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Application Note

Mineralogy-Geology

ICP

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Analysis of Trace Elements in a CeO_2 Matrix using ICP-OES

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Cerium is the most abundant Rare Earth Element and is found in many minerals. Monazite and bastnatite are the two most important sources of Cerium. Cerium is involved in metallurgy: added to cast iron it produces a malleable iron, it removes sulphides and oxides and completely degasifies steels, used to make aluminium alloys… Cerium is also used to polish precision optical glasses, as catalytic converter for the reduction of CO emissions in exhaust gases, in the fluid catalytic cracking for making gasoline and in permanent magnets.
This large range of applications makes Cerium an interesting element and there is a strong need to produce high purity Cerium.
High resolution ICP-OES is well suited for such application as it will help to solve all spectral interferences occurring to the line-rich spectrum emitted by Ce all over the spectral range. This application describes the analysis of trace elements in Ce matrix with evaluation of stability and accuracy.

Sample preparation

2g of sample was dissolved in 10 ml H_2O, 10 mL HNO_3 and 10 mL H_2O_2 then volume was made up to 100 mL. All standard solutions were prepared using Spex CertiPrep single element standard solution. For improved accuracy, the standard addition technique was used with addition of 0.5, 1 and 1.5 mg/L of Si, Ca, Fe, La, Nd, Pr, Sm and Y.

Operating conditions

The characteristics of the ULTIMA 2 High Resolution spectrometer used for this study are given in Table 1. Note that this instrument is equipped with the dual grating system that improves resolution for Rare Earth Elements based applications.

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 160 - 430 nm 2400 g/mm for 430 - 800 nm
Resolution (specification)	< 5 pm for 120 - 430 nm < 10 pm for 430 - 800 nm
Thermoregulation	32 ± 0.1°C
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

A concentric glass nebulizer and a cyclonic spray chamber were used to get the highest sensitivity. All details on the introduction system are given in Table 2.

Table 2. Specification of the sample introduction system

Nebulizer	Glass Concentric
Spray chamber	Glass cyclonic
Sample uptake	1 mL/min
Injector tube inner diameter	3 mm
Pump tubing	Black-black pump tubing for sample Grey-grey pump tubing for drain

All plasma parameters were optimized for sensitivity and robustness and are given in Table 3.

Table 3. Operating conditions

Power	1000 W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.3 L/min
Nebulizer flow	0.8 L/min (2.9 bars)
Pump speed	15 rpm

Acquisition was done using 3 replicates with Max mode and 2s integration time for analyte. A 20 µm / 15 µm slit combination was used for all wavelengths.

Results

Line selection

Lines used are given in Table 4. Selection of lines was done after performing profiles on samples to identify potential spectral interferences.

Table 4: List of lines used for the analysis

Wavelength (nm)	Wavelength (nm)
Fe 259.940	Sm 359.260
La 399.575	Y 377.433
Nd 406.109	Si 251.611
Pr 422.533	Ca 396.847

Calibration

The standard addition technique was used. Additions of 0.5, 1 and 1.5 mg/L were done for all elements. All calibration curves were validated with correlation coefficient r>0.999. Some calibration curves are displayed in Figures 1 to 3.

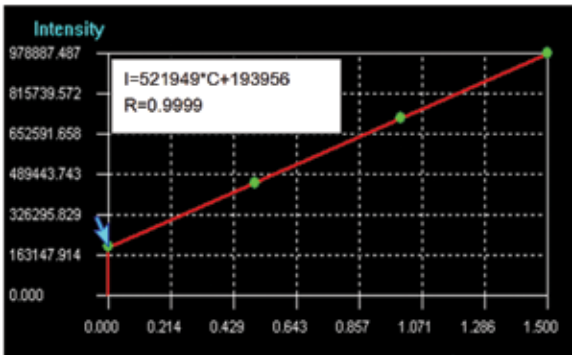

Figure 1: Calibration curve for La 399.575 nm.

