmental waters at the ultratrace level. Compared to single quadrupole ICP-MS, ICP-QQQ offers greater sensitivity and advanced interference removal using controlled reaction chemistry in the collision/reaction cell (CRC). Agilent ICP-QQQ instruments feature two quadrupoles (Q1 and Q2), one either side of the CRC, enabling double mass selection (MS/MS). Q1 rejects all nontarget ions before they enter the cell, allowing only analyte ions and on-mass interference ions to pass to the cell. These ions can then be separated using predictable, consistent, and reproducible reaction chemistry (4). Q2 then ensures that only the analyte ions (on mass mode) or analyte-product ions (mass-shift mode) pass to the detector, free of interferences.

In this study, an Agilent 8900 ICP-QQQ was used for the direct analysis of REEs in water that was collected at four different points along a Japanese river. Using an MS/MS mass-shift method with nitrous oxide (N₂O) as a reaction cell gas, any interferences were resolved quickly and effectively.

Experimental

Instrumentation

An Agilent 8900 ICP-QQQ (model #100 for advanced applications) was used in this study. The instrument was fitted with a quartz double-pass spray chamber, quartz torch with 2.5 mm id injector, and Ni interface cones. Sample delivery was via a peristaltic pump and PFA microflow nebulizer (G3139-65100 nebulizer) with a small dead volume. The samples were clean, natural waters, so 'low-matrix' preset plasma conditions were selected in the Agilent ICP-MS MassHunter software. The preset plasma setting automatically optimizes the plasma conditions for the routine analysis of samples with total dissolved solids < 0.1%.

Selection of reactive cell gas

Oxygen (O₂) and N₂O were investigated as reaction cell gases to remove spectral interferences on REEs using a MS/MS mass-shift method. The potential spectral interferences include BaO⁺ on Eu⁺, BaH⁺ on La⁺, or low mass REE-oxide ions on high mass REE ions.

Since the O atom transfer reaction of REE⁺ with N₂O (REE⁺ + N₂O → REEO⁺ + N₂) is exothermic for all REEs, good sensitivity was expected with N₂O. As shown in Figure 1, comparable or greater sensitivity was achieved for all REEs using N₂O compared to O₂ cell gas. Based on these results, N₂O was used as the reaction cell gas in this study.

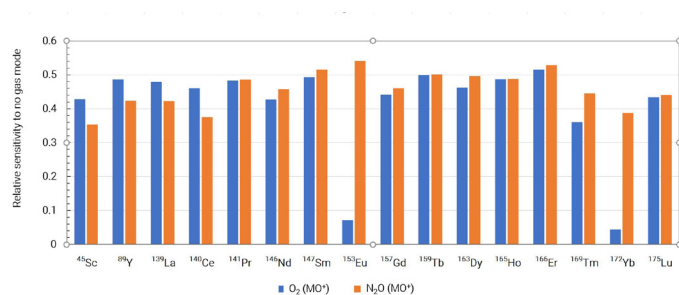


Figure 1. Comparison of the sensitivity of ICP-QQQ MS/MS mass-shift method with O₂ and N₂O cell gas.

All 8900 ICP-QQQ operating and tuning conditions are summarized in Table 1.

Table 1. ICP-QQQ tuning and operating conditions.

Parameter	Setting
RF Power (W)	1550
Sampling Depth (mm)	8.0
Nebulizer Gas Flow Rate (mL/min)	1.05
Makeup Gas Flow Rate (mL/min)	0.0
Extraction 1 Lens (V)	-5.0
Extraction 2 Lens (V)	-200
Omega Lens (V)	7.0
Omega Bias Lens (V)	-110
Octopole Bias (V)	-3.0
Cell Gas Flow Rate (% of full scale)	20
Axial Acceleration (V)	1.0

Method detection limits (MDLs)

MDLs for the REEs were calculated from three times the standard deviation of nine replicate measurements of a low-level standard (0.3 ppt each REE in 1% HNO₃). The results are summarized in Table 2. All the MDLs are sub ppt, confirming the suitability of the method for the determination of REEs at background levels in environmental waters.

Certified reference material analysis

A river water certified reference material (CRM), SLRS-6 (NRC-CNRC, Ottawa, Canada) was analyzed using the ICP-QQQ in MS/MS mode with N₂O. All REEs were measured as oxide ions, with a mass-shift of 16 u, as indicated in the Q1/Q2 settings provided in Table 2.

