

Determination of rare earth elements in geological samples using the Agilent SVDV ICP-OES

Application note

Geochemistry, mining and minerals

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Introduction

The chemical analysis of geological materials is required for a better understanding of mineral reserves but also for geological and geochemistry studies. The determination of rare earth elements (REEs) in geological materials can provide valuable information about the geochemical formation and origin. Nowadays, REEs are critically needed for high-technology and military applications [1] and some ores may be a rich source of REEs, such as Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th and Tm.



Among the spectrometric techniques available, instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) are commonly applied for REEs determination in mineral samples, due to multi-element capability, high sensitivity and low detection limits. However, those techniques are costly and suffer from interferences caused by long irradiation times and spectral overlaps, respectively.

X-ray fluorescence (XRF) gives the possibility of direct solid analysis, but it presents high detection limits not suitable for samples with low concentrations of REEs [2]. In this context, inductively coupled plasma optical emission spectrometry (ICP-OES) has been reported as a good alternative for REEs determination due to multi-element capacity, wide linear dynamic range and operational simplicity [2,3]. Moreover, in some cases it is important to have a sample profile to check for possible interfering elements on other target analytes when applying other instrumental methods, for example, compared to the magnitude of interferences caused by double-charged species, such as $^{150}\text{Sm}^{2+}$ and $^{150}\text{Nd}^{2+}$, on $^{75}\text{As}^+$ determination by ICP-MS [4], ICP-OES offers greater flexibility for choosing emission wavelengths and viewing position without interferences.

In this study the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES (this application is also applicable to the 5110 SVDV ICP-OES) was used for the determination of REEs (Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th and Tm) in geological samples. The 5100 and 5110 instruments allow for synchronous measurement capturing the axial and radial views of the plasma in one read, for SVDV viewing mode. Synchronous Vertical Dual View (SVDV) mode allows time saving for data acquisition which consequently reduces argon consumption per sample.

Experimental

Instrumentation

All measurements were performed using an Agilent 5100 SVDV ICP-OES with Dichroic Spectral Combiner (DSC) technology. The unique DSC component selects and combines the axial and radial light from the vertically-oriented plasma, with all wavelengths measured in a single reading. The VistaChip II CCD detector has the largest dynamic range. Full wavelength

range is available for analysis, meaning the best wavelength, free of spectral interferences can be used. The sample introduction system consisted of a SeaSpray nebulizer, single-pass spray chamber and 1.8 mm ID injector torch. Instrument operating conditions are presented in Table 1.

Table 1. Operating parameters used for the Agilent 5100 SVDV ICP-OES.

Instrument parameter	Setting
Read time (s)	20
Replicates	3
Sample uptake delay (s)	15
Fast Pump (80 rpm)	Yes
Stabilization time (s)	15
Pump Speed (rpm)	12
Sample tubing	white-white
Waste tubing	blue-blue
RF power (kW)	1.5
Aux flow rate (L/min)	1.0
Plasma flow rate (L/min)	12.0
Nebulizer flow rate (L/min)	0.60
Viewing modes	Radial and SVDV
Viewing height (mm)	8
Background correction	Auto

Reagents and standard solutions

All glassware was decontaminated by immersion in 10% v/v HNO_3 for at least 24 h and rinsed with distilled-deionized water (resistivity > 18.2 $\Omega\text{M cm}$), obtained from a Milli-Q® Water System (Millipore, Bedford, MA, USA). All calibration standards and blanks were prepared with ultrapure water and nitric acid obtained using a sub-boiling distillation apparatus (Milestone). A multi-element calibration standard (Agilent Technologies, USA) of 10 mg/L Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th and Tm was used to prepare working standards in the 0.05 – 5 mg/L concentration range.

Samples and sample preparation

Geological samples were obtained from a commercial mining company. These consisted of two samples (Sample 1 and Sample 2) with unknown concentrations of REEs. Approximately 100 mg of each sample were weighed directly into the Teflon-PFA digestion vessels followed by the addition of 9.0 mL of Aqua Regia. Following the addition of Aqua Regia, the samples were

left at room temperature overnight before digestion of the samples was carried out in a closed vessel microwave, cavity Ethos 1 Microwave oven (Milestone, Sorisole, Italy), according to the heating program presented in Table 2. After digestion, samples were transferred to 50 mL polypropylene flasks and made to a total of 50.0 mL with distilled-deionized water, resulting in 0.2% TDS. The accuracy of the proposed procedure was verified by addition and recovery of Sample 2 spiked at 2.5 mg/L with a multi-element calibration standard. This procedure was performed in triplicate.

