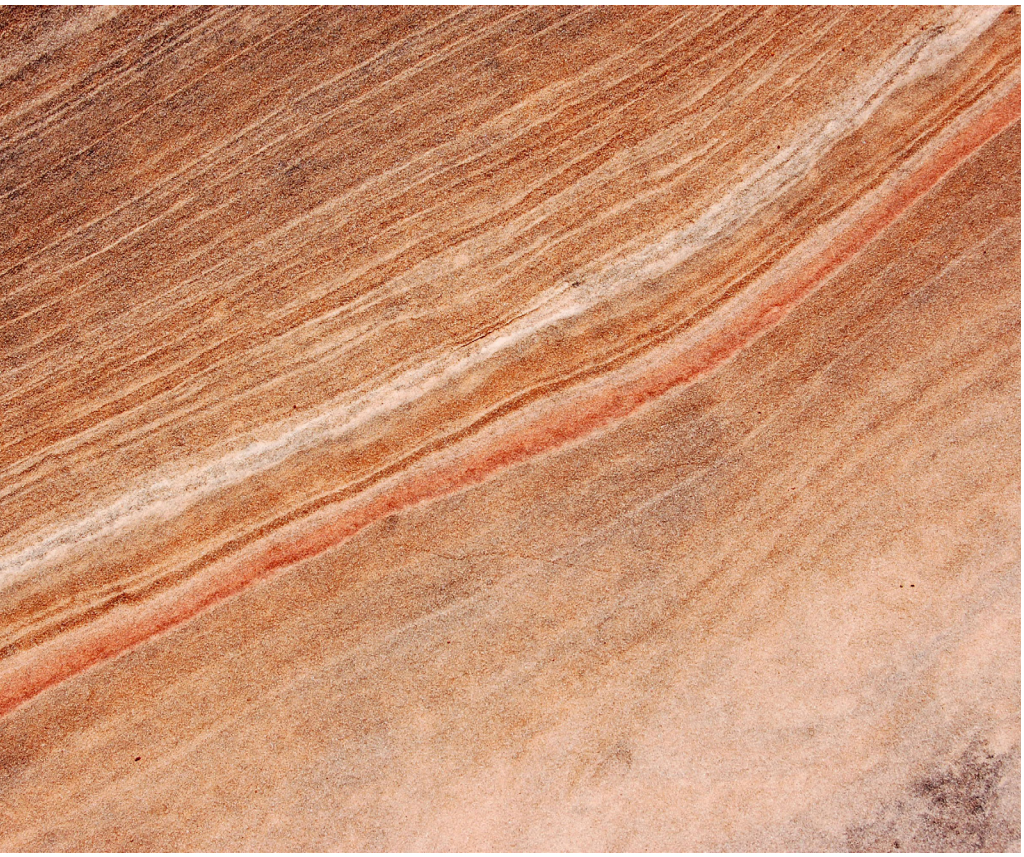

Challenge
Quantification of rare earth elements in line-rich geological materials, such as granite and sandstone.

Solution
HR ICP-OES with a high-resolution optical system and powerful CSI software capable of resolving spectral interferences from REE and the line-rich matrices of geological samples.

Intended audience
Geochemists and geologists, analytical scientists, laboratory personnel, quality control and reference material laboratories.

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, silica, iron and refractory metals etc. the high matrix contents of digested samples require an 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 is further contributes 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 9200 Elite.

Interference-free analysis in both granite and sandstone was possible for these REE thanks to the unique resolving power of the High-Resolution optics of the PlasmaQuant 9200 Elite. Prominent spectral interferences from cerium, erbium, iron und 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 excellent RSD values were obtained for granite (GSR-1) and sandstone (GSR-4). Matrix-specific detection limits are given.

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An Endress+Hauser Company

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 Na_2O_2). 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 9200 Elite without issues, proving the exceptional robustness of the efficient plasma.

Calibration

According to sample preparation with N_2O_2 and HNO_3, 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, while four exemplary calibration functions are shown in figure 1.

Table 1: Concentration of calibration standards for Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, and Yb

Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4
µg/L	0	10	50	100	500

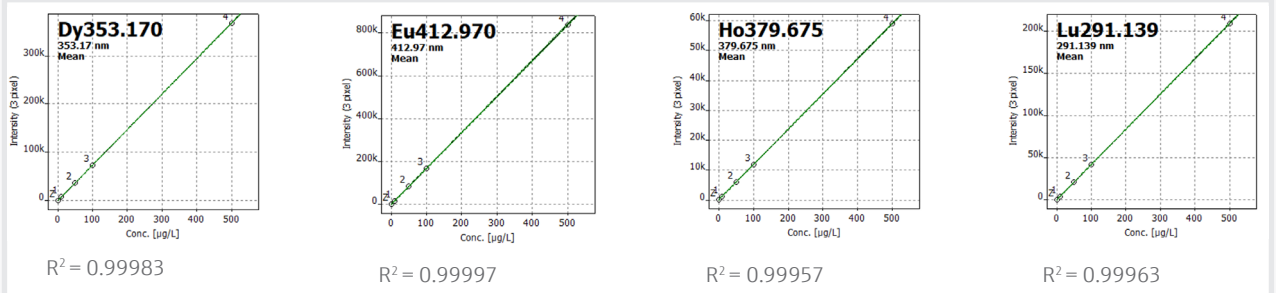


Figure 1: Exemplary calibration functions

Instrumentation

The analysis was performed on a PlasmaQuant 9200 Elite in combination with the Cetac ASX-560 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 PlasmaQuant 9200 Elite
Power	1,250 W
Plasma gas flow	8.5 L/min
Auxiliary gas flow	0.4 L/min
Nebulizer gas flow	0.6 L/min
Nebulizer	Concentric nebulizer for high salt content, borosilicate, 2.0 mL/min
Spray chamber	Cyclonic spray chamber with dip tube[1], 50 mL, borosilicate
Outer tube/inner tube	Quartz / quartz
Injector	Alumina[2], inner diameter 2 mm
Pump tubing	PVC
Sample pump rate	1.0 mL/min
Delay Time/ Rinse	45 s/ 45 s
Auto Sampler	Cetac ASX-560

1 ... the double-path geometry improves precision for high matrix-loadings
2 ... ceramic injector prolongs the lifetime of the torch in sodium-rich matrices

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	1	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

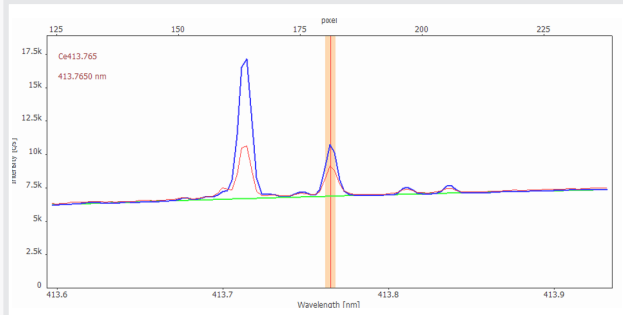
Table 4 summarizes the obtained results for the analysis of the certified reference materials GSR-1 and GSR-4 in comparison with the certified values. The utilization of a Na_2O_2 fusion digestion methodology rather than an acidic digestion allows for a full access to all REE in the investigated samples. The precise analysis (RSD values well below 3%) of the matrix rich digestions was ensured by the high plasma stability as well as the smart torch design of the PlasmaQuant 9200 Elite. Due to the high resolution of the instrument (2pm@200nm, FWHM Dy 353.170 ≤ 5.5 pm), even severe interferences can be spectrally resolved, resulting in the ability to analyze the majority of the REE without any further mathematical correction algorithms. As an example the interference-free spectra for cerium, neodymium and ytterbium are shown in figure 2. In this study only the elements dysprosium, erbium, lanthanum and samarium required a subsequent mathematical correction by the CSI software tool. For example, the erbium line at 369.265nm is interfered with an Iron line. The spectral differences between the emission maximum of erbium and the iron interference is only 1.5 pm, which can be discerned by comparing the peak center of the calibration standard with the peak of the sample. To overcome this interference, the CSI algorithm can be used with a pure iron spectrum (1 g/L Fe solution) as correction spectrum. This results in a perfect, not interfered peak of erbium. The uncorrected and interference-corrected spectra for erbium in GSR-1 are shown as an example in figure 3.

The excellent accuracy and precision achieved with the applied methodology demonstrates its suitability for the routine analysis of geological samples for REE.

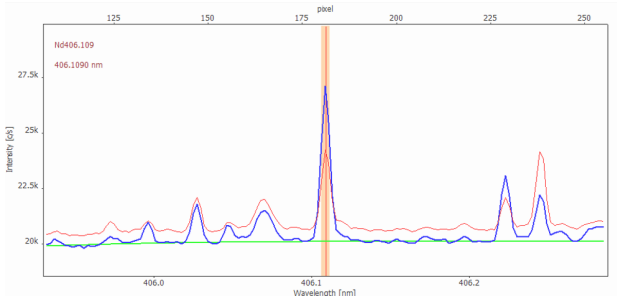
Table 4: Overview of results for two geological reference materials comprising of granite (GSR-1) and sandstone (GSR-4)

Element	GSR-1			GSR-4			LOD[1] [mg/kg]
	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	2.7	1.15 ± 0.09	0.257 ± 0.29	2.9	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	2.3	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

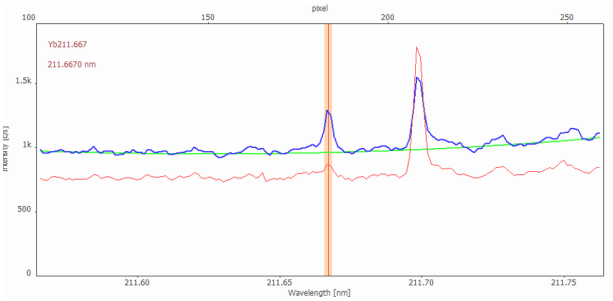
1 … Matrix-specific detection limit obtained from 3σ of SD for QC matrix blank (12 g/L Sodium peroxide)
2 … RSD values obtained from three replicate measurements per sample
3 … Confidence interval according to DIN 32645 and DIN 38402



