



## Application Note

# GEOLOGICAL SAMPLES BY ACTIVA-M ICP-AES

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## 1 Introduction

This application note describes the analysis of several elements (Ba, Be, Co, Cr, Cu, Nb, Ni, Rb, Sc, Sr, V, Y, Zn and Zr) in geological samples, with the ACTIVA-M ICP-AES instrument. Analysis of geological samples requires an ICP-AES instrument with good resolution and robustness, to compensate for the variability of matrix and the influence of the major elements.

The material was dissolved by fusion with  $\text{LiBO}_2$  in a Pt95Au5 crucible. The calibration was performed with 3 different certified reference materials (GSR-1 (Granite), GSR-2 (Andesite) and GSR-3 (Basalt)) from IGGE, China. A Kimberlite sample (SARM 39) was then analyzed to validate the analytical methodology. For the determination of low concentrations of Rb, a specific optimization was realized and is detailed.

## 2 Principle

The elemental analysis of these samples was done by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample, in liquid form, is nebulized and then transferred with an argon carrier gas stream to an argon plasma. The sample is dried, atomized and ionized, whereby the atoms and ions are excited. The intensity of the light is measured when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths which can be used for the identification of the element. The intensity of the light is used for the quantification.

## 3 Instrumental specifications and operating conditions

The work was done on the ACTIVA-M ICP-AES spectrometer. The specifications of the instrument and sample introduction system are listed in Table 1 and Table 2 respectively. For the determination of elements in geological samples, which are dissolved by alkaline fusion with  $\text{LiBO}_2$ , it is strongly recommended to use a nebulizer suitable to high salt concentration, to provide freedom from clogging. We used the

OpalMist nebulizer, which is made of PFA and resistant HF solutions. The operating conditions of the instrument are listed in Table 3.

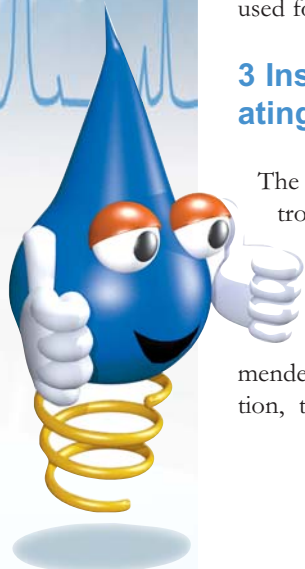
**Table 1: Specifications of the ACTIVA-M ICP spectrometer**

Parameter	Specification
Optical mounting	Czerny Turner
Focal length	0.64 m
Spectral range	120 – 800 nm
Nitrogen purge	Yes
Resolution	< 10 pm up to 430 nm < 18 pm in 430 – 800 nm
Gratings	Grating 1: 4343
grooves per mm	Grating 2: 2400
Order	1st order
Type of generator	Solid state
Frequency	40.68 MHz
Generator cooling	Air
Observation	Radial (view of total NAZ*)
Control of gas flow rates	By computer
Control of pump speed	By computer

\* Normal Analytical Zone

**Table 2: Specifications of the sample introduction system**

Parameter	Specification
Nebulizer	OpalMist (PFA concentric)
Nebulizer pressure	3 bar
Nebulizer Argon flow	0.84 L/min
Spray chamber	Cyclonic (glass)
Sample uptake	2 mL/min
Argon humidifier	No
Injector tube diameter	3 mm