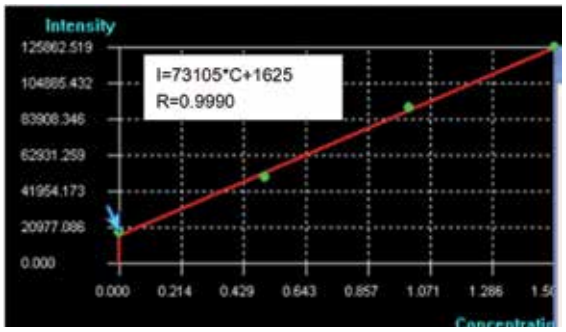

Figure 2: Calibration curve for Si 251.611 nm.

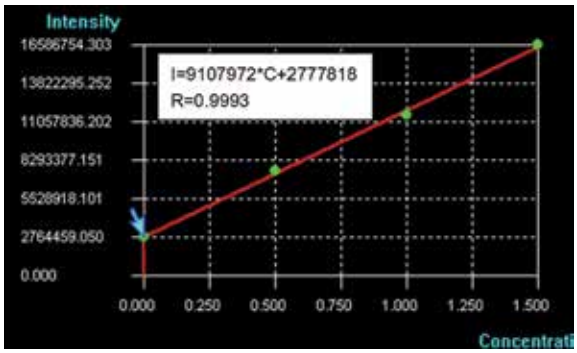

Figure 3: Calibration curve for Ca 396.847 nm.

Results on samples

Concentrations measured on sample are given in Table 5. The concentration is given for the prepared sample as well as for the original sample.

Table 5: Results obtained on sample

Element	Wavelength (nm)	Measured value (µg/L)	Concentration (mg/kg)
Fe	259.940	98.6	24.5
La	399.575	374	92.8
Nd	406.109	23.5	5.8
Pr	422.533	17.8	4.4
Sm	359.260	61.2	15.2
Y	377.433	9.04	2.2
Si	251.611	222	55.1
Ca	396.847	285	70.8

Recovery test

To evaluate the accuracy of the measurement, the sample was spiked and the spiked sample was analyzed to check for the recovery. Recoveries obtained are given in Table 6.

Table 6: Recoveries obtained on sample

Element	Wave-length (nm)	Original Conc. Measured (µg/L)	Spike (µg/L)	Measured Conc. (µg/L)	Recovery (%)
Fe	289.940	98.6	100	202	103
La	399.575	374	200	571	99
Nd	406.109	23.5	20	44.1	102
Pr	422.533	17.8	20	38.6	104
Sm	359.260	61.2	50	110	98
Y	377.433	9.04	10	19.4	103
Si	251.611	222	200	420	99
Ca	396.847	285	200	481	98

All recoveries obtained are in the range 98-104% that is excellent and proves the accuracy of results measured with the instrument.

Stability test

Stability was evaluated on the sample on Ca 396.847 nm line. The sample was measured every 5 minutes and the stability was evaluated by calculating the RSD of the measurements. Results of the stability test are given in Table 7.

Table 7: Stability test on Ca 396.847 nm

Time (Minutes)	Measured Concentration (mg/L)
0	0.283
5	0.281
10	0.275
15	0.275
20	0.283
25	0.284
30	0.276
35	0.283
40	0.278
45	0.279
50	0.282
Average value	0.280
RSD (%)	1.3

RSD obtained is less than 1.5%, proving the excellent stability of the ULTIMA 2 ICP-OES spectrometer for this application.

Conclusion

The results obtained on the analysis of trace elements in a CeO_2 matrix show that the ULTIMA 2 ICP-OES spectrometer offers accurate results and provides stability over the time. This makes the ULTIMA 2 High Resolution ICP-OES spectrometer the perfect instrument as this is the only instrument able to measure traces in CeO_2 matrices to ensure high purity materials production.

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