Ce 413.765 nm

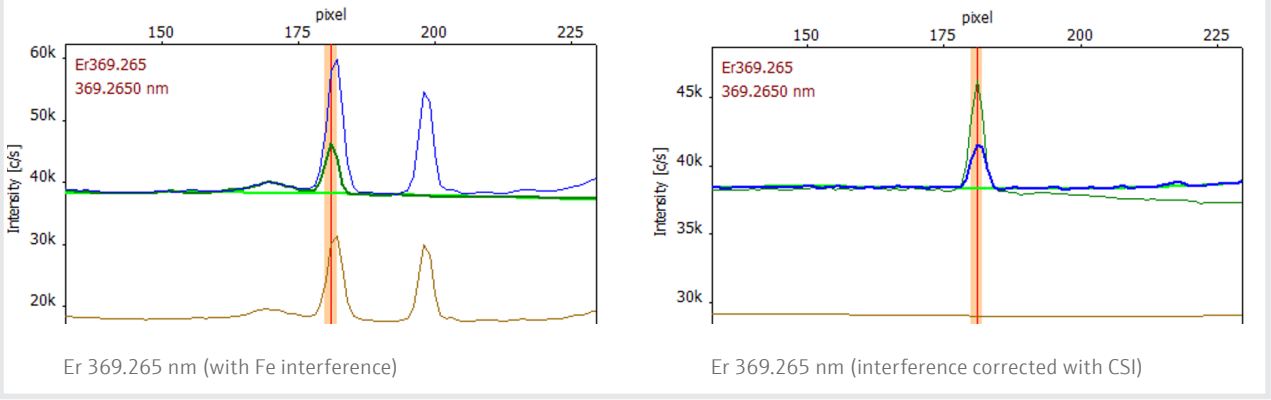


Nd 406.109 nm



Yb 211.667 nm

Figure 2: Collection of High-Resolution spectral data for granite, GSR-1 (blue) and sandstone, GSR-4 (red). Automatic baseline fit, ABC (green)



Er 369.265 nm (with Fe interference)

Er 369.265 nm (interference corrected with CSI)

Figure 3: Correction of spectral interference (CSI) of Fe (1 g/L, brown) on High-Resolution spectral data for granite, GSR-1 (blue). Automatic baseline fit, ABC (green). Calibration standard 10 µg/L (dark green). Intensity adjusted for better visibility.

Summary

The analysis of rare earth elements (REE) needs to overcome several obstacles, such as the need for complete digestion of the sample material as well as keeping all REE in solution, the analysis of matrix-rich samples and the high potential of severe spectral interferences. Herein, we presented an application methodology that combines a fusion digestion procedure using a Na_2O_2 flux with the analysis by High-Resolution ICP-OES on the PlasmaQuant 9200 Elite.

The fusion digestion allows residue-free digestion of complex geological matrices, hence all analytes, both light and heavy REE can be readily analyzed. Since the sample solutions carry both the sample and the flux matrix, a highly stable plasma performance as well as sample introduction system is required to perform a high precision and high accuracy analysis. Here, the PlasmaQuant 9200 Elite features a robust and highly efficient generator for best plasma stability with low argon consumption. Using the 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.

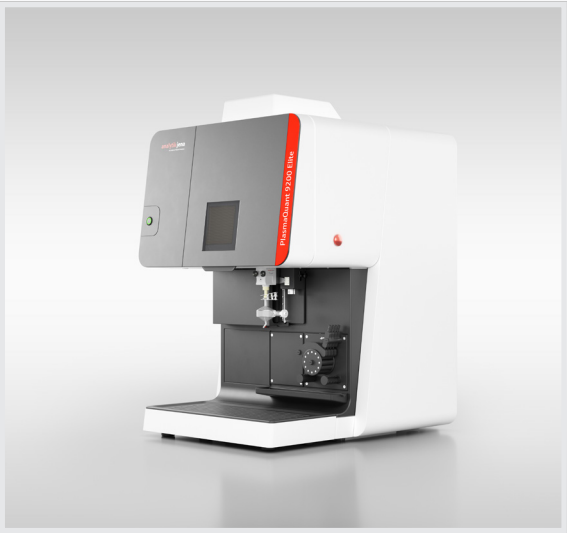


Figure 4: PlasmaQuant 9200 Elite

The PlasmaQuant 9200 Elite provides two powerful features to overcome such spectral interferences, the high resolution of the optical system and the CSI software tool. The former allows to spectrally resolve most interferences and the latter is able to correct even the most difficult interferences by applying a mathematical correction to provide an interference-free result making the PlasmaQuant 9200 Elite the perfect analytical tool for the analysis of REE in any geological sample.

Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
SALT Kit for PlasmaQuant 9x00 series	810-88009-0	Sample introduction kit for medium TDS concentrations
Teledyne Cetac ASX-560	810-88015-0	Autosampler with integrated rinse function

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