

Analysis of Rare Earth Elements in Base Metal Ores by ICP-OES

Overcoming complex spectral interferences using an
Agilent 5800 VDV ICP-OES



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Introduction

The Rare Earth Elements (REEs) are an important group of elements. They consist of the 15 lanthanide elements, from lanthanum (La) to lutetium (Lu). Some lists of REEs also include scandium (Sc) and yttrium (Y) due to the similarity of their physical and chemical attributes with the lanthanides. The unique properties of REEs make them especially useful in defense, energy, and industrial applications.

While REEs are not uncommon in the earth's crust, they are not often found in sufficient concentrations to make extraction commercially viable. The physical properties of rocks (lithology) of known deposits of REEs fall into a few major categories. The categories include carbonatites (carbonate-rich igneous rock types containing high Ca, Mg and/or Fe), peralkaline igneous (high in Na, Ca, K and lower in Si, Al), ion-adsorption clay deposits (leached from bedrock granite in tropical regions with moderate to high rainfall), and iron oxide/copper/gold (IOCG) deposits (1).

Due to its speed, robustness, and multi-element capabilities, many geological testing laboratories use ICP-OES for the high-throughput measurement of major and trace elements in base metal ores. However, the varied lithologies and associated elemental content of the common REE source-rocks can create challenges in assessing the REE content of mining deposit materials using ICP-OES. The close association that REEs have with each other, and the hundreds of spectral lines for each REE, make it difficult to find interference-free lines, or lines that can be easily corrected.

To deal with challenging samples, such as line-rich optical emission spectra of REEs and the associated spectral interferences, Agilent has focused developments on improving ICP-OES performance and simplifying operation. The Agilent 5800 and 5900 ICP-OES use freeform optics to enhance spectral resolution and an advanced detector that improves sensitivity. The higher resolution optics mean that more analyte lines are separated from neighboring lines, enabling the 5800 or 5900 to achieve lower detection limits for elements in complex matrices. Effective background correction and interference removal techniques, an easy-to-use sample introduction system, and intuitive maintenance tools also help achieve reliable, robust, and routine analysis of high matrix samples.

In this study, an Agilent 5800 Vertical Dual View (VDV) ICP-OES was used to measure 16 elements in three REE certified reference materials (CRMs) and four REE ores samples.

Experimental

Instrumentation

An Agilent 5800 Vertical Dual View (VDV) ICP-OES was fitted with a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, and demountable 1.8 mm i.d injector torch. The AVS 7 switching valve and SPS 4 autosampler were used for the fast and automated delivery of the samples to the ICP-OES. The AVS 7 features a seven-port valve and a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis without compromising on performance. The AVS 7 reduces maintenance and cleaning of the torch, as less sample digest passes through as compared to conventional sample introduction. The 5800 VDV uses an Agilent Vista Chip III charge-coupled device (CCD) detector. The detector provides high-speed, continuous wavelength coverage from 167 to 785 nm, allowing the analyst to choose multiple wavelengths for each element without adding any additional time to the analysis.

Selecting multiple wavelengths for an element increases the chance of finding interference-free lines. If a spectral overlap is recognized, the best correction tool can then be applied. Analysts can use IntelliQuant Screening within the ICP Expert software during method development to identify if any wavelengths are interfering on analyte lines (2, 3). IntelliQuant Screening recommends the best wavelength to use for the analysis via the star rating system. To obtain valuable information about this method, some of the CRM digests were analyzed using IntelliQuant Screening.

The vertical torch position of the 5800 VDV ICP-OES leads to excellent plasma robustness and long-term stability. The plug-and-play design automatically aligns the torch and connects the gases for a quick and simple start-up. Reproducible setup of the torch is needed for the repeatable analysis of challenging samples such as REE ores, especially if different analysts use the instrument. An internal standard (bismuth at 10 mg/L, added in-line) was used to correct for any matrix interferences.

