Challenge
Interference-free determination of rare earth elements at trace and ultratrace levels in geological materials

Solution
High-Resolution Array ICP-OES on PlasmaQuant 9100 Elite resolving spectral interferences and high-sensitivity ICP-MS on PlasmaQuant MS Elite using a method without traditional mathematical correction of polyatomic interferences

Analysis of Rare Earth Elements by ICP-OES and ICP-MS – Potentials and Limitations

Introduction

Contrary to their name, rare earth elements (REE) make up a substantial part of the earth's crust, where they occur dispersed among various minerals. In recent years, there has been a rising demand for REE in the fields of user electronics, catalysis, optical displays, high-performance magnets, batteries, aerospace manufacturing and medical applications. Therefore, reliable trace analysis procedures are needed in the assessment of potential mining sites, process control solutions (largely comprising of rare earth oxides, REO) and quality control of high-purity REE. Furthermore, there is a large interest from academic research in earth sciences involving trace and ultratrace level determination of REE in geology, geochemistry and mineralogy.
Quantification of REE in geological materials by Inductively Coupled Plasma Optical Emission Spectrometry (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 exceptional plasma robustness. This is especially the case when trace levels of REE ought to be detected and sample dilution has to be avoided. Adverse REO formation in plasma tail and severe spectral interferences due to the wealth of emission lines affect the detectability of REE by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) or ICP-OES. The High-Resolution Array ICP-OES PlasmaQuant 9100 Elite is capable to overcome these barriers. With its fast-sequential echelle-double monochromatic optical bench with versatile CCD detection, it nearly doubles the spectral resolution and halves the total analysis time with respect to currently available ICP-OES instrumentation with PMT detection that is solely used for REE analysis.
ICP-MS is a popular analytical technique for the determination of REE, from raw materials including soils, rocks and ores to impurities in highly refined rare earth products. The technique offers a fast multi-element

REE detection at concentrations down to the parts-per-quadrillion (ppq) range. However, challenges often faced by scientists in REE measurement include the occurrence of polyatomic and isobaric interferences that are not resolved by quadrupole ICP-MS. Collision gases can be applied to remove polyatomic interferences. With its integrated Collision Reaction Cell technology, the PlasmaQuant MS Elite offers an effective solution for such requirements. Furthermore sample preparation can also impose analytical constraints and must be considered in order to obtain accurate analytical data.

Materials and Methods

For the quantification of REE, it is important that a complete digestion of the sample is achieved because any insoluble residue will result in an underestimated concentration of these elements. When acid mixtures containing hydrofluoric acid (HF) are used, insoluble fluorides of REE may remain in the precipitate. Refractory minerals such as zircon, tourmaline, chromite, rutile, garnet, spinel and corundum are decomposed incompletely by an acid attack. Decomposition by lithium metaborate and tetraborate fusion provides a complete decomposition of silicate phases and accessory minerals. However, this results in a higher amount of total dissolved solids (TDS). Since ICP-MS is typically limited to TDS levels of less than 0.3% w/v, the fusion decomposition requires additional dilution prior to analysis. For several types of geological matrices, sintering with Na_2O_2 is a very attractive analytical decomposition procedure because it is highly effective in decomposing minerals rapidly and the resulting sinter residue is easy to dissolve. Additionally, it does not introduce high concentrations of reagent elements (e.g., Li, B) that may affect future analyses [1].

Therefore, this study considered a sintering digestion in the presence of Na_2O_2. Approximately 100 mg of sample grounded to pass a 200-mesh sieve was well mixed with 600 mg of Na_2O_2 and sintered at 480 ± 10 degrees Celsius for exactly 30 minutes in a Carbolite muffle furnace (CWF 1200) using porcelain crucibles (30 x 30 mm) lined with aluminum sheet. After cooling, the sinter residue was gently removed from the crucible with ultrapure water added dropwise into a 50 mL polypropylene tube. When the reaction finished, three drops of concentrated HCl and 2 mL of concentrated HNO_3 were added. The tube was filled to the mark with ultrapure water and the final solution was homogenized using a vortex stirrer.

The ICP-OES measured all samples undiluted, whereas for ICP-MS analysis, samples were diluted ten-fold with 1% HNO_3.

Samples and reagents

- Reference Material GBW 7103
- Deionized water (> 18.2 MΩ cm, Millipore MiliQ)
- Nitric acid Supra-quality 69% (ROTIPURAN Supra)
- Sodium peroxide (Na_2O_2) finely powdered, reagent grade, 97% (SIGMA-ALDRICH)

Calibration

For ICP-OES, calibration solutions were prepared in a matrix-matched solution containing 12 g/L Na_2O_2 in 1% HNO_3. The calibration concentrations ranged from 0.1 to 1 mg/L for all elements analyzed.

For ICP-MS measurements, calibration solutions were prepared from high-purity, single and multi-element solutions (SIGMA-ALDRICH) in 1% HNO_3 + 1.2 g/L of Na_2O_2. The calibration standards covered the concentration range from 0.25 to 25 µg/L for La, from 0.5 to 50 µg/L for Ce and Nd, and from 0.05 to 5 µg/L to Pr, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, Yb, and Lu.

