Application Note

The Determination of Aluminium, Iron and Silicon in Rock Samples

Introduction

Silica or silicates are a major constituent of materials such as rocks, lavas, minerals, slags, refractories, ceramics, glasses, cements and ashes. The analysis of such samples by atomic absorption presents some problems, and steps must be taken to overcome these. For the analysis of geological samples such as rocks, the major components include calcium, aluminium, magnesium and iron as well as silicon. There may be a number of interelement interferences or matrix interferences which cause suppression, enhancement or background effects. These difficulties need to be overcome before accurate analysis of such samples can be achieved.[1-4]

The choice of an appropriate dissolution procedure is also required. “Acid attack” methods generally involve the use of mixtures of hydrofluoric acid and nitric acid in conjunction with sulphuric or perchloric acid. Any mixture containing hydrofluoric acid may cause the complete removal of silicon by vaporization as the tetrafluoride.[1] The combination of hydrochloric acid and hydrogen peroxide has been used as a strong oxidising mixture to leach out metals from non-silicate minerals.[5] “Fusion” methods generally incorporate an alkaline fusion salt or mixture and are used to decompose these samples while allowing silicon to stay in solution. In recent times the use of lithium metaborate as a fusion agent has been recommended. However, it may not allow dissolution of silicates if strong acids (such as nitric acid) are used to dissolve the mixture. Alternatively, if the nitric acid concentration is too low, the fusion mixture will not dissolve.[6] Also, sodium carbonate can be used to provide “gentle fusion” for simple samples without sulphides and chromites.

The dissolution procedure chosen in this method used sodium hydroxide to provide a strongly alkaline fusion mixture in conjunction with sodium peroxide (as a strong oxidising agent), to dissolve any sulphides and chromites present in the rock samples.

Experimental

Instrumentation

A GBC 906 double beam atomic absorption spectrophotometer (AAS) equipped with the Ultra-pulse deuterium arc background correction system, and an FS3000 flame auto-sampler, were used. A GBC data station (AT-compatible computer with 40 megabyte hard disk drive) with 906 AAS operating software installed, was utilised for developing the flame atomic absorption application used for collecting and storing data and displaying all graphics traces. The real time colour graphics traces for the standards and sample signals allowed the analytical conditions to be optimized. The software allowed all diluted sample determinations to be converted to a final result in percentage oxide by performing a calculation for each sample using the in-built “Weight and Dilution Correction” feature. Method parameters, results, and graphics traces were printed for each analysis. The instrumental conditions for aluminium, iron and silicon are given in Table 1. Other elements that could be measured by the same procedure include magnesium and calcium.

	Aluminium	**Iron**	**Silicon**
Wavelength* (nm)	237.4	395.6	250.7
Lamp Current (mA)	10	6	15
Slit Width (nm)	0.5	0.2	0.2
Flame Type	N_2O-Acet.	N_2O-Acet.	N_2O-Acet.

* Standard hollow cathode lamps were used throughout, and alternative, less sensitive lines were chosen to reduce sensitivity.

***Table 1**: Instrument Parameters for aluminium, iron and silicon analysis.*

Apparatus and Reagents

All chemicals were analytical grade: sodium hydroxide (NaOH in pellet form) and sodium peroxide (Na_2O_2) were from Mallinckrodt (Australia). Hydrochloric acid (HCl) was from BDH Chemicals (Australia). Atomic Absorption standards for aluminium, iron and silicon, 1000 μg/mL, were from BDH Chemicals (Australia). Deionized water for washing and rinsing was obtained from a mixed-bed deionizing unit (Service Exchange Deionization System, Continental Water Systems Pty Ltd). Deionized water used for reagent preparation and analysis was from a reverse osmosis, mixed-bed deionizing unit that supplies Type I ultrapure water (Modulab, Reagent Grade Model Water Systems, Continental Water Systems Pty Ltd). Analytical standards were freshly prepared each day at the appropriate concentration for each element.

Digestion Procedure for Rock Samples

Samples of ground diabas rock (a form of basalt) were obtained for analysis. The samples were designated as Sample 4 and Sample 6.

