A Semi-Quantitative Method for Geological Samples

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1 Introduction

Geological samples contain major elements at high concentration present as oxides of Al, Ca, K, Mg, etc. and traces of rare earth elelements. Using a fast and simple semiquantitative method on a high-resolution ICP spectrometer with a robust radial plasma view we can obtain a complete sample screening with excellent accuracy for both trace and major elements present.

This application note will describe the semi-quantitative method as performed on the JY ULTIMA 2 ICP spectrometer.

2 Principle

2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

In this paper we describe a semiquantitative analysis where many elemental wavelengths are calibrated over a general concentration range to provide a screening of the sample.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the profile function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

3 Instrument specification

The work was done on a ULTIMA 2. The specifications of this instrument are listed below in Tables 1 and 2.

To analyze rare earth elements a high-resolution spectrometer is required in the 300 - 440 nm range. For this reason, we configure the ULTIMA 2 with a dual grating featuring a 4320 gr/mm grating providing 5 pm of resolution from 160 (120*) to 440 nm and a 2400 gr/mm grating providing 10 pm of resolution from 440 to 900 nm.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	4320 gr/mm 160-440 2400 gr/mm 440-900
Plasma viewing	Radial

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

`(*) if ULTIMA 2 is equipped with far UV option.`

4 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1100 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer flowrate	2.9 bars, 0.61 mL/min
Sample uptake	1 mL/min
Type of nebulizer	Meinhard (C1 type)
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm

The semi-quantitative method is simply calibrated with 2 points in deionized water. The different standards used are from SPEXCertiprep:

- ✓ QC21: 5 mg/L and Zr spiked at 5 mg/L
- ✓ QC7: 5 mg/L excepted 50 for K and 2.5 for and Rb spiked at 50
- ✓ Nb, P, S, W, Ge, Ta: 5 mg/L
- ✓ Hg, Sn: 1 mg/L
- ✓ Multi-element solution: 1.1 mg/L (rare earth elements, Claritas)
- ✓ Bi, Ga, In, U: 5 mg/L

Little or no matrix effects are seen through the combination of radial plasma viewing and a robust plasma. The high optical resolution allows for analysis of even complex samples from a calibration in water.

5 Sample preparation

0.1 g of sample was diluted in 50 mL. First it is dissolved in HF/HNO_3, evaporated to dryness and then completed with 45% HNO_3.

This sample preparation allows the analysis of all the elements, except Si, which is lost as SiF_6.

6 Results

3 samples were analyzed:

- BEN 5 Basalt
- 33 W 2 Diabas
- MRG 1 Gabbro

The results are displayed in Tables 4 through 6 on the following pages. Each table compared the concentration analyzed in solution, in the solid and at the percent of oxide, as well as the certifed concentration when available.

Table 4: Results, Sample BEN 5 (Basalt)

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Ag	328.068	< LD			
Al	308.215	105	52510	9.92	10.07
Al	396.152	102	51042	9.64	
As	189.042	0.014			
B	182.583	0.003			
Ba	455.403	1.805	905		1025
Be	313.042	0.003			
Bi	223.061	< LD			
Ca	317.933	193	96773	13.54	13.87
Cd	228.802	0.001			
Ce	413.765	0.306	153		152
Cl	134.724	0.475	237		300*
Co	228.616	0.159	79		61
Cr	267.716	0.714	357		360
Cu	324.754	0.137	68		72
Dy	353.170	0.013			
Er	369.265	0.010			
Eu	381.965	0.008	4.04		3.6
Fe	259.940	162	80839		
Ga	294.364	0.012	6.2		17*
Gd	376.840	0.020	9.8		9*
Ge	265.118	< LD			
Hf	264.141	0.011	5.3		5.4*
Hg	194.163	<LD			
Ho	345.600	< LD			
In	230.606	0.015			
K	766.490	22.44	11222	1.35	1.39
La	408.671	0.149	74.6		82
Li	670.784	0.045	22.56		12
Lu	291.139	< LD	< LD		0.24
Mg	279.806	148	74347	12.33	13.15
Mn	257.610	2.9	1490	0.19	0.2
Mo	202.030	0.004			
Na	589.592	45.1	22563	3.04	3.18
Nb	316.340	0.26	129		100*
Nd	406.109	0.13	65.6		70
Ni	231.604	0.47	235		267
P	178.229	8.31	4153	0.952	1.05
Pb	220.353	0.005	2.53		4
Pr	390.843	0.111			
Rb	780.023	0.109	54.4		47
S	181.978	0.556	278		300*
Sb	206.833	< LD			
Sc	361.384	0.041	20.3		22
Se	196.026	< LD			
Si	251.611	1.29			

* not certified

Table 4: Results, Sample BEN 5 (Basalt), (continued)

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Sm	359.260	0.024	11.9		12
Sn	189.989	0.03			
Sr	407.771	2.64	1320		1370
Ta	268.511	0.047	23.27		5.5
Tb	350.917	0.015	7.4		1.3*
Th	401.913	0.004	2.05		11
Ti	334.941	29.61	14804	2.47	2.61
Tl	190.864	< LD			
U	385.958	< LD	< LD		
U	409.014	0.034	17.1		2.4
V	311.071	0.627	313		235
W	207.911	0.071	35		29
Y	371.029	0.049	24		30
Yb	328.937	0.005	2.7		
Yb	369.420	0.004	2		1.8
Zn	206.200	0.230	115		120
Zr	343.823	0.511	255		265

Table 5: Results, Sample 33 W 2 (Diabase)

