THE DIRECT AND RAPID DETERMINATION OF ALUMINA AND SILICA IN SILICATE ROCKS AND MINERALS BY ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

Atomic absorption spectroscopy is a rapid and convenient method for the determination of silica and alumina in silicate rocks. NaOH fusion of the samples in nickel crucibles is more complete and superior to Na_2CO_3 fusion in platinum.

Non-resonance light absorption within the flame has been eliminated by: a) reduction of the solution feed-rate to about 75% of that yielding maximum absorption; b) application of the nitrous oxide-acetylene burner.

INTRODUCTION

The quantitative determination of Al_2O_3 and SiO_2 in silicate rocks and minerals remains one of the most difficult tasks in analytical geochemistry and mineralogy. Despite the investment of considerable effort towards the development of modern determinative methods for these and other oxides (Shapiro and Brannock, 1952, 1962; Riley, 1958; Riley and Williams, 1959; Weibel, 1961) much geochemical and petrological research still relies on the classical, well-established methods of analysis. These have remained basically unchanged since the beginning of the century, although some important improvements, with regard both to accuracy and time of execution, have recently been suggested (Peck, 1964).

The introduction of atomic absorption spectrophotometry in analytical chemistry (Walsh, 1955) has paved the way for the development of new methods of silicate rock analysis. Rapid and accurate atomic absorption techniques were developed for K, Na, Ca, Mg, Fe, Rb, Sr, Ni, Co, Cu, Zn and Cd in silicate minerals (Belt, 1964; Billings and Adams, 1964; Trent and Slavin, 1964; Firman, 1964).

No information has been published on silica and alumina determination *in silicates* by atomic absorption, although Al and Si analyses have been carried out on other materials (e.g. Chakrabarti, Lyles and Dowling, 1963; Slavin and Manning, 1963; Cartwright, Sebens and Manning, 1966; Slavin and Slavin, 1966).

The present paper describes methods which have been developed for silica and alumina determination in silicates by atomic absorption spectroscopy and the first results are given.

EXPERIMENTAL

A Perkin-Elmer atomic absorption spectrophotometer model 303 and recorder read-out accessory unit, mated to a 0–10 mV Leeds and

Northrup "Speedomax-G" recorder, were used. Perkin-Elmer hollow cathode single element tubes of Si and Al served as monochromatic light sources. The flame was furnished by a nitrous oxide-acetylene burner (Willis, 1965). All experiments were run on eight standard samples[1] comprising two granites (samples GH and GA), a basalt (BR), a tonalite (T-1), a syenite (CAAS), a soda-feldspar (NBS 99), a standard silica brick (BCS 267) and a standard firebrick (BCS 269). Standard calibration solutions were prepared for alumina from "Analar" grade (Hopkin & Williams) aluminum wire, and for silica from a powdered clear natural quartz crystal (98.40% SiO_2, sample No. 968 of the departmental collection, rock crystal from Elba).

The first attempts produced inconsistent and low results both for silica and alumina. The relative errors, however, were higher for silica than for alumina (about minus 5% and minus 2% respectively), increasing slightly with rock acidity. Careful inspection of the sample solutions (obtained by sodium carbonate fusion in platinum) invariably showed floating, white to colourless flakes which proved to be composed mainly of silica. Filtration of these particles followed by a second fusion (Na_2CO_3) lead to erratic results due to the high salt content of the analytical solutions (burner clogging was frequent).

The ordinary sodium carbonate fusion was rejected and instead the sample powders were decomposed with NaOH in nickel crucibles, followed by water-leaching and acidification (HCl). This procedure yielded clear solutions. Results obtained on these solutions were again in error, being systematically too high by 3–6% for both oxides. Attempts to correct for possible matrix and viscosity differences between sample and standard solutions by the method of additions and extrapolation to zero absorbance (Grimali, 1960) gave the same high results.

It was suspected that some "apparent absorption" contributed to the true, free-atom resonance absorption. This may be caused by solid refractory particles which scatter light within the flame (David, 1961; Willis, 1964; Billings, 1965b) and/or by true molecular absorption (Koirtyohann and Pickett, 1965, 1966a, 1966b). The existence of such apparent absorption was confirmed by observing significant absorption using non-resonance lines in the vicinity of the Si and Al analytical lines. However, suitable corrections could not be made because of the poor signal-to-noise ratio of the non-resonance lines.

[1] Additional information on sample composition, mineralogy and location can be obtained from the following sources: BR basalt, GA granite, GH granite (Roubault, et al., 1966); T-1 tonalite (Commissioner, Geological Survey, P.O. Box 69, Dodoma, Tanganyika); CAAS syenite (Weber, 1965); BCS 267 silica brick, BCS 269 firebrick (British Bureau of Analysed Samples); NBS 99 soda feldspar (U. S. National Bureau of Standards).