Table 1: Configuration of the PlasmaQuant 9100 Elite, equipped with HF kit

Instrumentation

The ICP-OES system used an HF kit for the sample introduction. Table 1 and 2 list the system configurations for ICP-OES and ICP-MS respectively.

Table 1: Configuration of the PlasmaQuant 9100 Elite, equipped with HF kit

Parameter	Settings
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.0 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	Parallel path nebulizer, PFA, 1.0 L/min
Spray chamber	PTFE cyclonic, 50 mL
Injector	Alumina, inner diameter 2 mm
Outer tube /Inner tube	SiAlON/alumina
Pump tubing	PVC
Sample pump flow	1 mL/min
Rinse/Read delay	60 sec
Integration time	3 sec (3 replicates)
Plasma view	axial

Table 2: Configuration of the PlasmaQuant MS Elite

Parameter	Settings
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.35 L/min
Nebulizer gas flow	0.97 L/min
iCRC settings	No gas mode, Gas mode with Helium
Plasma RF power	1,300 W
Dwell time	30 ms
Scans per replicate	10
Acquisition mode	Peak hopping, 1 pt/peak
Number of replicates	5
Pump rate/tubing	8 rpm, black/black PVC
Sample uptake delay	30 s
Stabilization time	20 s
Ion optics	Auto-optimized for highest sensitivity

Results and Discussion

In ICP-MS, the formation of polyatomic species like MO$^+$ and MOH$^+$ is greatly influenced by the chemical nature of the respective element. Since oxide and hydroxide formation will follow particular stoichiometric reactions, their contribution to an analyte signal can be corrected by a fixed numerical coefficient (correction equation), determined for the specific analysis conditions. Cerium for example has a strong affinity for oxygen with oxide levels of less than 2% being typical under optimized instrument conditions. Oxide interferences can be reduced to negligible levels by injecting a helium gas into the iCRC interference management system (Figure 1). Thus, the CRMs were investigated by ICP-MS with helium as collision gas within the iCRC. No corrections for oxide and hydroxide polyatomic interferences were applied, although isobaric interferences were accounted for.

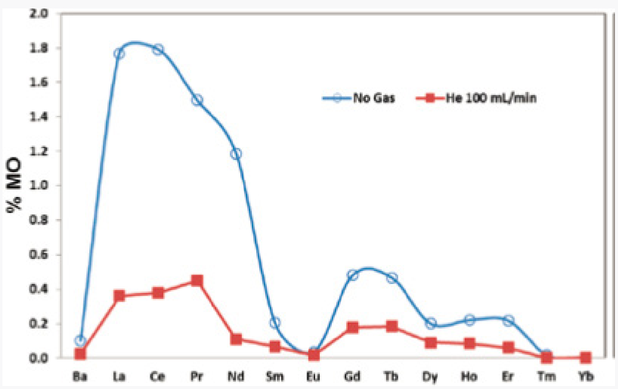

Table 3 shows the concentration values of REE in CRM GBW07103 (GSR-1) measured by HR ICP-OES and ICP-MS. Concentrations range from µg/kg to mg/kg with excellent recoveries for both techniques used. The analysis by ICP-OES obtained RSD-values smaller than 2% for most elements. This proves that the precision achieved with HR ICP-OES is best suited for REE-trace analysis. Moreover, the total analysis time per sample including rinse and read delays was less than 120 seconds.

Table 3: Results for CRM GBW07103 obtained by HR ICP-OES and ICP-MS

Element	CRM GBW 7103 (GSR-1) Granite powder [mg/kg]	HR ICP-OES PlasmaQuant 9100 Elite			ICP-MS PlasmaQuant MS Elite		
		Measured [mg/kg]	Recovery [%]	MDL [mg/kg]	Measured [mg/kg]	Recovery [%]	MDL [µg/kg]
La	54 ± 4	53.4	99	0.14	60.9	113	3.5
Ce	108 ± 7	112	104	0.85	114	106	0.9
Pr	12.7 ± 0.8	12.2	96	1.55	13.2	104	0.6
Nd	47 ± 4	48.6	103	0.34	51.2	109	2.6
Sm	9.7 ± 0.8	9.23	95	0.65	10.6	108	2.7
Eu	0.85 ± 0.07	0.71	84	0.04	0.82	96	2.7
Tb	1.65 ± 0.09	n.a.*			1.68	102	0.8
Gd	9.3 ± 0.7	10.3	111	0.36	9.69	104	1.4
Dy	10.2 ± 0.4	10.6	104	0.32	10.8	106	0.4
Er	6.5 ± 0.3	7.0	108	0.15	7.01	108	0.3
Ho	2.05 ± 0.17	2.22	108	0.11	2.24	109	1.6
Tm	1.06	n.a.*			1.11	105	0.8
Yb	7.4 ± 0.5	7.67	104	0.34	8.23	111	1.5
Lu	1.15 ± 0.09	1.11	97	0.19	1.17	102	0.4

* this element was not analyzed by ICP-OES

The unique potential of the PlasmaQuant 9100 Elite becomes even clearer when inspecting the Nd/Ce-line pair at about 401.2 nm (Figure 2). With a line spacing of only 14 pm, the Nd 401.225 nm (orange) is severely overlapping with Ce 401.239 nm (black) in conventional ICP-OES systems and thus only a high-resolution ICP-OES can resolve the individual lines for analysis. The Nd 401.225 nm is the most sensitive Neodymium line and hence optimal for trace analysis.