There is good agreement between the CRM reported values (5) and measured concentrations for all elements except for Sc (Table 2). To investigate the discrepancy, Sc was analyzed in the CRM using no gas and helium (He) collision (kinetic energy discrimination) mode. The measured concentrations were 367 and 33.3 ppt, respectively. No detailed information is given for the reported value for Sc on the CRM certificate. Since the reported concentration (333.0 ppt) agrees with the measured value obtained in no gas mode (367 ppt), the author suspects the CRM reported value provided for Sc is not correct. Because the CRM contains Si at the ppm level, a spectral interference on Sc⁺ by SiO⁺ or SiOH⁺ may account for the high reported value.

Using the ICP-QQQ method, any Si-based interferences on Sc⁺ would be avoided. In MS/MS mode, Q1 operates as a single (1 u) mass filter so that only ions with the targeted *m/z* enter the CRC and react with the cell gas. Q1 rejects all other masses (including Si ions), avoiding any subsequent interferences by SiO⁺ or SiOH⁺ on Sc⁺.

River water analysis

River water samples were collected at four points (A to D) of the Tama River, Japan. Two of the samples were collected at wastewater treatment plant (WWTP) discharge points (C and D), as shown in Figure 2. Three samples were collected from each sampling point, then filtered through a 0.45 μm filter, and acidified to 1% HNO₃.

Table 2. MDLs and SLRS-6 river water CRM reported values (5) and ICP-QQQ measured results.

Element	Q1/Q2	Integration Time (s)	MDL (ppt)	SLRS-6 Reported (ppt)	SLRS-6 This Study (ppt)
Sc	45/61	1.0	0.127	333.0	16.3
Y	89/105	1.0	0.053	128.0	125.7
La	139/155	1.0	0.062	248.3	241.3
Ce	140/156	1.0	0.061	292.7	288.5
Pr	141/157	1.0	0.057	59.1	57.3
Nd	146/162	3.0	0.066	227.8	221.3
Sm	147/163	3.0	0.096	39.5	37.8
Eu	153/169	1.0	0.082	7.26	6.50
Gd	157/173	3.0	0.078	31.6	29.9
Tb	159/175	1.0	0.059	4.07	3.75
Dy	163/179	3.0	0.073	21.9	21.1
Ho	165/181	1.0	0.100	4.30	4.14
Er	166/182	1.0	0.092	12.4	11.7
Tm	169/185	1.0	0.079	1.79	1.63
Yb	172/188	3.0	0.096	11.2	10.7
Lu	175/191	1.0	0.052	1.91	1.74

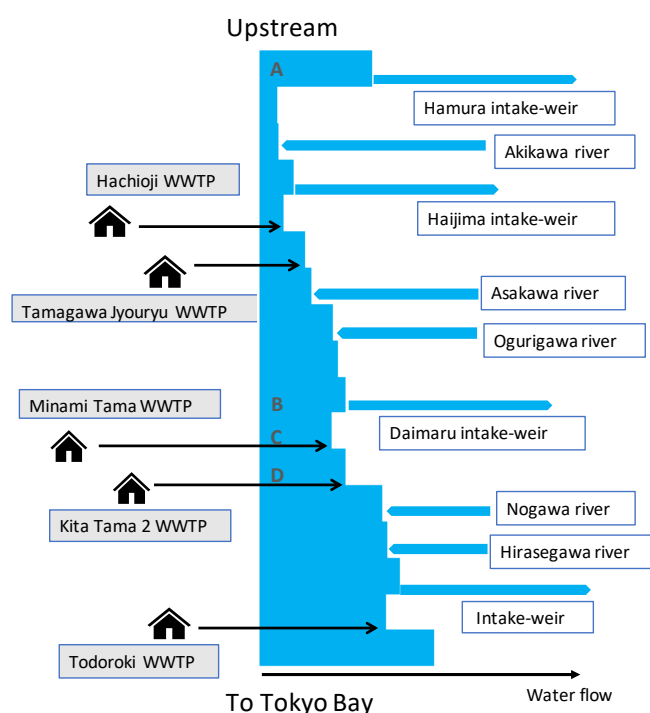


Figure 2. Tama River water flow balance and sample collection points A to D. The water flow balance is based on data provided by the Japanese Ministry of Land, Infrastructure, Transport, and Tourism, 1999.

