



Challenge

Quantification of rare earth elements in line-rich geological materials, such as granite and sandstone.

Solution

HR ICP-OES with high-resolution optical system in combination with a powerful software routine (CSI), being able to resolve spectral interferences originating from REE as well as from the line-rich matrix of typical geological matrices.

Analysis of Rare Earth Elements in Granite and Sandstone by HR ICP-OES

Introduction

Quantification of rare earth elements (REE) in geological materials by ICP-OES is one of the most challenging analytical routines. Often containing large amounts of alumina and silica, sulfur and refractory metals, etc., the high matrix contents of digested samples require for exceptional plasma robustness, in particular when trace levels of REE ought to be detected and sample dilution has to be avoided. The vast number of emission lines arising from both matrix and rare earth elements further adds to the complexity, which can be resolved by high spectral resolution only.

This application note describes a method for the analysis of two geological reference materials for granite (GSR-1) and sandstone (GSR-4) for its rare earth constituents including Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, and Yb by high-resolution Array ICP-OES on a PlasmaQuant 9100 Elite equipped with HF Kit.

Interference-free analysis in both granite and sandstone was possible for most REE elements thanks to the unique resolving power of the high-resolution optics of the PlasmaQuant 9100 Elite. Prominent spectral interferences from cerium, erbium, iron, and neodymium on sensitive emission lines of dysprosium, erbium, lanthanum, and samarium were successfully corrected by the CSI-Software Tool. Excellent agreement with the certified values and quality RSD values were obtained for granite (GSR-1) and sandstone (GSR-2). Matrix-specific detection limits are given.

Materials and Methods

Samples and reagents

- Geological reference materials for granite (GSR-1) and sandstone (GSR-4)
- Sodium peroxide
- Deionized water
- Nitric acid
- REE single element standards

Sample preparation

Samples were digested by alkaline fusion (0.1 g sample + 0.6 g Na₂O₂). To the fusions, 2 mL of nitric acid were added and afterwards filled up to 50 mL. The resulting nominal matrix content was approximately 12 g/L. These solutions were directly submitted to the PlasmaQuant 9100 Elite.

Calibration

Matrix matched calibration standards were produced from a Sodium Peroxide digestion blank using REE-single elements standards (1000 mg/L, Sigma Aldrich) according to the expected concentration range in the investigated samples. The prepared calibration levels are given in Table 1.

Table 1: Concentration of calibration standards

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4
Ce	mg/L	0	0.040	0.100	0.250	0.500
Dy	mg/L	0	0.004	0.010	0.025	0.05
Er	mg/L	0	0.004	0.010	0.025	0.05
Eu	mg/L	0	0.004	0.010	0.025	0.05
Gd	mg/L	0	0.004	0.010	0.025	0.05
Ho	mg/L	0	0.004	0.010	0.025	0.05
La	mg/L	0	0.020	0.050	0.125	0.250
Lu	mg/L	0	0.004	0.010	0.025	0.05
Nd	mg/L	0	0.040	0.100	0.250	0.500
Pr	mg/L	0	0.004	0.010	0.025	0.05
Sm	mg/L	0	0.004	0.010	0.025	0.05
Yb	mg/L	0	0.004	0.010	0.025	0.05