The 5800 VDV ICP-OES operating conditions are given in Table 1 and the AVS 7 parameters are listed in Table 2.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Settings
Read Time (s)	20
Replicates	2
Sample Uptake Delay (s)	-
Stabilization Time (s)	5
Rinse Time (s)	-
Pump Speed (rpm)	12
RF Power (kW)	1.5
Auxillary Flow (L/min)	1
Plasma Flow (L/min)	12
Nebulizer Flow (L/min)	0.70
Sample Pump Tubing	White/white
Internal Standard Pump Tubing	Orange/green
Waste Pump Tubing	Blue/blue
Background Correction	FBC/FACT/ Off-peak
Viewing Mode	Axial

Table 2. Agilent AVS 7 switching valve system parameters.

Parameter	Setting
Sample Loop Size (mL)	1.0
Pump Rate - Uptake (mL/min)	35
Pump Rate - Inject (mL/min)	5
Valve Uptake Delay (s)	6
Bubble Inject Time (s)	1.8
Pre-emptive Rinse Time (s)	2

Sample preparation

Three ores CRMs, REE-1, REE-2, and REE-3, Natural Resources Canada (NRC), were used to validate the 5800 VDV ICP-OES method. The reference ores contain significant levels of REEs, as shown in the certificates of analysis (4). REE-1 is an ore containing REEs, zirconium (Zr), and niobium (Nb), from the Strange Lake deposit, Quebec, Canada. REE-2 is a carbonatite with REEs obtained from a Canadian mining company. REE-3 is an ore with REEs and zirconium.

Four raw REE rhyolite ore samples, ores 1 to 4, were obtained from a rare earth mining group in the USA. To ensure that the sample was homogeneous before microwave digestion, the samples were ground to a fine powder. The samples, CRMs, and method blanks were prepared and digested at CEM Corporation.

High purity acids and 18 MΩ de-ionized water (DIW) were used throughout. First, 0.250 g of each sample was weighed into EasyPrep iWave vessels (CEM) and 2 mL of HNO₃ and 6 mL of concentrated HCl were then added. The vessels were capped and placed in the CEM MARS 6 iWave microwave for digestion. The microwave program is detailed in Table 3. On completion of the digestion program, solutions were left to cool to room temperature before being diluted to a final volume of 50 mL with DIW. The final matrix of the samples was 4% HNO₃ and 12% HCl.

Table 3. Microwave method parameters.

Parameter	Value
Power (W)	1800
Temperature (°C)	210
Ramp Time (min)	20
Hold Time (min)	20

Wavelength selection using IntelliQuant Screening

IntelliQuant Screening allows analysts to run a quick, semiquantitative screening of unknown samples (2). In this study, IntelliQuant Screening was used during method development, particularly for wavelength selection, and to determine the approximate concentration of elements in some of the ore CRM digests. Figure 1 shows the IntelliQuant Screening results for erbium (Er) in a CRM sample. The star ranking system was used to select (or to confirm) the best wavelength for each element.

The wavelengths with the highest confidence rating indicate which lines are likely to be suitable for the quantitative method. The red question marks next to the low-star rated wavelengths highlight an issue with the primary lines. The pop-up tip provides a reason for the low confidence in the lines, typically due to a strong interference from another element. Based on the IntelliQuant Screening data, the primary lines for Er at 349.910 and 337.275 nm were excluded from the final method. Both primary lines were given a one star rating, due to interferences, so Er 369.265 was selected based on its five star rating.

Element	Used	Flags	Wavelength	Rating	Concentration	Intensity	Background
Er			349.910	* ?	912.7	7211.1	
			337.275	* ?	8.09E	7766.3	
			369.265	*****	1.14E	8611.1	
			390.631	*****	1.06E	7622.4	
			323.058	*****	1.23E	7128.1	
			389.623	*****	949.85	93392.5	28374.5

Figure 1. IntelliQuant Screening star ratings for Er wavelengths in a CRM sample. Hovering the cursor over the red question mark opens a dialog box. The dialog box for Er 349.910 nm suggests a likely interference from Ti 349.908 nm.

