Analysis of Traces of Rare Earth Elements in a Rare Earth Element matrix using High Resolution ICP-OES

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Because of their ability to readily give up and accept electrons, the Rare Earth Elements (REEs) have become uniquely indispensable in many electronic, optical, magnetic and catalytic applications. From iPODs to catalytic converters, from wind power generators to computer disc drives and hybrid electric vehicles – Rare Earth applications are ubiquitous and critical from all days life to advanced R&D.

Most of Rare Earth Resources are actually located in China but there is a need of alternative resources in some other countries such as Brazil, Australia, Canada, South Africa, Greenland and USA. Electronic wastes are also a potential alternative source for REEs.

Once extracted, REEs-bearing minerals contain as many as 14 Rare Earth Elements and Yttrium. Complex extraction and refining should be conducted and the refined material should be analyzed to check for its purity.

Analysis by ICP-OES

ICP-OES is the most adequate technique to analyze traces of Rare Earth Elements in a matrix of another Rare Earth Element. Its major advantages compared to other techniques are the speed of analysis, its ability to analyze all elements in a single run and its tolerance to high concentration of major elements. For Rare Earth Elements, the ICP-OES should also offer High Resolution as Rare Earth Elements exhibit line-rich emission spectra.

Rare Earth Elements matrices

In this study, three matrices were studied and according to the matrix different traces of Rare Earth Elements were determined.

Matrix 1: CeO_2 nitrate (500 g/L) – Analysis of La_2O_3
Matrix 2: Gd_2O_3 nitrate (100 g/L) – Analysis of Tm_2O_3, Yb_2O_3 and Lu_2O_3
Matrix 3: CeO_2 nitrate (200 g/L) – Analysis of Ca, Na and K

Instrument

To ensure the best resolution available, an ULTIMA 2 ICP-OES was used for this study (Figure 1). The characteristics of the ULTIMA 2 and of the operating conditions are given in Tables below.

Figure 1: ULTIMA 2 High Resolution ICP-OES

Table 1. Characteristics of ULTIMA 2 ICP-OES Spectrometer

Optical mounting	Czerny-Turner
Focal length	1 meter
Gratings	Back-to-back gratings used in the 1st order
	4343 g/mm for 120-430 nm
	2400 g/mm for 430-800 nm
Resolution	<5 pm for 120-430 nm
(specification)	<11 pm for 430-800 nm
RF Generator	40.68 MHz solid state, water cooled
Torch	Vertical with Radial Viewing and Total plasma View*

* Total Plasma View: Measurement of the whole Normal Analytical Zone for enhanced sensitivity and reduced matrix effects

Table 2. Sample introduction system

Nebulizer	Glass concentric nebulizer
	0.8 L/min at 2.8 bars
Spray chamber	Glass cyclonic spray chamber
Sample uptake	1 mL/min
Injector tube inner diameter	3 mm

Table 3. Measurement conditions

Acquisition mode	Max mode
Measurement points	1
Integration time	4 s
Entrance slit	10 or 20 µm
Exit slit	15 or 80 µm

The ULTIMA 2 has a variable resolution thanks to its selectable slits. Thus the resolution effect can be studied before selecting the best slit combination. Measurement were done using max mode to avoid any bias to potential spectral interferences close to the analyte line.

Line selection

As REE are emitting line-rich spectra, line selection for analyte is a crucial step and should be conducted with great care. Main issue with such elements is that all lines are not reported in the literature and thus not identified. The huge knowledge of HORIBA Jobin Yvon for such kind of matrices allowed us to select adequate wavelengths for this analysis only with the knowledge of the major REE involved. Wavelengths selected for the analysis are given in Table below.

Table 4. Wavelengths used for the analysis

Matrix 1	La 333.749 nm
Matrix 2	Tm 313.126 nm, Yb 289.138 nm, Lu 261.542 nm
Matrix 3	Ca 396.847 nm, Na 588.995 nm, K 769.696 nm

Calibration strategy

Standard addition method was used as purest material than our samples is not available for matrix matching. External calibration has to be avoided as the difference between calibration standards and samples will be too important and a bias will be observed on final results.

For the analysis, matrices 1 and 2 were diluted to 20 g/L and matrix 3 was diluted to 100 g/L. The concentrations added were defined according to the expected result in the sample as it is a known value. Standard additions for each matrix are given in the table below.