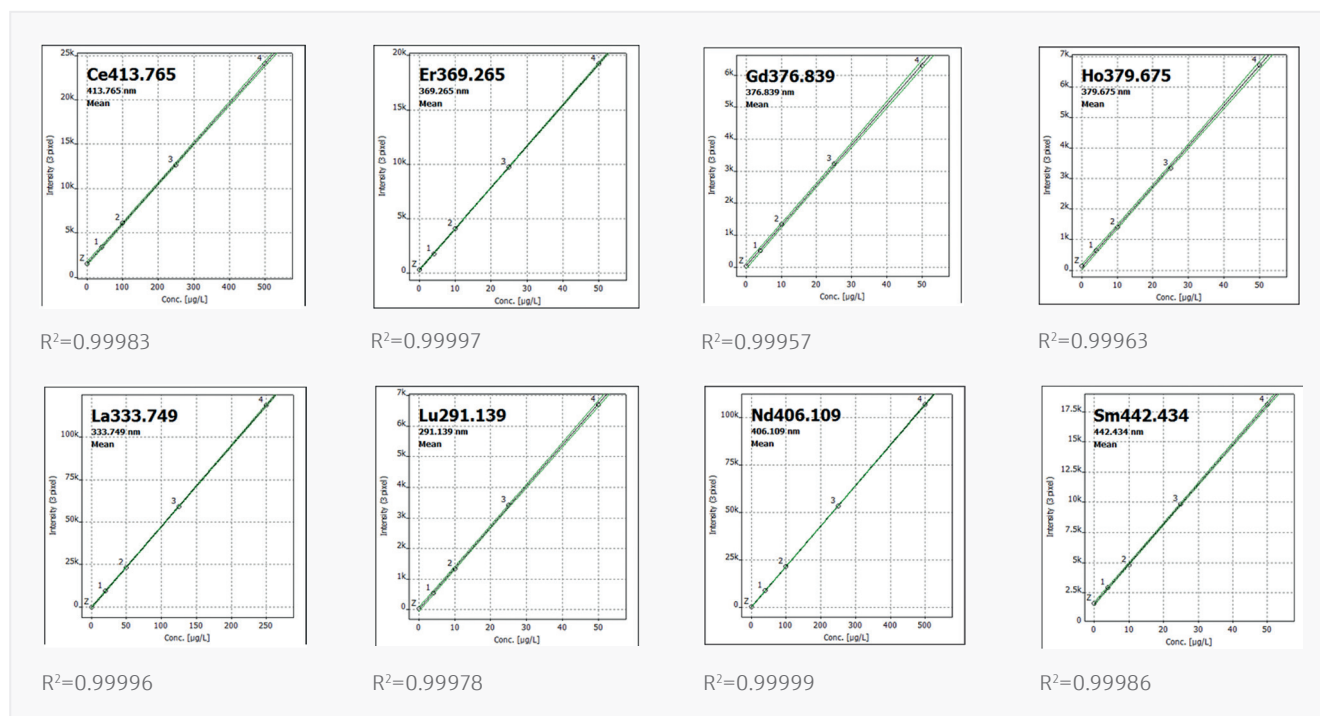


Figure 1 - 8: Calibration curves

Instrumentation

The analysis was performed on a PlasmaQuant 9100 Elite in combination with the ASPQ 3300 autosampler and HF sample introduction kit. Method settings as well as a detailed description of the parts of the sample introduction system are given in Table 2.

Table 2: Plasma configurations and set-up of the sample introduction system

Parameter	Settings
Power	1250 W
Plasma gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.6 L/min
Nebulizer ¹	PFA parallel path nebulizer, 1.0 mL/min
Spray chamber ¹	PTFE cyclonic spray chamber, 50 mL
Outer tube/Inner tube ¹	Syalon / alumina
Injector ¹	Alumina, inner diameter 2 mm
Pump tubing	PVC
Sample pump rate	1.0 mL/min
Read delay/ Rinse	45 s/ 20 s
Auto Sampler	Yes

¹ Salt Kit may be used, too, for samples that do not contain hydrofluoric acid (HF)

Evaluation parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Ce	413.765	axial	peak	3	3	ABC ¹	auto	-
Dy	353.170	axial	peak	3	3	ABC	auto	CSI ²
Er	369.265	axial	peak	3	3	ABC	auto	CSI ³
Eu	412.970	axial	peak	3	3	ABC	auto	-
Gd	376.839	axial	peak	3	3	ABC	auto	-
Ho	379.675	axial	peak	3	3	ABC	auto	-
La	333.749	axial	peak	3	3	ABC	auto	CSI ^{2,4}
Lu	291.139	axial	peak	3	3	ABC	auto	-
Nd	406.109	axial	peak	3	3	ABC	auto	-
Pr	532.276	axial	peak	3	3	ABC	auto	-
Sm	442.434	axial	peak	3	3	static	auto	CSI ^{2,5}
Yb	211.667	axial	peak	3	3	ABC	auto	-