Five-gram aliquots of NaOH were added to seven clean nickel crucibles. The NaOH was melted at 400°C in the bottom of the crucibles. When the melt was cool, 0.5 to 0.6 g of ground rock samples were added to the top of the melt. Also included was a blank which was taken through the sample treatment process. Three replicates of each of the 2 samples were prepared. Additional NaOH (2g) and 0.5 to 1.5 g Na_2O_2 were added to the top of the sample. The crucibles were covered with a loose fitting nickel lid.

The crucibles were gently heated until any frothing stopped. The heat was gradually increased until the contents were molten and the contents were occasionally swirled to ensure complete mixing.

Fusion required only 3 to 5 minutes because the rock was finely ground. (A longer time period is necessary if the sample is not less than 200 mesh).

The crucibles were allowed to cool and the outside was rinsed (with 6 M HCl). The washings were discarded.

Each crucible and its contents were added to a 250 mL plastic beaker along with 30–40 mL of distilled water and covered with a watch glass.

When the reaction had cleared, each crucible and lid were cleaned with 6M HCl (10–20 mL only) and the washings were added to the aqueous leach. Each crucible and lid were removed with clean tweezers.

The solutions were diluted to an appropriate volume for atomic absorption determination.

Sample Preparation

The dilution for the samples depended on the element to be measured. For iron the dilution was 1+1 with deionized water (factor of 2), for aluminium the dilution was 3+10 with deionized water (factor of 10/3 or 3.33) and for silicon the dilution was 1+4 with deionized water (factor of 5). Iron and silicon were measured using the standard (analyte) additions technique. The preparation of the sample tubes and additions of standard for the silicon determination are given in Table 2. The silicon standard concentration was 500 μg/mL.

	Sample Vol (mL)	**Std Vol (mL)**	**Water Vol (mL)**	**Addition Conc μg Si/mL**
Sample	2.0	-	8.0	-
Addition 1	2.0	1.0	7.0	50
Addition 2	2.0	2.5	5.5	125
Addition 3	2.0	5.0	3.0	250

***Table 2**: Standard additions table for Si.*

Sodium, at 2000 μg/mL, is generally added to samples for silicon analysis to suppress the ionization that can occur in the nitrous oxide-acetylene flame. These samples already contained sufficient sodium due to the fusion technique. When the composition of the sample matrix is the same for all samples, one set of additions is used and other samples measured directly from the calibration graph. Otherwise, standard additions must be used for each sample.

Initially, aluminium was measured by standard additions, but because the calibration graph was curved, the results could not be relied upon. The standard additions technique relies upon a linear calibration graph to obtain accurate results. Hence aluminium was measured by direct calibration. To suppress ionization of aluminium, potassium was added to all standards and sample dilutions at a final concentration of 2000 µg/mL.

Results and Discussion

Analyte and oxide concentrations were calculated using Equations 1 and 2 respectively.

Equation 1

analyte concentration (µg/g) =

undiluted sample concentration (µg/mL x volume (mL) x 1/sample weight (g)

Equation 2

oxide concentration (%) =

analyte concentration (µg/g)

$$\times \frac{\text{molecular wt. of oxide}}{\text{atomic wt. of analyte}} \times 100$$

All calculations were performed using the “Weight and Dilution Correction” file of the 906 AAS software for each sample dilution and analyte.

Table 3 contains measured data for silicon for one of the samples, while the corresponding standard additions calibration graph is reproduced in Fig. 1.

Sample Type	Conc. mg/mL	RSD %	Replicate Readings mean absorbance			
Blank	0	0.002	0.003	0.003	0.001	0.001
Addition 1	50	0.71	0.370	0.368	0.369	0.373
Addition 2	125	1.07	0.466	0.471	0.466	0.461
Addition 3	250	1.08	0.603	0.609	0.596	0.603

***Table 3**: Silicon data for sample 4 (No.1)*

Table 4 summarises the mean percent oxide concentrations based on all the results obtained for sample 4 and sample 6.