Table 5. Standard additions

	Addition 1	Addition 2
La (Matrix 1)	20 ppm (0.4 mg/L)	40 ppm (0.8 mg/L)
Tm, Yb, Lu (Matrix 2)	5 ppm (0.1 mg/L)	10 ppm (0.2 mg/L)
Ca, Na, K (Matrix 3)	25 ppm (2.5 mg/L)	50 ppm (5 mg/L)

Study of resolution

To definitely set up the analytical method, it was necessary to define the slit combination that should be used. Profiles were then acquired using a 10/15 µm slits combination (high resolution setting) and a 20/80 µm slits combination (low resolution setting) for the La wavelength at 333.749 nm in Matrix 1 for standard addition 2.
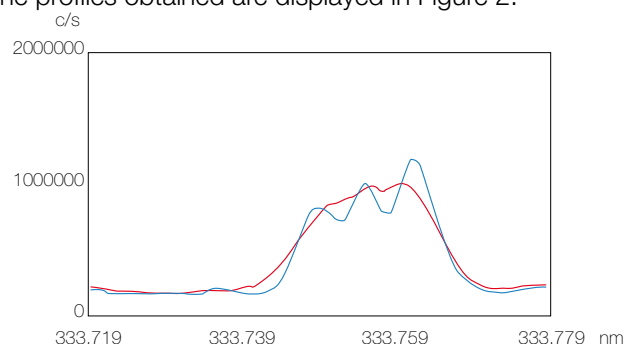The profiles obtained are displayed in Figure 2.

Figure 2: Profiles of La 333.749 nm for Standard Addition 2 of Matrix 1. In red, 20/80 µm slits combination (measured resolution 7.8 pm), in blue 10/15 µm slits combination (measured resolution 3.8 pm)

With low resolution (red profile), measurement of La is not possible due to Ce spectral interference. With High Resolution, measurement is possible as the La 333.749 nm wavelength and the doublet of Ce lines nearby are separated.

To ensure the highest reliability, it was decided to use the 10/15 µm slits combination for all wavelengths of REEs.

The profiles of samples and standard additions were acquired for all samples. The profiles obtained for La 333.749 nm are displayed in Figure 3 when Figure 4 displays the profiles for Lu 261.542 nm.
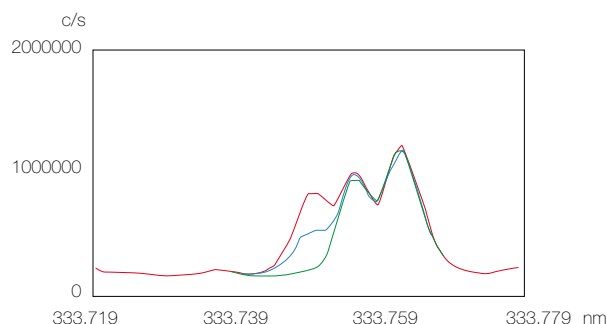

Figure 3: Profiles of La 333.749 nm for Matrix 1 (green profile), standard addition 1 (20 ppm – blue profile) and standard addition 2 (40 ppm – red profile) with 10/15 µm slits combination.
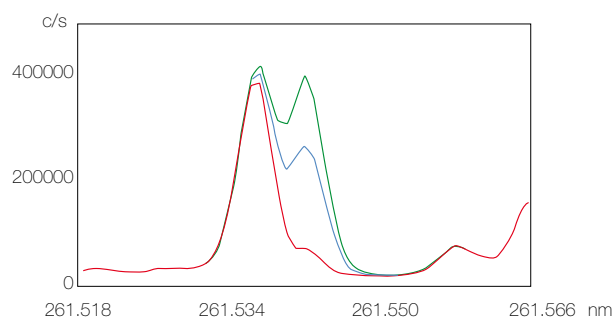

Figure 4: Profiles of Lu 261.542 nm for Matrix 2 (red profile), standard addition 1 (5 ppm – blue profile) and standard addition 2 (10 ppm – green profile) with 10/15 µm slits combination.

As shown in Figures 3 and 4, the analysis should be easy to conduct as the high resolution allows separating peaks from analyte and from matrix. The high sensitivity of the ULTIMA 2 ICP-OES spectrometer thanks to the Total Plasma View allows reaching the required detection limits for this application.

Evaluation of stability

Due to the low concentrations of trace Rare Earth Elements that have to be determined, the major element concentration is high, ranging from 20 to 100 g/L. To ensure reliability of the final result, the ICP-OES should allow long term stability over hours with such samples. The unique vertical torch and its 3 mm inner diameter injector associated with the sheath gas device, originally patented by HORIBA Jobin Yvon, helps to achieve unrivaled stability with such samples.