Table 2. Microwave-assisted acid digestion heating program for REEs determination in geological samples.

Step	Applied power (W)	Time (min)	Temperature (°C)
1	500	10	120
2	1000	20	220
3	1000	5	220

Results and discussion

Method detection limits

For determination of rare earth elements in geological samples, external calibration was employed. Method Detection Limits (MDLs) were obtained considering background equivalent concentrations (BEC) and relative standard deviations (RSD) for 10 measurements of the digested blank samples.

MDLs are shown in Table 3. Three wavelengths were selected for each element for all measurements, and the optimal wavelength for each element in SVDV and radial viewing modes are displayed. Low MDL values were reached and, in general, lower MDLs were obtained using the SVDV viewing mode. Traditional REEs are measured radially with a vertical plasma, due to the heavy matrix nature of geological samples. SVDV mode allows for wavelengths to be read axially from the vertically-oriented plasma, ideal for geological samples as it provides much lower MDLs than radial view.

Table 3. BEC and MDL values obtained for SVDV and radial viewing modes.

Radial			SVDV		
Element & wavelength (nm)	BEC (mg/L)	MDL (mg/kg)	Element & wavelength (nm)	BEC (mg/L)	MDL (mg/kg)
Dy 353.171	0.009	1.1	Dy 340.780	0.0007	0.6
Er 349.910	0.004	1.1	Er 369.265	0.00008	0.1
Eu 397.197	0.0004	0.09	Eu 397.197	0.003	2.6
Gd 336.224	0.003	0.6	Gd 335.048	0.001	0.5
Ho 341.644	0.008	0.9	Ho 339.895	0.0009	0.8
La 379.477	0.001	0.2	La 408.671	0.0007	0.5
Lu 307.760	0.003	0.7	Lu 307.760	0.0005	0.4
Nd 406.108	0.04	2.8	Nd 401.224	0.002	1.0
Pr 422.532	0.009	1.8	Pr 422.532	0.00008	0.02
Sc 363.074	0.0005	0.2	Sc 335.372	0.00005	0.05
Sm 360.949	0.008	2.7	Sm 360.949	0.002	1.3
Tb 367.636	0.01	1.7	Tb 350.914	0.0006	0.7
Th 283.730	0.02	3.7	Th 283.730	0.003	1.6
Tm 342.508	0.003	0.9	Tm 346.220	0.00008	0.08

Spike recoveries

Spike recoveries were performed to check the accuracy of the proposed method. Results presented in Table 4 show good accuracy was obtained in both radial and SVDV viewing modes. La, Nd and Pr were present at high concentrations in both samples, thus a 4-fold additional dilution was necessary. Recoveries ranged from 90.1 to 107% for both viewing modes.

Calibration linearity

Excellent linearity was achieved with calibration coefficients greater than 0.9990 obtained for all analytes, with less than 5% error for each calibration point for both radial and SVDV measurements. Figures 1 and 2 display the calibration curve for Lu 307.760 nm in radial and SVDV modes, respectively.

Table 4. Spike recoveries for REEs (mean \pm standard deviation, n=3) in a 2.5 mg/L spiked geological sample. obtained for SVDV and radial viewing modes.

SVDV mode		Radial mode	
Element & wavelength (nm)	Recovery (%)	Element & wavelength (nm)	Recovery (%)
Dy 340.780	94.4 \pm 0.9	Dy 353.171	97 \pm 1
Er 369.265	97.4 \pm 0.2	Er 349.910	96.6 \pm 0.4
Eu 381.967	96.6 \pm 0.1	Eu 397.197	96.1 \pm 0.4
Gd 335.048	94.4 \pm 0.4	Gd 336.224	95.3 \pm 0.8
Ho 339.895	94.8 \pm 0.1	Ho 341.644	97.4 \pm 0.7
La 333.749	105 \pm 5	La 379.477	107 \pm 7
Lu 261.541	96.1 \pm 0.1	Lu 307.760	97.4 \pm 0.6
Nd 406.108	106 \pm 3	Nd 406.108	104 \pm 5
Pr 417.939	100 \pm 1	Pr 422.532	99 \pm 1
Sc 363.074	96.1 \pm 0.3	Sc 363.074	98.7 \pm 0.6
Sm 360.949	91.8 \pm 0.5	Sm 360.949	95.7 \pm 0.4
Tb 367.636	97.9 \pm 0.3	Tb 367.636	96.6 \pm 0.6
Th 283.730	97.4 \pm 0.4	Th 283.730	90.1 \pm 0.7
Tm 342.508	94.0 \pm 0.1	Tm 342.508	96.6 \pm 0.4