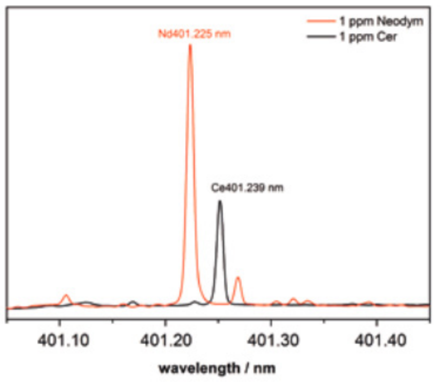

Figure 2: HR ICP optical emission spectra of the Nd 401.225 (orange) and the Ce 401.239 nm line (black) as in the highest calibration standard

Summary

For the analysis of REE in geological samples, ICP-OES and ICP-MS are ideal analytical techniques because of the multi-element detection capabilities. However, line-rich emission spectra and isotope-rich mass spectra plus polyatomic interferences from e.g., oxides require highest performance and high-end technological solutions to meet today's requirements.

ICP-MS with its high detection power is an ideal technique, especially since collision cell techniques help to eliminate interferences. The improvements made during the last decade to make the instruments reliable and easy to use for routine applications are the reason for the wide acceptance of this technology. The high-detection power especially for REE allows detection limits in the ppt to ppb range. However, limited matrix tolerance and complex optimization of many parameters still require an experienced operator to reach the full performance of this technique.

Figure 4: PlasmaQuant 9100 Elite and PlasmaQuant MS Elite

ICP-OES systems are robust and reliable instruments used as a workhorse in many analytical laboratories. Improved optics and detector designs led to much lower detection limits over the past decades. High-resolution instruments make it possible to use typically interfered lines, making them ideally suited for the analysis of complex matrices. The easier handling and robust introduction system allow for analysis without previous sample dilution. This leads to an instrument performance that fits for many applications.

Table 4 presents a summary of potentials and limitations for both techniques. Each ICP technique shows strengths and weaknesses. Less matrix tolerance and higher running costs compensate for the better detection limits of ICP-MS. The robustness and higher matrix tolerance of ICP-OES comes with more frequent cleaning and careful configuration of the sample introduction system.

Table 4: Comparison of potential and limitations for ICP-OES and ICP-MS

PlasmaQuant 9100 Elite HR-ICP-OES	Potential/Limitations	PlasmaQuant MS Elite ICP-MS
▪ TDS > 30% are tolerated ▪ Direct analysis	Heavy matrix (fusion or acid digest)	▪ TDS typically < 0.3% ▪ Dilution strategies required
▪ Overlap of emission lines ▪ High resolution required ▪ Mathematical correction tools used	Spectral Interferences	▪ Molecular interferences, e.g. REO ▪ Correction equations used ▪ Interference management systems required
▪ ng to µg/L or µg to mg/kg (ppm$_w$)	Detection limits (DL)	▪ pg/L to ng/L or ng/kg to µg/kg (ppb$_w$)
▪ RSD typically < 3% for REE ▪ Recovery typically ± 5% for REE	Precision	▪ RSD typically < 1% for REE ▪ Recovery typically ± 2% for REE
▪ High resolution with CCD ▪ Time saving single line evaluation with automated algorithms	Throughput	▪ High sensitivity allows short dwell times ▪ Fast wash-out using discrete sample introduction
▪ Workhorse for REE analysis with mg/kg detectability	Performance	▪ Advanced analytical capabilities incl. high-purity REE, isotope ratio analysis and µg/kg detectability

Continuation of table 4: Comparison of potential and limitations for ICP-OES and ICP-MS

PlasmaQuant 9100 Elite HR-ICP-OES	Potential/Limitations	PlasmaQuant MS Elite ICP-MS
▪ Direct analysis ▪ Quick method development ▪ Robust system (sealed optic) ▪ Easy maintenance (cleaning)	Handling	▪ Dilution strategies ▪ High operator skills ▪ More prone to contaminations ▪ Frequent cleaning required
▪ Lower cost of technology ▪ Glassware (consumables) ▪ Normal chemicals ▪ Less stringent lab requirements	Cost of Ownership	▪ High costs of technology ▪ Consumables (cones, glassware) ▪ High purity chemicals ▪ High lab standard

The comparison shows the high performance of both analytical techniques for the analysis of REE in geological samples. The PlasmaQuant 9100 Elite and the PlasmaQuant MS Elite offer outstanding features to overcome the challenges in the analysis of REE. Interference removal by either the high-resolution optical system or collision cell technology (iCRC) in combination with low gas consumption underline the high performance of these instruments.

References

[1] T. Meisel et al., *Geostandard Newslett 2002, 26, 53-61.*

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