



Analysis in Geology: 1% HF and 4 g/L Boric Acid, 10 g/L Lithium Metaborate and 10 g/L Lithium Tetraborate

Nathalie Le Corre
HORIBA Scientific
Longjumeau, France

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1 Introduction

The analysis of geological samples is undertaken in several ways, depending on the original rocks and the elements to be determined. In this document, we present two types of sample preparation. The first uses hydrofluoric acid with boric acid for passivation and the second is a fusion procedure. Sample analysis results, including detection limits, are presented for both sample preparation techniques.

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.

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.

2.3 Limits of detection estimation

The limits of detection are calculated using the following formula:

$$\text{LOD} = k \times \text{BEC} \times \text{RSD}_0$$

With:

LOD = limits of detection,
k= 3 for the normal 3-sigma values,
BEC = Background equivalent concentration,
RSD₀ = relative standard deviation of the blank.

To calculate the LOD, a calibration curve is constructed using two points, 0 ppm and 5 ppm, or some concentration where the calibration is linear; this gives the BEC. The RSD₀ is evaluated by running the blank ten times.

3 Sample preparation

Boric acid was added to the HF to soak up the excess free HF and to create BF₃⁻, which has a better solubility than F⁻. This technique is often used with the determination of traces in geological samples.

4 Instrument specification

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

**Table 1: Specification of spectrometer**

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1 m
Thermoregulation	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
1st order resolution	0.010 nm
2nd order resolution	0.005 nm
Order	2nd order

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

5 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameters	Specifications
RF Generator power	1120 W or 1200 W
Plasma gas flowrate	15 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer gas flowrate	1 L/min
Nebulizer flowrate	3.6 bars (54 psi)
Sample uptake	1 mL/min
Type of nebulizer	Inert tangential
Argon humidifier	Yes
Injector tube diameter	3.0 mm

6 Wavelength selection and analytical conditions

The line with the highest sensitivity was used for each of the elements, as there were no interference problems.

Table 4: Analysis conditions

Element	Slits μm	Analysis Mode	Integration Time (sec)
Al, Hg, Zn	20 x 15	3 points on peak	0.5 or 2
Pb, Bi, Cd, Ni			
B, Mn, Fe, Cr			
Mg, Cu, Ag, Al			
Sr, Na, Li, K			
Al, Sn, Ti, Co	20 x 15	Gaussian	1
Ba			

7 Discussion

7.1 Calibration

A two-point calibration was made: using 0 and 1 mg/L standards for each sample preparation technique.

7.2 Limits of Detection

The results are shown in Tables 5 and 6.

7.3 Analysis

Using the calibration curve, a solution of 20 $\mu\text{g/L}$ in both matrices was analyzed. The results are given in $\mu\text{g/L}$ in Table 7.

8 Summary

These samples would normally present problems due to the dissolved solids and the presence of HF. The use of the argon humidifier, sheath gas and the large ID injector tube from HORIBA Scientific ensures smooth running of these samples. For HF samples the use of the inert tangential nebulizer and the inert Scott spray chamber is required. The results show excellent detection limits for the original sample. A typical dilution factor would have degraded these figures by a factor of 10 when calculated in the original material.

Table 5: Limits of Detection (1 % HF + 4 g/L H₃BO₃)

Element	Wavelength (nm)	BEC (mg/L)	RSD0 (%)	LOD (µg/L)
Ag	328.068	0.093	0.53	1.5
Al	167.020	0.036	2.2	2.4
Ba	455.403	0.007	0.49	0.1
Bi	223.061	0.320	0.6	5.8
Cd	228.802	0.023	0.47	0.3
Co	228.616	0.029	0.89	0.8
Cr	267.716	0.032	0.9	0.9
Cu	324.754	0.080	0.29	0.7
Fe	259.940	0.04	1.09	1.3
K	766.490	1.55	0.42	19.5
Li	670.784	0.073	0.76	1.7
Mn	257.610	0.005	0.84	0.1
Mg	279.553	0.001	1.1	0.02
Na	589.592	0.405	0.35	4.2
Ni	231.604	0.052	0.6	0.9
Pb	220.353	0.0248	0.41	3
Tl	190.864	0.112	0.97	3.3
Zn	213.856	0.015	0.57	0.3

