

## Determination of majors in geological samples by ICP-AES

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### Introduction

The classical analysis of silicate rocks for the major element constituents requires the determination of  $Al_2O_3$ ,  $CaO$ ,  $Fe_2O_3$ ,  $K_2O$ ,  $MgO$ ,  $MnO$ ,  $Na_2O$ ,  $P_2O_5$ ,  $SiO_2$  and  $TiO_2$ . These have traditionally been determined and expressed as the oxides<sup>1</sup>.

The fusion method is applicable for the decomposition of geological samples<sup>2,3</sup> and for their subsequent analysis by ICP-AES. Lithium tetraborate or lithium metaborate is used to decompose the samples. Lithium metaborate is a better flux for highly siliceous ores and lithium tetraborate better for high iron containing ores. The fused bead is dissolved in 10% nitric acid and the resultant solution analyzed directly.

### Experimental

#### Instrumentation

A Varian Liberty Vacuum 200 Inductively Coupled Plasma Atomic Emission Spectrometer was used for all measurements. The inert 'V' groove nebulizer was chosen because of the corrosive matrix. The operating parameters are listed in table 1. The instrument was controlled by an Epson EL 2 PC.

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#### Nebulizer

Type	V-groove
Pressure	195 kPa
Plasma power	1.0 kW
Torch	Demountable with alumina injector

#### Argon flow rate

Plasma	15.0 L/min
Auxiliary	1.5 L/min
Pump rate	15 rpm
Integration time	3 s
Replicates	3
Viewing height	Optimized on SBR
PMT voltage	650 V
Grating order	Default
Filter position	Default
Background correction	Dynamic
Snout purge	High

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Table 1: Instrument Operating Conditions

#### Reagent preparation<sup>4</sup>

Anhydrous lithium carbonate (73.89 g) and boric acid (122.6 g) were well mixed in a porcelain dish and slowly heated for four hours in a muffle furnace at 400°C. This produced a compound which was predominantly lithium metaborate  $LiBO_2$ .

The fused mass was ground to pass a BSS 250 mesh sieve. Lithium metaborate and lithium tetraborate were mixed in a 1:1 ratio to produce the borate flux.

All reagents used were Analytical Reagent Grade.

#### Sample preparation<sup>4,5</sup>

The samples (0.5000 g) were mixed with 2.5 g of the previously prepared borate flux in a 30 mL platinum crucible and fused in a muffle furnace at 1000°C for 30–45 minutes. The crucibles were removed from the muffle furnace and the contents were carefully swirled. If the fusion was incomplete the crucible was returned to the muffle furnace for a further 10 minutes. When the fusion was complete the crucible was removed from the furnace and allowed to cool.

The crucible was placed in a tall 150 mL beaker. A Teflon coated stirring bar was placed in the crucible and 125 mL of 1.6 M nitric acid solution was added. The beaker was placed on a hotplate stirrer, heated to 40–60°C with vigorous stirring until complete dissolution was obtained.

Precautions<sup>4</sup> required during this procedure are:-

- (i) The melt should be clear and not have any dark spots of sample or any floating material otherwise the process should be repeated.
- (ii) The melt and the acid must be at ambient temperature before commencing the dissolution process or the silica in the sample may form polymeric hydrated silicic acid.
- (iii) Excessive heating of the solution may also cause the same polymerization to occur.
- (iv) If constant stirring is not maintained some of the rock constituents may precipitate from solution.

When dissolution was complete, the solutions were quantitatively transferred to 250 mL standard flasks and made to volume with distilled/deionized water. The solutions were transferred to screwtop plastic bottles until required for analysis.

### Reference Rock samples

Five U.S. Geological Survey Rock Standards were used.

G-2, SY-2, BCR-1 and PCC-1 were presented as unknowns.

SY-3 was used as the standard for calibration purposes for this study.

### Standard preparation

SY-3 was prepared according to the sample preparation procedure described and was used as the working standard. The concentrations used for calibration were those values ascribed to the rock sample as shown in table 2.

A blank solution was prepared by performing the sample preparation without any sample present.