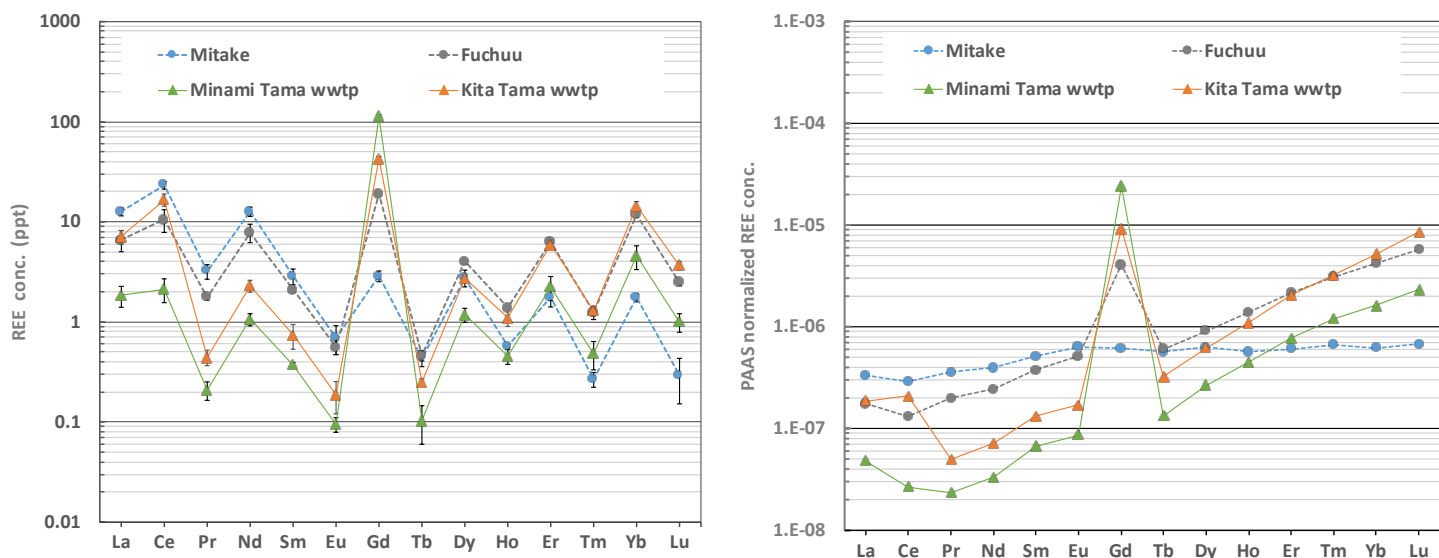


Figure 3. Concentrations of REEs in Tama River water samples by ICP-QQQ. Left: Average of three samples from each site with error bars showing two times the standard deviation. Right: Same REE results normalized to PAAS values.

Results and discussion

Each water sample was analyzed in triplicate using the 8900 ICP-QQQ method, and the average REE concentration for each site is shown in Figure 3 (left). The REEs are a chemically similar group of elements, so tend to behave consistently. However, in most natural materials, the REEs alternate between high and low concentrations, giving a saw-tooth profile which makes it difficult to see anomalies. For this reason, geochemists often normalize REE data by dividing the concentration of each REE measured in the sample by that element's value in a reference material. In this case, the reference material used was Post-Archean Australian Shales (PAAS) (6), as shown in Figure 3 (right).

Apart from gadolinium (Gd), the normalized REE results for waters from different points on the river gave consistent, smooth profiles, despite the low concentrations. Gd was consistent with the other REEs in the river water collected at the upstream location (Mitake). But there was a spike in the Gd concentration in the samples taken at the other three sites. The results indicate contamination by Gd compounds, which were not removed by WWTP and so were discharged into the river. A possible source is widely used Gd-based magnetic resonance imaging (MRI) contrast agents.

The plots in Figure 3 also suggest that the light REEs were depleted in the WWTP effluents, but the higher mass REEs were somewhat enriched. There is also a suggestion that Ce might be anomalously high in the water from the Kita Tama WWTP, as this element lies above the smooth line formed by the other light REEs.

These patterns may indicate other sources of REE contamination from local industry, although most REE concentrations apart from Gd were at the single ppt level or below.

Conclusion

The study demonstrates the suitability of the Agilent 8900 ICP-QQQ with MS/MS mode for the direct measurement of 16 REEs in river water. All potential polyatomic interferences arising from Ba oxide or low mass REE-based hydride, oxide, and hydroxide polyatomic interferences were resolved using the N_2O mass-shift method.

Sub ppt MDLs were achieved for all the REEs using the MS/MS method. The high sensitivity and low background provided by the 8900 are needed for the determination of emerging pollutants in environmental samples, which are typically present at ultratrace concentrations.

The results from the analysis of the Japanese river water samples collected at different points along the river highlighted an interesting finding for Gd. While all the other REEs were measured below 50 ppt in all samples, there was a spike in the Gd concentration in samples collected at or near to wastewater discharge points. Gd MRI reagents may be the source of the contamination.

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