Table 6: Limits of Detection (10 g/L LiBO₂ + 10 g/L Li₂BO₄)

Element	Wavelength (nm)	BEC (mg/L)	RSD0 (%)	LOD (µg/L)
Ag	328.068	0.120	0.49	1.8
Al	167.020	0.069	3.1	6.5
Ba	455.403	0.014	0.37	0.15
Bi	223.061	0.315	0.46	4.3
Cd	228.802	0.028	0.77	0.6
Co	228.616	0.054	0.86	1.4
Cr	267.716	0.424	1.53	19.5 (*)
Cu	324.754	0.723	0.88	19 (*)
Fe	259.940	1.535	2.47	114 (*)
K	766.490	0.535	4.25	64
Mg	279.553	0.165	1.57	7.8 (*)
Mn	257.610	0.04	1.43	1.7
Na	589.592	1.806	0.69	38 (*)
Ni	231.604	0.269	1.2	9.5 (*)
Pb	220.353	0.315	0.33	3.1
Sr	346.446	0.004	0.49	0.06
Tl	190.864	0.184	0.51	2.8
Zn	213.856	0.072	1.35	2.9

(*) blank contaminated



Table 7: Results

Element	Wavelength (nm)	1 % HF + 4 g/L H ₃ BO ₃	10 g/L LiBO ₂ + 10 g/L Li ₂ BO
Ag	328.068	19.3	19.4
Al	167.020	21.9	28.4
B	249.773	/	/
Ba	455.403	19.95	20.2
Bi	223.061	22.5	17.7
Cd	228.802	20.6	18.7
Co	228.616	19.1	19.4
Cr	267.716	21.7	/
Cu	324.754	19.2	/
Fe	259.940	27.7	/
Hg	194.227	/	/
Li	670.754	19.5	/
Mg	279.553	21.3	13.2
Mn	257.610	20.8	17.9
Na	589.592	14.4	/
Ni	231.604	22.9	19.4
Pb	220.353	17.5	17.3
Sn	189.989	/	/
Sr	346.446	21.5	21.1
Tl	190.864	21.5	20.7
Zn	213.856	21.4	15

/ = not measured

info-sci.fr@horiba.com
www.horiba.com/scientific

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France: HORIBA Jobin Yvon S.A.S., 16-18 rue du Canal, 91165 Longjumeau Cedex - Tel: +33 (0)1 64 54 13 00 - Fax: +33 (0)1 69 09 07 21 - Email: info-sci.fr@horiba.com
USA: HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Toll-free: +1-866-jobinyvon - Tel: +1-732-494-8660 - Fax: +1-732-549-5125
 Email: info-sci.us@horiba.com
Japan: HORIBA Ltd., Scientific Instruments Sales Dept., Alte-Building Higashi-Kanda, 1-7-8 Higashi-Kanda, Chiyoda-ku, 101-0031 Tokyo - Tel: +81 (0)3 3861 8231
 Fax: +81 (0)3 3861 8259 - Email: info-sci.jp@horiba.com
Germany: HORIBA Jobin Yvon GmbH, Hauptstrasse 1, 82008 Unterhaching - Tel: +49 (0)89 46 23 17-0 - Fax: +49 (0)89 46 23 17-99 - Email: info-sci.de@horiba.com
Italy: HORIBA Jobin Yvon Srl, Via Cesare Pavese 35/AB, 20090 Opera (Milano) - Tel: +39 0 2 57 60 30 50 - Fax: +39 0 2 57 60 08 76 - Email: info-sci.it@horiba.com
UK: HORIBA Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ - Tel: +44 (0)20 8204 8142 - Fax: +44 (0)20 8204 6142 - Email: info-sci.uk@horiba.com
China: HORIBA Jobin Yvon SAS, Room 1801, Capital Tower No.6, Jianguomenwai Av., Chaoyang District, Beijing 100022 - Tel: +86 (0)10 8567 9966 - Fax: +86 (0)10 8567 9066
 Email: info-sci.cn@horiba.com
Other Countries: Tel: +33 (0)1 64 54 13 00 - Email: info.sci@horiba.com