### Standard SY-3

	Standard values used (wt%)	Uncertainty (wt%)
Al <sub>2</sub> O <sub>3</sub>	11.76	0.30
CaO	8.25	0.18
Fe <sub>2</sub> O <sub>3</sub>	6.49	0.16
K <sub>2</sub> O	4.23	0.12
MgO	2.67	0.13
MnO	0.32	0.02
Na <sub>2</sub> O	4.12	0.15
P <sub>2</sub> O <sub>5</sub>	0.54	0.03
SiO <sub>2</sub>	59.68	0.41
TiO <sub>2</sub>	0.15	0.02
TOTAL	98.21	1.87

Table 2: Standard values used for calibration

## Results

The V-groove nebulizer was used because it has a lower susceptibility to degradation in comparison with the glass concentric nebulizer particularly for fusion samples. It is also less susceptible to clogging than glass concentric nebulizers.

### Analytical line selection

Al 396.152 nm This line was chosen because it has the maximum sensitivity while having the minimum interferences from other elements as shown in figure 1. The high resolution of the Liberty ICP-AES minimizes spectral interference from Ca. The performance is therefore better than the "traditional" 308.215 nm Al line which suffers from an OH band structure.

Ca 317.933 nm The two primary Ca lines are too sensitive for the levels of Ca found in the fusion samples. There is a weak Fe line which directly overlaps, however the concentration of the Fe is not high enough to cause an interference.

Fe 238.204 nm The structured background due to NO band emission can be reduced by using a lower viewing height or by using a higher plasma auxiliary flow.

K 769.869 nm This line was chosen to avoid a Mg interference found with the 766.490 nm K line.

Mg 279.079 nm This line was chosen because it has sufficient signal while having minimum interferences from other elements. The only documented interference is Mn. For the Mg/Mn ratios found in these fusion samples the effect is minimal.

Mn 257.610 nm This primary line has minimum interferences from other elements. High Al concentrations will cause an elevated background which can be corrected using Dynamic background correction. The Fe line directly overlaps on the Mn line. For very high Fe to Mn ratios this will become significant. However for these fusion samples the effect is minimal.

Na 588.995 nm This line was chosen because it has the maximum sensitivity while having the minimum interferences from other elements. The wing of the nearby Ar lines causes a sloping background which can be minimized by using a higher viewing height and Dynamic background correction.

P 177.495 nm There is a nearby weak Cu line which overlaps the analyte peak however the concentrations are not significant to cause an interference.

Si 288.158 nm This line was chosen because it has minimum interferences from other elements. A demountable torch with an alumina injector is recommended for Si determination.

Ti 334.941 nm The structured background due to OH band emission presents no problem.

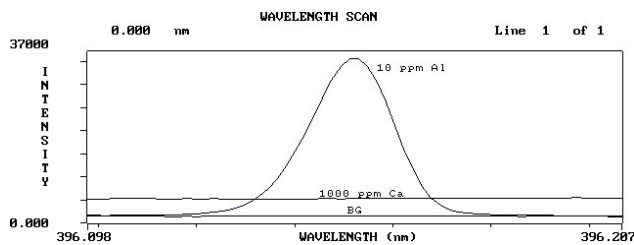


Figure 1. Wavelength scans of 10 ppm Al standard, blank and 1000 ppm Ca

### Detection limit

The detection limit was determined as twice the standard deviation of the blank solution (the borate flux) measured 10 times with a 5 sec integration time. The analytical wavelengths used and detection limits obtained are listed in table 3.

Element	Wavelength (nm)	Detection limit in rock (wt%)
Al <sub>2</sub> O <sub>3</sub>	396.152	0.0007
CaO	317.933	0.0005
Fe <sub>2</sub> O <sub>3</sub>	238.204	0.0007
K <sub>2</sub> O	769.869	0.0015
MgO	279.079	0.0003
MnO	257.610	0.00002
Na <sub>2</sub> O	588.995	0.0003
P <sub>2</sub> O <sub>5</sub>	177.495	0.003
SiO <sub>2</sub>	288.158	0.0009
TiO <sub>2</sub>	334.941	0.00003

Table 3: Wavelengths used and detection limits obtained

The results for the measurement of four US Geological Rock standards are shown in table 4. The %RSD typically varies from 0.1%–7% depending on the level of the element present.