1 automatic baseline correction (ABC)

2 mathematical correction of spectral interferences from Neodymium

3 mathematical correction of spectral interferences from Iron

4 mathematical correction of spectral interferences from Erbium

5 mathematical correction of spectral interferences from Cerium

Results and Discussion

Table 4 summarizes the obtained results for the analysis of the certified reference materials GSR-1 and GSR-4 in comparison with the certified values. The utilization of a Na₂O₂ fusion digestion methodology rather than an acidic digestion allows for a full access to all REE in the investigated samples. The precise analysis (RSD values well below 5%) of the as-prepared, matrix rich digestions was ensured by the high plasma stability as well as the smart torch design of the PlasmaQuant 9100 Elite. Due to the high resolution of the instrument (FWHM Dy 353.170 ≤ 5.5 pm), also severe interferences can be spectrally resolved, resulting in the ability to analyze the majority of the REE without any further mathematical correction algorithms. In this investigation only the elements dysprosium, erbium, lanthanum and samarium required a subsequent mathematical correction by the CSI software tool. The excellent accuracy and precision achieved with the applied methodology demonstrates its suitability for the routine analysis of geological samples for REE.

Table 4: Overview of results for two geological reference materials comprising of granite (GSR-1) and sandstone (GSR-4)

Element	GSR-1			GSR-4			DL ¹ [µg/L]
	Measured value [mg/kg]	RSD ² [%]	Certified value [mg/kg]	Measured value ³ [mg/kg]	RSD [%]	Certified value [mg/kg]	
Ce	112 ± 2.3	0.09	108 ± 7	52.6 ± 2.2	0.92	48 ± 4	0.85
Dy	10.6 ± 0.97	2.7	10.2 ± 0.4	4.18 ± 0.96	1.8	4.1 ± 0.4	0.32
Er	7.0 ± 0.099	0.87	6.5 ± 0.3	2.15 ± 0.10	0.48	2 ± 0.3	0.15
Eu	0.705 ± 0.56	3.0	0.85 ± 0.07	1.00 ± 0.52	1.6	1.02 ± 0.08	0.04
Gd	10.3 ± 0.37	1.7	9.3 ± 0.7	4.76 ± 0.36	3.0	4.5 ± 0.4	0.36
Ho	2.22 ± 0.38	5.0	2.05 ± 0.17	0.841 ± 0.37	2.3	0.75 ± 0.12	0.11
La	53.4 ± 0.53	1.9	54 ± 4	21.9 ± 0.52	0.73	21 ± 2	0.14
Lu	1.11 ± 0.30	4.7	1.15 ± 0.09	0.257 ± 0.29	5.9	0.3 ± 0.03	0.19
Nd	48.6 ± 0.67	0.72	47 ± 4	23.8 ± 0.67	0.49	21 ± 2	0.34
Pr	12.2 ± 1.3	2.1	12.7 ± 0.8	5.65 ± 1.2	1.3	5.4 ± 0.6	1.55
Sm	9.23 ± 0.20	1.4	9.7 ± 0.8	4.70 ± 0.20	5.3	4.7 ± 0.3	0.65
Yb	7.67 ± 0.36	1.3	7.4 ± 0.5	2.15 ± 0.38	1.6	1.9 ± 0.2	0.34