Calibration

Single element (1000 mg/L) and multi-element calibration standards (Agilent) were used in this study. Calibration solutions were prepared at 0.01, 0.1, 1.0, and 10 mg/L from the single element stock solutions into a matrix of 4% HNO₃/12% HCl (Aristar Plus, VWR) to match the sample matrix. A matrix-matched calibration blank and an initial calibration blank were also prepared. 18.2 MΩ DIW (Merck Millipore) was used to dilute all solutions.

The concentration range used for the elements was based on semiquantitative data obtained using IntelliQuant Screening. Linear calibration curves were used for all elements. All elements displayed excellent correlation coefficients of greater than 0.9999 (Table 4).

Table 4. Background correction method, calibration range, and calibration coefficients.

Element, Wavelength (nm)	Background Correction Technique	Concentration Range (mg/L)	Correlation Coefficient
Ce 418.659	FACT	0.01 – 10	1.00000
Dy 353.171	Off-peak	0.01 – 10	1.00000
Er 369.265	FBC	0.01 – 10	1.00000
Eu 397.197	FACT	0.10 – 10	1.00000
Gd 376.840	FBC	0.01 – 10	1.00000
Ho 345.600	FBC	0.01 – 10	0.99999
La 399.575	FBC	0.01 – 10	1.00000
Lu 290.030	FBC	0.01 – 10	0.99997
Nd 401.224	FACT	0.01 – 10	0.99999
Pr 410.072	FACT	0.01 – 10	0.99999
Sm 360.949	Off-peak	0.01 – 10	1.00000
Tb 332.440	FACT	0.01 – 10	0.99999
Tm 379.576	Off-peak	0.01 – 10	0.99999
Y 321.668	FBC	0.01 – 10	0.99999
Yb 328.937	FBC	0.01 – 10	0.99998
Sc 255.235	FBC	0.01 – 10	0.99999

Quality control

A midrange range calibration standard was used as the continuous calibration verification (CCV) sample to check the long-term stability of the instrument.

Background correction and interference correction

Due to the complexity of REE ore samples, multiple background correction methods were used in this application. The ICP Expert software includes several easy-to-use background correction techniques including Fitted Background Correction (FBC), Fast Automated Curve-Fitting Technique (FACT) modeling, and off-peak background correction.

FBC was used for correction where there were no direct overlaps, as demonstrated in Figure 2 for Gd 376.840. FBC has accurately modeled the cerium, Ce 376.877, interfering peak on Gd 376.840, allowing easy correction. By eliminating the need for the analyst to manually determine off-peak background correction points, FBC simplifies method development (5). Alternatively, with careful placement of background points, off-peak background correction can also be used.

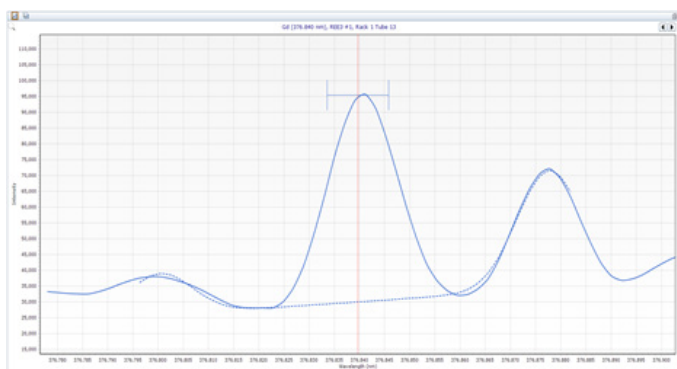


Figure 2. Automatic background correction using FBC to accurately model the Ce 376.877 nm interfering peak on Gd 376.840 nm.