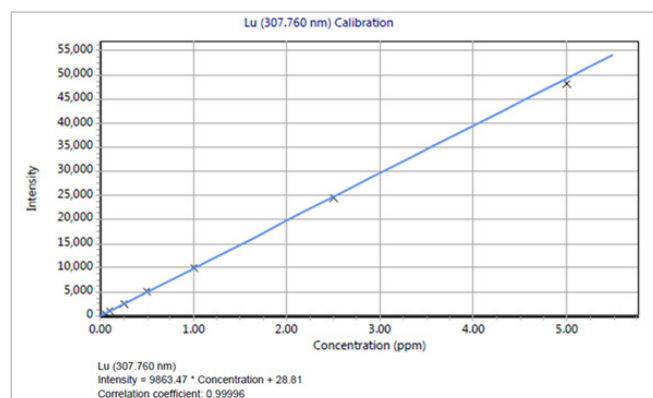


Figure 1. Calibration curve for Lu 307.760 nm in radial mode.

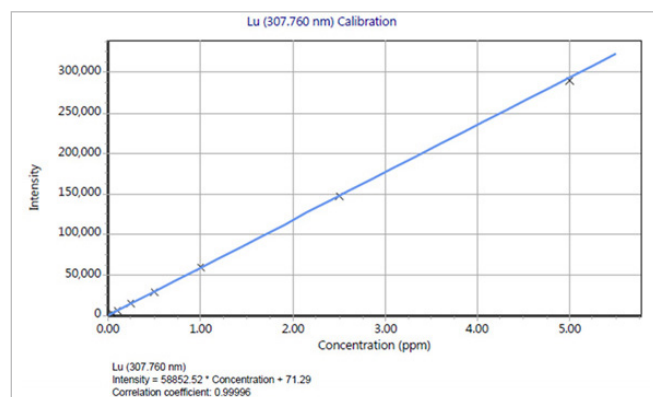


Figure 2. Calibration curve for Lu 307.760 nm in SVDV mode.

Sample analysis

Determination of REEs in geological samples is displayed in Table 5. Once again, due to the high concentrations of La, Nd and Pr in the samples, further dilution was required, but the expansion of the linear range of calibration curves is also feasible.

Application of a t-test showed no statistically significant differences with a 95% confidence level observed between SVDV and radial viewing modes. Therefore, only the results for SVDV mode are displayed in Table 5.

Sample 1 contained higher concentrations of REEs than sample 2, of all analytes except Sc. The REEs determination by ICP-OES in SVDV mode was fast and the excellent results for the spike recoveries showed that spectral interferences were not an issue. For each element, three emission lines were measured requiring 3 mL of sample and less than 2 min acquisition of all data in both radial and SVDV viewing modes, which led to desirable sample throughput.

Table 5. Determination of rare earth elements (mean \pm standard deviation, n = 3) in geological samples by Agilent 5100 ICP-OES with SVDV viewing.

Element & wavelength (nm)	Sample 1	Sample 2
	Determined (mg/kg)	
Dy 340.780	60 \pm 8	<0.6
Er 369.265	18 \pm 4	<0.1
Eu 381.967	148 \pm 11	58 \pm 4
Gd 335.048	330 \pm 30	<0.5
Ho 339.895	<0.8	<0.8
La 333.749	8005 \pm 744	2798 \pm 150
Lu 261.541	<0.4	<0.4
Nd 406.108	6332 \pm 592	1730 \pm 96
Pr 417.939	2160 \pm 191	568 \pm 30
Sc 363.074	83 \pm 8	153 \pm 9
Sm 360.949	513 \pm 45	<1.3
Tb 367.636	155 \pm 19	128 \pm 8
Th 283.730	345 \pm 30	225 \pm 13
Tm 342.508	35 \pm 4	<0.08

Conclusions

In this study, the Agilent 5100 SVDV ICP-OES proved well suited to the determination of REEs in geological samples.

The instrument's multi-element capabilities and expansive wavelength selection ensured the spectral interferences associated with complex geological samples were not an issue.

Axial readings of the vertical-oriented plasma in SVDV meant, that in most cases, lower MDLs for REEs in geological samples could be achieved in SVDV mode than in radial.

The high sample throughput, accuracy and precision of the proposed procedure indicates that the Agilent 5100 or 5110 SVDV ICP-OES, running in SVDV viewing mode are a simple and cost effective alternative for REE determination in geological samples.

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Verified for Agilent
5110 ICP-OES



Results presented in this document were obtained using the 5100 instrument, but performance is also verified for the 5110 ICP-OES

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