Stability was evaluated on a spiked sample for Matrix 1 on 3 hours and for Matrix 2 on 90 minutes. Stability is displayed in Figures 5 and 6 for Matrix 1 and Matrix 2, respectively.
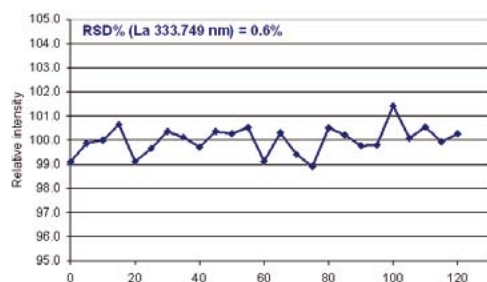

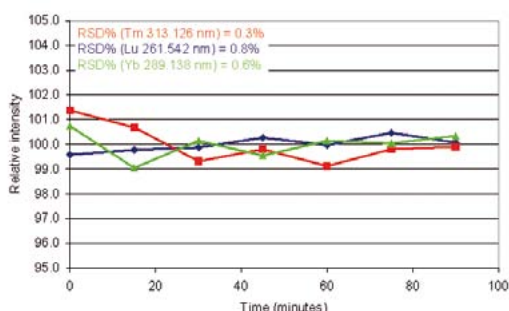Figure 5: Stability measured on La 333.749 nm for Matrix 1 over 3 hours

Figure 6: Stability measured on Tm 313.126 nm, Lu 261.542 nm and Yb 289.138 nm for Matrix 2 over 90 minutes

Stability obtained on Matrix 1 and Matrix 2 samples is identical to stability in water, proving the robustness of the ULTIMA 2 ICP-OES spectrometer.

Results

The results obtained on the samples are given in tables below. Results in ppm are for original sample when results in µg/L are for diluted sample. For Matrix 1 and Matrix 2, two different samples were analyzed, one unspiked and the other spiked. Note that the spike was done on a different batch of the sample, explaining some variations of the recovery rate. The aim of the spike was to check that the instrument allows detecting low values of the analyte in a given sample.

Table 6. Results obtained for Matrix 1 (Ce_2O_3 matrix analyzed at 20 g/L)

	Measured value	Expected value
La 333.749 nm	3 ppm (59 µg/L)	≤ 3 ppm
La 333.749 nm (spiked)	4.6 ppm (90 µg/L)	≤ 3 ppm then spiked with 1 ppm (20 µg/L)

Table 7. Results obtained for Matrix 2 (Gd_2O_3 matrix analyzed at 20 g/L)

	Measured value	Expected value
Lu 261.542 nm	0.3 ppm (5.9 µg/L)	≤ 3 ppm
Lu 261.542 nm (spiked)	1.4 ppm (27 µg/L)	3 ppm then spiked with 1 ppm (20 µg/L)
Tm 313.126 nm	0.4 ppm (8.4 µg/L)	≤ 1 ppm
Tm 313.126 nm (spiked)	1.4 ppm (28 µg/L)	1 ppm then spiked with 1 ppm (20 µg/L)
Yb 289.138 nm	0.5 ppm (8.2 µg/L)	≤ 3 ppm
Yb 289.138 nm (spiked)	1.4 ppm (23.9 µg/L)	≤ 3 ppm then spiked with 1ppm (20 µg/L)

Table 8. Results obtained for Matrix 3 (Ce_2O_3 matrix analyzed at 100 g/L)

	Measured value	Expected value
Ca 396.847 nm	2.1 ppm (206 µg/L)	≤ 2 ppm
Na 588.995 nm	1.4 ppm (138 µg/L)	
K 769.896 nm	0.6 ppm (56 µg/L)	

Results obtained are perfectly consistent with the expected values. The recovery of the spikes, even if the batch of the samples are different, are really good, all close to 100%

Conclusion

Analysis of traces of REEs in a major REE is not an easy task due to the line-rich emission spectra of these elements. Nevertheless, using a High Resolution ICP-OES spectrometer such as the HORIBA Jobin Yvon ULTIMA 2 with its unrivaled spectral resolution of <5 pm for the 120-430 nm wavelength range helps reaching high performance on such matrices.

The experimental profiles, the stability obtained on real samples and the consistence between expected results and measured concentrations prove that the ULTIMA 2 is a perfect tool for this particular application, from extraction, refining, standard applications to advanced R&D applications.

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