For elements that were affected by more complex background signals, FACT was used. FACT modeling is used to correct for spectral overlap, but it can also be used to correct for highly complex background structures (6). FACT can help achieve lower detection limits for some elements because of its ability to completely remove all the background structure. For example, there is a spectral interference from elemental cerium (Ce) on neodymium (Nd). In the FACT spectrum (Figure 3), the contribution to the Nd signal from Ce can be removed by modeling the Ce interference peak, improving the accuracy of the measurement.

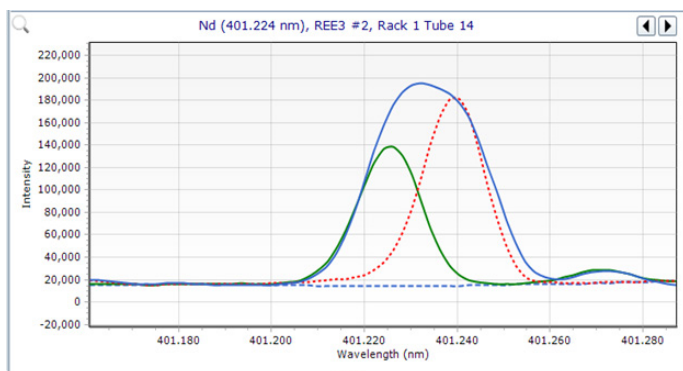


Figure 3. FACT correction of a Ce interference on Nd (shown in blue). The Ce 401.239 nm (red dotted) line is overlapping the Nd 401.224 nm (green) line.

Results and discussion

Method detection limits

Method Detection Limits (MDLs) were determined by analyzing a blank solution spiked with all elements at 10 ppb ten times. The MDL was calculated as three times the standard deviation (SD) of the ten measurements of the blank spike. The MDLs given in Table 5 take into account the dilution required to bring the analytes within the analytical range of the instrument.

Table 5. Method detection limits.

Element, Wavelength (nm)	MDL (solution) $\mu\text{g/mL}$ (3σ)	MDL (solid) $\mu\text{g/g}$
Ce 418.659	0.0030	0.59
Dy 353.171	0.0026	0.52
Er 369.265	0.0028	0.56
Eu 397.197	0.0023	0.45
Gd 376.840	0.0025	0.50
Ho 345.600	0.0026	0.53
La 399.575	0.0025	0.49
Lu 290.030	0.0018	0.36
Nd 401.224	0.0026	0.51
Pr 410.072	0.0036	0.73
Sc 255.235	0.0024	0.48
Sm 360.949	0.0019	0.38
Tb 332.440	0.0032	0.64
Th 401.913	0.0014	0.28
Tm 379.576	0.0023	0.46
Y 321.668	0.0023	0.46
Yb 328.937	0.0023	0.46

Accuracy and precision of the method

To validate the sample preparation procedure and the accuracy of the 5800 VDV ICP-OES, the three CRMs (REE-1, REE-2, and REE-3) were analyzed in triplicate, with the results averaged over three separate runs. The results are given in Tables 6 to 8.

The quantitative recoveries for all certified elements that were measured above the MDL in the CRMs were within $\pm 10\%$ of the certified value. The recoveries demonstrate the accuracy of the instrument when analyzing samples with difficult matrices. The results also demonstrate the robustness of the method to measure trace REEs in the presence of high concentration elements such as Al, Ca, K, Na, Fe, Mg, Mn, S, Si, and Ti (4).

Table 6. Average measured results for three sample digests of REE-1 CRM.