To eliminate this apparent absorption the solution feed rate into the burner was reduced from the initial 5.2 ml/min to 4.5 ml/min, resulting in a sensitivity reduction to about 75% that of its original value. The elimination of apparent absorption by this method is explained as follows: a) in a given flame a larger proportion of the introduced compounds is dissociated to free atoms when the same energy provided by the flame per unit time is applied to smaller quantities of solution; b) the flame temperature is raised significantly by feed-rate reduction because less water (per time) is aspirated (Dean, 1960, p. 20).

Sample solutions demonstrate the effect much more strongly than do standards because the possibility that various molecules and/or solid

TABLE 1. SiO_2 ANALYSES

Sample	Reported Range	Average or Preferred Value	Results Obtained			Average Difference
			Lower	Higher	Average	
BR	37.33–39.50	38.49	38.10	38.42	38.26	−0.23
BCS 269	56.5–56.8	56.7	56.43	56.81	56.62	−0.08
CAAS	57.54–60.65	59.45	58.99	59.31	59.16	−0.29
T-1	62.30–63.11	62.69	62.02	62.80	62.41	−0.28
NBS 99	not specified	68.66	68.48	68.50	68.49	−0.17
GA	68.75–70.51	69.71	69.80	69.98	69.89	+0.18
GH	74.60–76.46	75.58	75.72	75.92	75.82	+0.24
BCS 267	95.7–96.1	95.9	96.11	96.19	96.15	+0.25

refractories will form is much greater for the sample solution, containing as it does a great variety of chemical species normally encountered in rocks.

RESULTS

The results obtained on the eight standard samples are given in tables 1 and 2. Duplicate analytical values are reported and compared with the data available for these samples.

The results are presented in tables 1 and 2, and are arranged in increasing order of SiO_2 and Al_2O_3. They show good agreement with previous data. As regards silica, the new averages fall within the reported data range, except for sample BCS-267, but even here the deviation of the new mean value (96.15%) from the maximal reported value (96.1%) is negligible. The differences between the duplicate runs are small and always smaller than the reported differences between the maximal and minimal values. The differences between the new mean values and the reported means of SiO_2 show a distinct tendency (table 1) to increase

gradually with increasing silica content. The differences are negative (maximal difference $= -0.29\%$) for rocks with less than about 68–70% SiO_2, and are positive (maximal difference $= +0.25\%$) for rocks containing more SiO_2. No explanation could be found for this trend, but it should be stated that this is not caused by apparent absorption for the following reasons: (a) such absorption may account only for positive errors; (b) no such trend was observed during the initial experiments when apparent absorption definitely took place.

The alumina results (table 2) are again in good agreement with reported data. The new data averages fall within the reported data range. The new averages are, however, higher than the reported averages (ex-

TABLE 2. Al_2O_3 ANALYSES

Sample	Reported Range	Average or Preferred Value	Results Obtained			Averages Difference
			Lower	Higher	Average	
BCS 267	0.83–0.88	0.85	1.30	1.52	1.41	+0.56
CAAS	8.53–11.08	9.58	10.19	10.30	10.24	+0.66
BR	9.19–11.42	10.31	10.40	10.58	10.49	+0.18
GH	12.02–13.25	12.63	13.00	13.41	13.20	+0.57
GA	14.10–15.44	14.61	14.77	14.79	14.78	+0.17
T-1	16.0–16.93	16.55	16.50	16.53	16.52	−0.03
NBS 99	not specified	19.06	19.00	19.38	19.19	+0.13
BCS 269	33.7–34.1	33.9	34.01	34.23	34.12	+0.22

cept for sample T-1). The absolute differences between the averages (new vs. reported) show a tendency to become smaller with increasing alumina content. Sample BCS-267 shows a very high relative difference between the averages (new average 1.41% Al_2O_3 against reported 0.85% Al_2O_3). It is believed that these differences might be explained by the incomplete precipitation of Al_2O_3 with the ammonia group as frequently occurs during classical analysis when the pH is not strictly controlled.

Recording indicates the favourable signal to noise ratio obtained for both silica and alumina, the ratio being slightly better for alumina. The recording procedure is considered superior to direct meter readings, since the readjustment of zero absorption between readings is eliminated and any change in the flame due to burner clogging is readily shown up.

The method is recommended for application in any geochemical laboratory possessing an atomic absorption spectrophotometer with equivalent specifications. A detailed procedure is presented in the appendix.