1 Matrix-specific detection limit obtained from 3σ of SD for QC matrix blank (12 g/L Sodium peroxide),

2 RSD values obtained from three replicate measurements per sample

3 Confidence interval according to DIN 32645 and DIN 38402

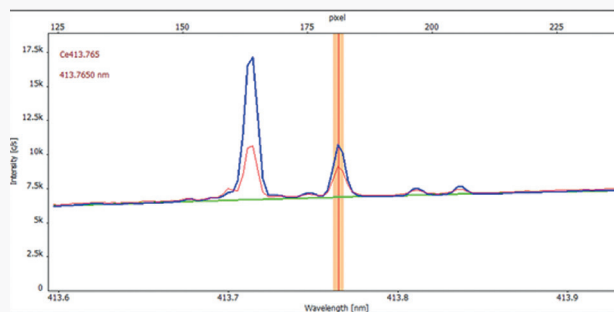


Figure 9: Ce 413.765 nm

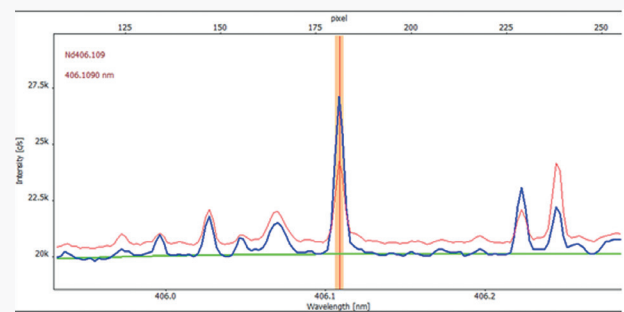


Figure 10: Nd 406.109 nm

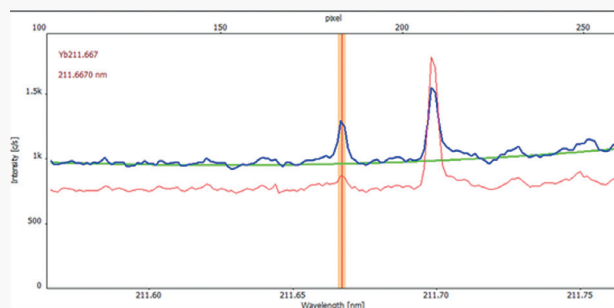


Figure 11: Yb 211.667 nm

Figures 9-11: Collection of High-Resolution spectral data for granite, GSR-1 (blue) and sandstone, GSR-4 (red). Automatic baseline fit, ABC (green).

Conclusion

The analysis of rare earth elements (REE) exhibits several obstacles, such as the ability for complete access to all REE, analysis of matrix-rich samples, and the high potential of severe spectral interferences. The application methodology presented here combines a fusion digestion procedure using a Na₂O₂ flux with the analysis by high-resolution ICP-OES on the PlasmaQuant 9100 Elite.

The fusion digestion allows residue-free digestion of complex geological matrices, hence all analytes, including both light and heavy REE, can be readily analyzed. Since the solutions as prepared carry both the sample and the flux matrix, a highly stable plasma performance and a sample introduction system are required to perform a high-precision and high-accuracy analysis. Here, the PlasmaQuant 9100 Elite features a high-frequency generator for the best plasma stability among ICP-OES instrumentation. Using its V-Shuttle torch, a fully demountable vertically-oriented torch, the analysis of highest matrix content (e.g. 12 g/L fusion flux) is ensured without further dilution that benefits REE detection limits. Matrix specific detection limits in the ng/L to low µg/L range can be achieved.

Severe spectral interferences arising from other REE or elements that often accompany REE, such as iron, complicate their accurate analysis in geological materials. The PlasmaQuant 9100 Elite exhibits two powerful features to overcome such spectral interferences: the high resolution of the optical system and the CSI software tool. The former makes it possible to spectrally resolve even severe interferences without further mathematical correction schemes, and the latter is able to correct for most difficult interferences by applying a mathematical correction to provide an interference-free result, making the PlasmaQuant 9100 Elite the perfect analytical tool for the analysis of REE in any geological sample.

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