Analysis of rock samples by fusion techniques requires a high degree of analytical precision. The variation in the results in Table 4 indicates that analytical variation from aliquot to aliquot of each sample is an important consideration in the final result for the samples. Hence, it is important to use high purity reagents and keep the number of additions of fusing material to a minimum to reduce variation in the sample result caused by contamination effects.

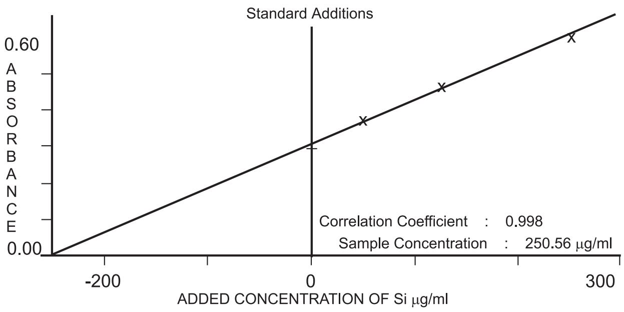

***Figure 1**: Calibration graph for silicon analysis.*

	Fe_2O_3	Al_2O_3	SiO_2
Sample 4	-	13.2 (0.4)	50.7 (2.0)
Sample 6	10.2 (2.6)	19.8 (1.7)	42.3 (1.2)

***Table 4**: Mean oxide concentrations, %, with standard deviations given in parentheses.*

The fusion procedure described is a general method which allows the majority of samples to be decomposed in a routine way. A ten to twenty-fold ratio of the NaOH flux to the sample weight is required. The use of alkali metal hydroxides may liberate variable amounts of water during the fusion process, causing the fusion melt to foam, froth and spatter in the worst cases. The procedure therefore requires the formation of the NaOH melt prior to the addition of sample.

Fusion with hydroxides is used to decompose quartz, silicates, sand, clay, natural oxides, some ores and rocks. The decomposition of silicates depends on the structure of the minerals concerned. Layered clay minerals may react very rapidly, even at low temperatures (400–430°C). Sodium hydroxide causes iron compounds to be reduced in the melt if the samples contain silicates. Iron forms an alloy with nickel in proportion to the iron content of the mineral sample. The addition of sodium peroxide allows complete oxidation of the sample for these difficult matrices, especially when sulphides and chromites are in the samples.

Fusion with NaOH is usually carried out in an iron, nickel, silver or gold crucible, but never in platinum. Platinum crucibles are known to corrode at 500°C with sodium hydroxide and at 400°C with potassium hydroxide. A nickel crucible is only marginally corroded by either hydroxide below 400°C. However it must not come into direct contact with a burner flame. When a nickel crucible is used for a prolonged fusion, the formation of nickel oxides may result due to the effect of atmospheric oxygen, alkaline nitrate, or sodium peroxide. When hydrochloric acid is later added to the melt, the oxides will cause evolution of chlorine which may cause severe problems with subsequent determinations. Corrosion of crucibles may cause difficulties in the analysis of elements at trace concentrations. Also, some of these elements may be adsorbed onto the crucible wall, while other elements may exchange with the crucible material.

Many other fusion procedures are available for use. Lithium tetraborate has been used alone[7] and in conjunction with lithium carbonate[8], but both methods suffer because silicon dioxide is not readily taken up into the melt. The incorporation of lithium carbonate has improved the lithium tetraborate method but it still suffers from the evolution of carbon dioxide and the resultant sputtering. A lithium carbonate/boric acid mixture is known to be less than satisfactory due to the incomplete evolution of carbon dioxide and the inability to obtain a complete melt of the sample.[9] All the above methods, except for the lithium carbonate/boric acid mixture, require fusion temperatures of approximately 1000°C. The method outlined here requires temperatures up to 400°C only.

The method described herein is a general procedure allowing decomposition of most of the sample types that will be encountered. The combination of sodium hydroxide and sodium peroxide allows for the use of an aggressive decomposition mixture suitable for not only simple samples but complex matrices as well.

References

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