APPENDIX

Detailed analytical procedure. 0.5 gm of the finely powdered sample (minus 200 mesh) was weighed to the nearest 0.1 mg into a 100 ml nickel crucible. About a gram of NaOH pellets (Merck, analytical grade) was added and the crucible heated *uncovered* on a very low bunsen flame for 2–3 minutes until all the NaOH melted. If the crucible is covered, the adjustment of the flame to slow melting of the flux is impossible and material loss through spattering often occurs. The heat was then increased slightly and the crucible occasionally swirled until a homogeneous clear melt was obtained. The time required is 5–10 minutes.

After cooling, about 50 ml of doubly distilled water was introduced into the crucible and carefully stirred by means of a nickel spatula. The water was poured off into a polythene 500 ml beaker and a second 50 ml water portion added to the crucible. The crucible was then transferred to a hot-plate and carefully heated, without boiling, until (ca. 10 minutes) the entire fused mass became loose, after which it was removed from the crucible into the plastic beaker containing the poured-out solution. The crucible was washed several times with water and the washings added to the beaker. The beaker was placed on a magnetic stirrer and its contents stirred until all solid fusion lumps dissolved. Without interrupting the stirring, some 50 ml concentrated HCl (Analar grade) were slowly added and the solution tested (litmus) to be distinctly acid. The solution was transferred into a volumetric 500 ml flask, cooled to room temperature, diluted to volume with water, shaken and immediately transferred to a 500 ml well stoppered plastic bottle. The entire procedure (including weighing and fusion) can be carried out within 30 minutes. Several samples can be run in parallel.

25 ml of this solution, diluted to volume with water in a 100 ml volumetric flask and immediately transferred to a suitable small plastic bottle, served for silica determination. For alumina determination 50 ml of the sample solution were placed in a 100 ml volumetric flask, to which 3 ml of a 4% KCl solution (in water) were added in order to repress ionization effects, and the solution made up to volume.

Standard calibration solutions for silica were prepared by fusion of 1.000 gm of powdered quartz (the SiO_2 content having been determined on a separate portion by conventional procedures and found to be 98.4%) with 2 gms of NaOH followed by the above treatment and brought to a final volume of 500 ml. This stock solution had a concentration of 2000 ppm silica (correction factor—0.9840) and was diluted to yield standard working solutions of 100, 150 and 250 ppm silica. The use of natural quartz was preferred to artificial silica compounds (silica gel or sodium silicate) because the weighing is more accurate with quartz powder than with the extremely hygroscopic artificial compounds.

Standard stock solution for alumina was prepared by dissolving 1.0000 gram of analytical-grade aluminium wire in a minimal amount of dilute (1:3) hydrochloric acid followed by dilution with water to 1 liter. The solution contained 1000 ppm Al and was appropriately diluted to yield working standards of 20, 50 and 80 ppm Al. Blank runs were analysed alongside the samples but they were later omitted since no detectable reagent contamination was found. This obviously applies only to the specific substances used in the course of the present investigation and the situation should be rechecked for every new batch of chemicals.

After sample and standard preparation the spectrophotometer and recorder were al-

lowed to warm up for 10 minutes with the silicon lamp lighted. A sample solution was aspirated and the capillary supporting-screw rotated counter clockwise until a "blow back" bubbling from the capillary was observed. The screw was then rotated backwards until a maximum absorption signal was obtained on the read-out meter. The percent-absorption was recorded and the aspiration rate again reduced by means of the same screw until the meter reading dropped to a value approximately 75% that of the maximum value. The screw was fastened and this position maintained for all following silica and alumina determinations.

The following instrumental settings were used:

	SiO_2		Al_2O_3
Analytical line	2516 Å		3093 Å[3]
Range	UV		UV
Slit	3		3
Source: Hollow Cathode	30 ma	Hollow cathode	30 ma
	Fuel: Acetylene[1]		Acetylene[1]
	Oxidizer: N_2O[2]		N_2O[2]

Recorder read-out scale expansion was set to 1 and noise suppression to 3 for both silica and alumina.

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[1] Acetylene pressure was set to 9 psig and flow was set above 15 at the flowmeter. After ignition of the flame, the acetylene flow-rate was readjusted to yield maximum absorption while aspirating a standard solution. The flame required for silica analysis is fuel-rich and bright; for alumina a "hard," lean oxidizing flame is suitable.

[2] N_2O cylinder regulator was set to 45 psig and the burner regulator to 30 psig. The flow meter was set to 7.5.

[3] The 3961.5 Å line for Al was found to be equally suitable as the 3093 Å line.

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