Element, Wavelength (nm)	Background	Measured Conc ($\mu\text{g/g}$)	REE-1 Certified Conc ($\mu\text{g/g}$)	Recovery (%)
Ce 418.659	FACT	3939	3961	99
Dy 353.171	Off-peak	889	848	105
Er 369.265	FBC	738	701	105
Eu 397.197	FACT	24.30	23.5	103
Gd 376.840	FBC	469	433	108
Ho 345.600	FBC	214	208	103
La 399.575	FBC	1670	1661	101
Lu 290.030	FBC	88.9	92.4	96
Nd 401.224	FACT	1509	1457	104
Pr 410.072	FACT	454	435	104
Sm 360.949	Off-peak	407	381	107
Tb 332.440	FACT	107	107.2	100
Tm 379.576	Off-peak	109	106	103
Y 321.668	FBC	5582	5480	102
Yb 328.937	FBC	649	678	96
*Sc 255.235	FBC	2.23	8.0	-

*Informative (semiquantitative) concentration (4)

Table 7. Average measured results for three sample digests of REE-2 CRM.

Element, Wavelength (nm)	Background	Measured Conc ($\mu\text{g/g}$)	REE-2 Certified Conc ($\mu\text{g/g}$)	Recovery (%)
Ce 418.659	FACT	9232	9610	96
Dy 353.171	Off-peak	67.2	69.2	97
Er 369.265	Off-peak	14.4	14.0	103
Eu 397.197	FACT	105.6	96.6	109
Gd 376.840	FBC	207.7	219	96
Ho 345.600	FACT	7.68	7.87	98
La 399.575	FBC	4931	5130	96
Lu 290.030	Off-peak	0.84	0.92	91
Nd 401.224	FACT	3497	3660	96
Pr 410.072	FACT	1123	1075	104
Sm 360.949	Off-peak	421	410	103
Tb 332.440	FACT	18.6	20.3	92
Tm 379.576	Off-peak	1.49	1.383	108
Y 321.668	FBC	188	176	107
Yb 328.937	FACT	7.0	7.2	97
Sc 255.372	FBC	59.8	57.5	104

Table 8. Average measured results for three sample digests of REE-3 CRM.

Element, Wavelength (nm)	Background	Measured Conc ($\mu\text{g/g}$)	REE-3 Certified Conc ($\mu\text{g/g}$)	Recovery (%)
Ce 418.659	FACT	4508	4541	99
Dy 353.171	Off-peak	346	330.3	105
Er 369.265	FBC	201.6	187	108
Eu 397.197	FACT	20.52	20.85	98
Gd 376.840	FBC	365	346	105
Ho 345.600	FBC	67	65	103
La 399.575	FBC	2142	2121	101
Lu 290.030	FBC	21.8	21.5	98
Nd 401.224	FACT	2132	2084	102
Pr 410.072	FACT	586	550	107
Sm 360.949	Off-peak	401	398	101
Tb 332.440	FACT	59	56.2	105
Tm 379.576	Off-peak	27	25.8	105
Y 321.668	FBC	1852	1725	107
Yb 328.937	FBC	159	159	99
*Sc	FBC	1.48	3.0	-

*Indicative (semiquantitative) concentration (4)

Sample analysis

Each rhyolite ore was digested three times and each digest was run three times. The sample to sample measurement time was 1:01 minutes. The quantitative results from the measurement of the four rhyolite ore samples using the 5800 VDV ICP-OES are shown in Table 9. Precision data for the three independent readings of each ore is also shown.

Table 9. Determination of REEs in four rhyolite ore samples by Agilent 5800 VDV ICP-OES.

