MASTER-SOS assistance for Analysis of Rare Earth Elements in geological samples

Agnès Cosnier, Sophie Lebouil, Sébastien Vélasquez, HORIBA Jobin Yvon, Longjumeau, France

Instrument: ACTIVA-M

1 Introduction

To achieve reliable results, HORIBA Jobin Yvon has developed specific software tools[1] for the ACTIVA-M ICP-AES system. Among them, the MASTER[2]: Multi-line Analysis, Selection Tool for Enhanced Reliability (for lines selection) and the SOS: Statistical Outlier Survey (for detection and rejection of outliers).
The assistance is illustrated here with a geological application: analysis of europium, neodymium and scandium in rocks.

2 Operating conditions

The use of the multi-line analysis dedicated software tools is ideal for a geological application, where the nature of the samples is inherently variable.

• Sample description
Certified Reference Materials were used for MASTER selection and calibration procedures: granite AC-E, anorthosite AN-G, diorite DR-N, granite GS-N, all Geostandards were from CRPG (Centre de Recherche Pétrographiques et Géochimiques), France.
The basalt BE-N Geostandard (CRPG, France) was selected as the sample.

• Sample preparation
Sample preparation was based on an acid digestion classically used for rare earth elements in non-refractory samples : 0.5 g of sample, dissolved slowly with 15 mL HF/4 mL $HClO_4$ (Pure Grade, VWR) using hot plate, evaporated to dryness, picked up with 4 mL HCl (Pure Grade, VWR) and warmed, and finally diluted with de-ionized water to 250 mL.
Tables 1 and 2 give plasma and instrument parameters.

Table 1: Plasma parameters

Parameter	Specification
Power	1100 W
Plasma gas	12 L/min
Auxiliary	0
Sheath gas	0.2 L/min
Nebuliser gas	0.7 L/min (3 bar)
Sample uptake	1 mL/min (20 rpm)
Plasma view	Radial*

* Total Plasma View (observation of the complete NAZ, Normal Analytical Zone), for minimised matrix effects and optimum sensitivity.

Table 2: Specifications of the ACTIVA-M ICP spectrometer

Parameter	Specification
Generator	40.68 MHz, solid state, water-cooled
Optical System	Czerny-Turner (0.64 m Focal)
Gratings	4343 / 2400 g/mm
Spectral range	120 - 800 nm
Resolution	10 pm in 120 - 430 nm range
Sample introduction	Parallel Flow/Cyclone
Pump tubing	Black/black Tygon (sample) Grey/grey Tygon (drain)
Torch design	Vertical, demountable 3 mm i.d. injector

3 Method development

Table 3 is the list of elements and their concentration range defined in MASTER according to the different samples to be measured. Table 4 is the list of lines validated by MASTER for Eu, Nd and Sc and Figure 1 illustrates the validation of the 394.151 nm Nd line.

Table 3: Elements and concentration range defined in MASTER

Element	Min	Max	Unit	Element	Min	Max	Unit
SiO_2	46.3	70.3	%	Hf	0.38	27.9	ppm
TiO_2	0.11	1.09	%	La	2.2	75	ppm
Al_2O_3	14.7	29.8	%	Li	12.5	93	ppm
Fe_2O_3	2.53	9.7	%	Lu	0.12	2.45	ppm
MnO	0.056	0.22	%	Mo	0.9	2.5	ppm
MgO	0.03	4.4	%	Nb	0.9	110	ppm
CaO	0.34	15.9	%	Nd	2.4	92	ppm
Na_2O	1.63	6.54	%	Ni	1.5	35	ppm
K_2O	0.13	4.63	%	Pb	2	55	ppm
P_2O_5	0.01	0.28	%	Rb	1	185	ppm
As	0	3	ppm	S	70	350	ppm
B	0	21	ppm	Sc	0.11	28	ppm
Ba	34	1400	ppm	Sm	0.7	24.2	ppm
Be	0.3	12	ppm	Sn	2	13	ppm
Ce	4.7	154	ppm	Sr	3	570	ppm
Cl	180	450	ppm	Ta	0.6	6.4	ppm
Co	0.2	65	ppm	Tb	0	0.77	ppm
Cr	3.4	55	ppm	Th	0.04	42	ppm
Cs	0	6.3	ppm	U	0	1.5	ppm
Cu	4	50	ppm	V	3	220	ppm
Dy	1.2	29	ppm	W	1.5	490	ppm
Er	0.75	2.5	ppm	Y	8	184	ppm
Eu	0.37	2	ppm	Yb	0.8	17.4	ppm
Ga	18	39	ppm	Zn	20	224	ppm
Gd	0.9	26	ppm	Zr	15	780	ppm