### Standard G-2

	Measured value (wt%)	Certified Value (wt%)	
Al <sub>2</sub> O <sub>3</sub>	15.15	15.37 ± 0.55	
CaO	2.02	1.94 ± 0.06	
Fe <sub>2</sub> O <sub>3</sub>	2.66	2.71 ± 0.06	
K <sub>2</sub> O	4.37	4.45 ± 0.11	
MgO	0.77	0.799 ± 0.03	
MnO	0.03	0.03 ± 0.0001	
Na <sub>2</sub> O	3.84	4.06 ± 0.13	
P <sub>2</sub> O <sub>5</sub>	0.03	0.135 ± 0.005	
SiO <sub>2</sub>	71.54	69.03 ± 0.43	
TiO <sub>2</sub>	0.52	0.480 ± 0.012	
TOTAL	100.93	99.00 ± 1.39	

### Standard PCC - 1

	Measured value (wt%)	Certified Value (wt%)	
Al <sub>2</sub> O <sub>3</sub>	0.60	0.590 ± 0.02	
CaO	0.57	0.518 ± 0.017	
Fe <sub>2</sub> O <sub>3</sub>	8.27	8.07 ± 0.18	
K <sub>2</sub> O	0.01	0.038 ± 0.048	
MgO	45.70	43.40 ± 1.30	
MnO	0.12	0.092 ± 0.003	
Na <sub>2</sub> O	0.02	0.07 ± 0.10	
P <sub>2</sub> O <sub>5</sub>	<0.01	0.02 ± 0.01	
SiO <sub>2</sub>	42.33	41.94 ± 0.37	
TiO <sub>2</sub>	<0.01	0.004 ± 0.0002	
TOTAL	97.64	94.74 ± 2.05	

### Standard SY - 2

	Measured value (wt%)	Certified Value (wt%)	
Al <sub>2</sub> O <sub>3</sub>	11.88	12.04 ± 0.23	
CaO	8.92	7.96 ± 0.15	
Fe <sub>2</sub> O <sub>3</sub>	6.57	6.31 ± 0.17	
K <sub>2</sub> O	4.31	4.45 ± 0.11	
MgO	2.91	2.69 ± 0.12	
MnO	0.34	0.32 ± 0.01	
Na <sub>2</sub> O	4.05	4.31 ± 0.13	
P <sub>2</sub> O <sub>5</sub>	0.27	0.43 ± 0.03	
SiO <sub>2</sub>	63.32	60.11 ± 0.43	
TiO <sub>2</sub>	0.15	0.15 ± 0.02	
TOTAL	102.72	98.77 ± 1.40	

### BCR - 1

	Measured value (wt%)	Certified Value (wt%)	
Al <sub>2</sub> O <sub>3</sub>	12.86	13.49 ± 0.49	
CaO	7.36	6.67 ± 0.22	
Fe <sub>2</sub> O <sub>3</sub>	13.42	13.15 ± 0.29	
K <sub>2</sub> O	1.63	1.70 ± 0.04	
MgO	3.67	3.45 ± 0.11	
MnO	0.19	0.14 ± 0.004	
Na <sub>2</sub> O	3.09	3.34 ± 0.11	
P <sub>2</sub> O <sub>5</sub>	0.17	0.351 ± 0.009	
SiO <sub>2</sub>	55.64	54.23 ± 0.67	
TiO <sub>2</sub>	2.40	2.20 ± 0.055	
TOTAL	100.43	99.02 ± 2.00	

Table 4: Results of the US Geological Rock standards analyses

## Conclusion

The determination of majors in geological samples by ICP-AES has been described. The values found compare very well with the certified values indicating that this methodology is totally suitable for these geological samples.

The high resolution of the Liberty ICP-AES allows the user to choose the desired wavelength depending on the precision and detection limits required.

## References

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