Element	Ore 1		Ore 2		Ore 3		Ore 4	
	Mean Measured Conc (µg/g)	RSD (%)	Mean Measured Conc (µg/g)	RSD (%)	Mean Measured Conc (µg/g)	RSD (%)	Mean Measured Conc (µg/g)	RSD (%)
Ce	82.6	0.9	84.3	2.1	79.0	4.5	82.4	4.5
Dy	31.2	5.9	31.4	6.8	30.2	6.7	33.3	6.2
Er	26.4	11.0	27.3	9.7	25.0	11.6	30.0	7.2
Eu	<MDL	-	<MDL	-	<MDL	-	<MDL	-
Gd	11.0	1.4	10.7	2.2	10.9	3.6	11.5	2.1
Ho	7.6	13.8	7.8	13.5	7.5	24.8	8.5	14.4
La	19.7	2.4	17.5	4.2	18.2	3.5	18.9	2.9
Lu	5.8	23.7	6.8	20.8	5.4	27.3	7.6	17.9
Nd	28.3	5.4	24.1	3.6	25.0	2.2	25.5	4.3
Pr	10.8	9.5	9.4	5.9	9.8	5.2	9.7	5.4
Sc	<MDL	-	<MDL	-	1.2	13.2	<MDL	-
Sm	12.1	3.4	10.7	4.0	11.0	7.3	11.5	7.5
Tb	<MDL	-	<MDL	-	3.7	95.3	<MDL	-
Tm	5.6	9.4	6.0	8.1	5.1	11.9	6.6	8.5
Y	210.1	2.0	193.3	2.4	196.7	2.0	214.4	2.2
Yb	45.7	1.6	51.1	2.0	43.3	1.6	55.4	1.9

Long-term stability

Approximately 100 digested samples were run over a five-hour period without recalibrating. During the run, a QC sample was analyzed every 10 samples and plotted to show the stability of the method. Figure 4 shows the recovery of all elements over the five-hour period to be within $\pm 10\%$. The relative standard deviation (RSD) of this data was less than 3% for all elements, indicating excellent precision over the extended run. The excellent stability of the 5800 VDV ICP-OES throughout the run highlights the suitability of the method for the routine analysis of REE ore raw materials.

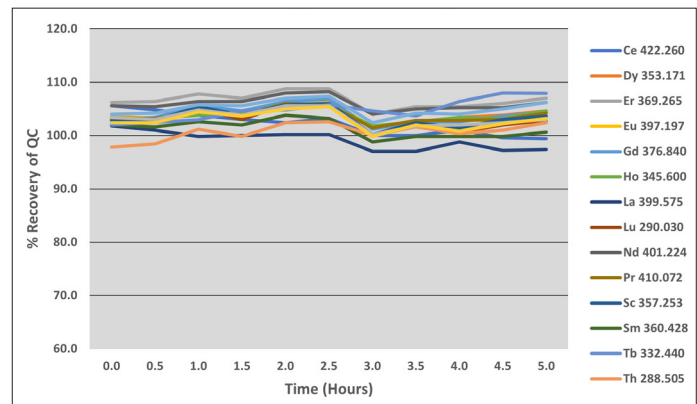


Figure 4. Long-term stability test showing the recovery of elements in a QC sample that was analyzed every 10 samples over a five-hour period.

Conclusion

The high performance of the Agilent 5800 ICP-OES enabled the accurate measurement of REEs in geological samples—a challenging application because of interferences caused by the REE line-rich emission spectra.

The 5800 ICP-OES uses freeform optics and an advanced detector design to lower detection limits and increase resolution, ensuring that a suitable line can be selected when analyzing complex matrices. To help with method development, IntelliQuant Screening semiquantitative data was used to select or confirm the best wavelengths and was used to help with selecting the best background correction technique for the REEs.

All REEs in three ore CRMs were measured within $\pm 10\%$ of the certified values, demonstrating the accuracy of the microwave digestion procedure and 5800 VDV ICP-OES method. The matrix tolerance and robustness of the 5800 was shown by the excellent recoveries of all elements measured throughout the analysis in the long-term stability test. Also, good precision data was obtained for most of the REEs, based on three independent readings of each of the four rhyolite ore samples.

To meet the productivity needs of many mining labs, the 5800 ICP-OES was fitted with an AVS 7, which increased sample throughput and minimized carry over from previous samples. A sample to sample measurement time of 1:01 minutes was achieved. The plug-and play torch and maintenance tools also ensured that the 5800 was operationally ready for the analysis. The excellent long-term stability results demonstrated the matrix tolerance, robustness, and simple operation provided by the 5800 VDV ICP-OES.

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