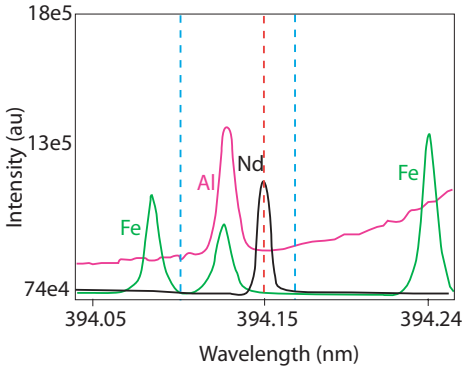

Figure 1: Validated 394.151 nm Nd line and background correction set-up (blue dashed lines)

Table 4: Validated lines by MASTER

Element	Line 1	Line 2	Line 3	Line 4	Line 5	Line 6
Eu	372.494	381.967	390.170	412.970	420.505	
Nd	378.425	394.151	404.080	406.109	410.946	430.358
Sc	335.372	353.573	357.634	361.383	364.531	424.682

4 Analytical results

Table 5: Analytical results of BE-N sample with SOS applied (values in red are outliers; the standard deviation SD associated to the mean concentration is corrected by the Student coefficient)

Element	Line (nm)	Concentration (ppm in the rock)	SD (ppm)	Certified concentration (ppm)	Recovery %
	372.494	4.94	0.18		
	381.967	3.94	0.07		
	390.170	3.71	0.21		
	412.970	3.69	0.11		
	420.505	3.53	0.17		
Eu	**Mean**	**3.64**		**3.60**	**101.1**
	SD	**0.19**			
	378.425	72.54	1.04		
	394.151	69.93	5.09		
	404.080	70.48	1.83		
	406.109	69.18	0.67		
	410.946	67.66	1.13		
	430.358	71.04	1.41		
Nd	**Mean**	**70.14**		**70**	**100.2**
	SD	**2.83**			
	335.372	24.24	0.17		
	353.573	31.55	0.31		
	357.634	24.52	0.40		
	361.383	23.79	0.23		
	364.531	23.65	0.13		
	424.682	22.89	0.12		
Sc	**Mean**	**23.72**		**23.0**	**103.1**
	SD	**0.30**			

The basalt BE-N Geostandard (CRPG, France) was analyzed, using 5 replicates for each line. The data processing is then automatically applied by SOS for detection of outliers and rejection, to get a final reliable result, as shown in Table 5.

The maximum concentration of Ti oxide was defined in MASTER at 1.09 %. In the BE-N sample, its concentration is 2.61 %, generating an interference on the 372 nm Eu line and the 353 nm Sc line. The positive biases were detected by SOS and rejected. Some other lines have been rejected due to a high variation in the replicates (for example, the 357 nm Sc line) or a high dispersion from the mean.
The final element concentration value is then the mean of the remaining concentration values. Results obtained for Eu, Nd and Sc were of high reliability, as proved by the recovery values.

References:
(1) ACTIVA-M brochure, HORIBA Jobin Yvon, www.jobinyvon.com
(2) Application Note No. 46 "MASTER assistance for impurities and major analysis in Nb/Ni/Zr matrix", Agnès Cosnier, HORIBA Jobin Yon, Longjumeau, France ; Jean-Claude Birolleau, CEA Le Ripault, Monts, France