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Ag	328.068	< LD			
Al	308.215	158	79277	14.98	15.45
Al	396.152	155	77785	14.70	
As	189.042	< LD	< LD		1*
B	182.583	0.013			
Ba	455.403	0.318	158.8		174
Be	313.042	0.002			
Bi	223.061	< LD			
Ca	317.933	159	79632	11.14	10.86
Cd	228.802	< LD			
Ce	413.765	0.022	11.07		23
Cl	134.724	0.950			
Co	228.616	0.102	51		43
Cr	267.716	0.167	84		92
Cu	324.754	0.217	109		106
Dy	353.170	0.013	0.007		
Er	369.265	0.010	0.007		
Eu	381.965	0.008	0.003	1.3	1.1
Fe	259.940	162	137	68506	

* not certified

Table 5: Results, Sample 33 W 2 (Diabase), continued

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Ga	294.364	0.048	24.15		16.8*
Gd	376.840	0.005			
Ge	265.118	0.001			
Hf	264.141	< LD			2.6*
Hg	194.163	< LD			
Ho	345.600	0.001			
In	230.606	< LD			
K	766.490	11.2	5605	0.68	0.63
La	408.671	0.017	8.7		10.4
Li	670.784	0.032	16.2		9.6*
Lu	291.139	< LD	< LD		0.33*
Mg	279.806	79.8	39898	6.62	6.37
Mn	257.610	2.7	1351	0.174	0.167
Mo	202.030	0.001			
Na	589.592	33	16532	2.2	2.2
Nb	316.340	0.109	54.68		6.8*
Nd	406.109	0.033	16.7		13.4*
Ni	231.604	0.139	69.3		70
P	178.229	1.014	506.9	0.116	0.141
Pb	220.353	< LD			
Pr	390.843	0.017			
Rb	780.023	0.192	96.01		21
S	181.978	0.259			
Sb	206.833	< LD	< LD		0.85*
Sc	361.384	0.074	36.77		36
Se	196.026	< LD			
Si	251.611	0.488			
Sm	359.260	< LD	< LD		3.3*
Sn	189.989	0.009			
Sr	407.771	0.390	194.95		0.5*
Ta	268.511	0.047	23.5		0.5*
Tb	350.917	0.013	6.34		0.66*
Th	401.913	0.003	1.35		2.4
Ti	334.941	11.28	5641	0.94	1.062
Tl	190.864	0.003			
U	385.958	< LD	< LD		0.5*
U	409.014	< LD	< LD		
V	311.071	0.592	296		259
W	207.911	< LD			
Y	371.029	0.040	19.86		23*
Yb	328.937	0.006	3.17		
Yb	369.420	0.005	2.28		2.1
Zn	206.200	0.154	77.9		80
Zr	343.823	0.240	120		100*

* Not certified

Table 6: Results, Sample MGR 1 (Gabbro)

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Ag	328.068	< LD			0.14*
Al	308.215	96.15	47075	9.08	
Al	396.152	89	44777	8.46	8.5
As	189.042	0.005	2.527		0.7
B	182.583	< LD	< LD		13*
Ba	455.403	0.100	49.8		50
Be	313.042	0.001	0.571		0.6*
Bi	223.061	< LD			
Ca	317.933	219	109436	15.31	14.77
Cd	228.802	0.001			
Ce	413.765	0.044	22.10		25*
Cl	134.724	0.897	447.3		150*
Co	228.616	0.253	127		86
Cr	267.716	0.742	371		450
Cu	324.754	0.309	154		135
Dy	353.170	0.04	2.009		3*
Er	369.265	0.007			
Eu	381.965	0.004	1.99		1.4*
Fe	259.940	249	124429		
Ga	294.364	0.037	18.4		18*
Gd	376.840	0.006			
Ge	265.118	< LD			
Hf	264.141	0.001			
Hg	194.163	< LD			
Ho	345.600	< LD	< LD		0.5*
In	230.606	< LD			
K	766.490	3.27	1635		
La	408.671	0.019	9.7		
Li	670.784	0.014	6.9		
Lu	291.139	< LD	< LD		0.2*
Mg	279.806	173	86701	14.38	13.49
Mn	257.610	2.89	1443	0.186	0.17
Mo	202.030	0.001			
Na	589.592	11.3	5651	0.76	0.71
Nb	316.340	0.06	27.74		20*
Nd	406.109	0.04	18.9		19*
Ni	231.604	0.38	190		195
P	178.229	0.47	235	0.054	0.06
Pb	220.353	0.010	4.96		10
Pr	390.843	0.029			
Rb	780.023	< LD			8
S	181.978	1.446	723		600
Sb	206.833	< LD			0.4
Sc	361.384	0.108	53.7		48*
Se	196.026	< LD			
Si	251.611	1.527			

* not certified

Table 6: Results, Sample MGR 1 (Gabbro) continued

El	Wavelength nm	Cc mg/L	Cc ppm solid	Cc % oxide	Cc Certified
Sm	359.260	0.008	4.2		5*
Sn	189.989	0.005	2.58		3.2
Sr	407.771	0.563	281		260
Ta	268.511	0.056			
Tb	350.917	0.009			
Th	401.913	< LD			
Ti	334.941	44.44	22220	3.71	3.69
Tl	190.864	< LD			
U	385.958	< LD			
U	409.014	0.027	13.62		1
V	311.071	1.445	722		520
W	207.911	0.008			
Y	371.029	0.024	12.2		16*
Yb	328.937	0.005	2.45		
Yb	369.420	0.002	1.24		1*
Zn	206.200	0.372	186		190
Zr	343.823	0.192	96		105

* not certified

7 Conclusion

The semiquantitative results obtained for these 3 samples were close and often very close to the certified results. This high level of accuracy is due mainly to the high resolution of the ULTIMA 2 combined with the robust, radial view plasma. The high resolution eliminates spectral interferences and the robust, radial plasma provides few matrix effects, even in complex samples. Few matrix effects alllow for rapid, easy method development.

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