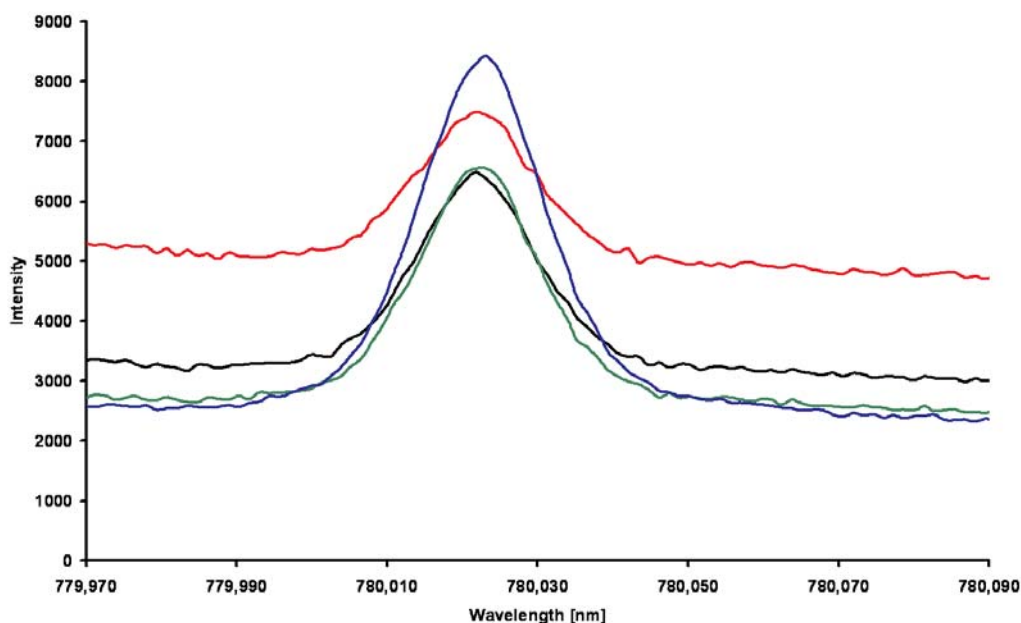


**Table 3: Operating conditions of plasma**

Parameter	Specification
RF generator power	1000 W
Plasma gas	12 L/min
Auxiliary gas	0.3 L/min
Sheath gas	0.2 L/min for normal conditions 0.8 L/min for Rb
Sheath gas stabilization time	8 s

The use of auxiliary gas is usually dedicated for organic samples. However, for high salt concentration solutions, some auxiliary gas mimizes salt deposit at the tip on the inner tube and ensures then an excellent long-term stability.

In addition, the sheath gas can be optimized for each line for sensitivity purpose and all elements can be measured with the same method. For the determination of low concentrations of Rb, the sheath gas flow rate was optimized to improve the sensitivity on this element. Figure 1 illustrates that a higher flow rate improves the SBR (Signal-to-Background Ratio) of the Rb 780.023 nm line. The optimum value of 0.8 L/min was defined then in the method for the argon sheath gas flow rate, specifically for Rb (other elements are measured with a flow rate of 0.2 L/min).



**Figure 1: Sensitivity enhancement for Rb (1 mg/L) by the use of higher sheath gas: red = 0.2 L Argon/min, black = 0.4 L Argon/min, green = 0.6 L Argon/min and blue = 0.8 L Argon/min.**

#### 4 Sample preparation for geological samples

The sample preparation is based on an alkaline fusion of the material with  $\text{LiBO}_2$  (Spectroflux 100 from Johnson Matthey) in a Pt95Au5 crucible. 1.5 g of  $\text{LiBO}_2$  was mixed with 0.5 g of the sample and melted for 30 min at 900 to 1000 °C (depending on the material). The sample was cooled down to room temperature and the melting cake was then dissolved in 50 mL of 1 M  $\text{HNO}_3$  and transferred into a 100 mL flask. The flask is filled up to 100 mL with 1 M  $\text{HNO}_3$ . This sample preparation induces a dilution factor of 200.

The same sample preparation is used for both samples and certified standards used for calibration.

#### 5 Calibration samples

Three different certified reference materials (GSR-1 (Granite), GSR-2 (Andesite) and GSR-3 (Basalt)) were used for the calibration. Table 4 lists the concentrations of the different standards.

A blank of fusion was added in the calibration procedure to get a 4 points calibration graph.

**Table 4: Concentrations of the different standards (values in the solid)**

Element	Wavelength nm	GSR-1 Granite ppm	GSR-2 Andesite ppm	GSR-3 Basalt ppm
Ba	455.403	343	1020	526
Be	313.042	12.4	1.1	2.5
Co	228.616	3.4	13.2	46.5
Cr	267.716	5.0	32.4	134
Cu	324.754	3.2	55.4	48.6
Nb	316.340	40.0	6.8	68.0
Ni	231.604	2.3	17.0	140
Rb	780.023	466	37.6	37.0
Sc	361.384	6.1	9.5	15.2
Sr	421.552	106	790	1100
V	292.402	24.0	95.5	167
Y	371.029	62.0	9.3	22.0
Zn	213.856	28.0	71.0	150
Zr	343.823	167	99.0	277

## 6 Results for the geological samples

The results of a Kimberlite sample (SARM 39) are listed in Table 5. The good recoveries obtained, even for low concentrations, validate the global analytical methodology (sample preparation + analytical method).

**Table 5: Concentrations of the SARM 39 certified sample (values in the solid)**

Element	SARM 39 Kimberlite measured ppm	SARM Kimberlite certified ppm	Recovery %
Ba	1740	1700	97.7
Be	1	1	100
Co	75	77	102.6
Cr	1264	1300	102.8
Cu	55	58	105.4
Nb	108	110	101.9
Ni	1021	994	97.4
Rb	51	52	102.0
Sc	14	13	92.9
Sr	1369	1400	102.3
V	111	109	98.2
Y	16	17	106.3
Zn	67	70	104.5
Zr	231	239	103.5

## 7 Conclusion

This application note demonstrates the performance of the ACTIVA-M ICP instrument for geological samples.

In addition, the ACTIVA-M instrument can offer a complete assistance for the development and validation of the method, based on the multi-line analysis concept which is described in Reference [1].

[1] *Application of Unique Software Tools Dedicated to Multiline Analysis by CCD-Based ICP-AES for Geological Samples*, Agnès Cosnier, Jean-Michel Mermet, Sébastien Vélasquez and Sophie Lebonil; *Applications of ICP & ICP-MS Techniques for Today's Spectroscopist*, October 2007

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