GEOLOGICAL SURVEY OF CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES, OTTAWA

PAPER 74-19

MC82
.8C21R
74-19 c5

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

ANALYSIS OF ROCKS AND MINERALS USING AN ATOMIC ABSORPTION SPECTROPHOTOMETER

Part 5. An Improved Lithium-Fluoborate Scheme for Fourteen Elements

BIBLIOTHÈQUE
PUBLICATIONS
6 MAI 1974
UNIVERSITÉ LAVAL

SYDNEY ABBEY, NAOMI J. LEE and J.L. BOUVIER

LIBRARY / BIBLIOTHÈQUE
FEB 14 1975
GEOLOGICAL SURVEY
COMMISSION GÉOLOGIQUE

1974

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

GEOLOGICAL SURVEY
PAPER 74-19

ANALYSIS OF ROCKS AND MINERALS USING AN ATOMIC ABSORPTION SPECTROPHOTOMETER

Part 5. An Improved Lithium-Fluoborate Scheme for Fourteen Elements

(Report, 1 figure and 20 tables)

SYDNEY ABBEY, NAOMI J. LEE and J.L. BOUVIER

1974

© Crown Copyrights reserved
Available by mail from *Information Canada*, Ottawa

from the Geological Survey of Canada
601 Booth St., Ottawa

and

Information Canada bookshops in

HALIFAX - 1683 Barrington Street
MONTREAL - 640 St. Catherine Street W.
OTTAWA - 171 Slater Street
TORONTO - 221 Yonge Street
WINNIPEG - 393 Portage Avenue
VANCOUVER - 800 Granville Street

or through your bookseller

Price: $2.00 Catalogue No. M44-74-19

Price subject to change without notice

Information Canada
Ottawa
1974

CONTENTS

	Page
Abstract/ Résumé	iv
Introduction	1
Acknowledgments	1
Apparatus	1
The Goguel burner	2
Colorimetric measurements with an Atomic Absorption Instrument	2
"Standard samples"	3
Decomposition technique	3
Determination of silica	5
Experimental	6
Determination of phosphorus	8
Atomic absorption measurements	9
Determination of magnesium and calcium	9
Determination of sodium and potassium	9
Determination of manganese, chromium and nickel	10
Determination of titanium	10
Determination of barium and strontium	11
The lithium-fluoborate scheme in general	12
Comparison with similar methods	12
Possible further work	19
References	20
Appendix – Operating procedures	23
Special reagents	23
Sample decomposition	24
Solution for Al, Mn, Cr, Ni and approximate Si	24
Solution for Mg, Ca, Na, K and total Fe	24
Solution for Ti	24
Solution for Ba and Sr	24
Atomic absorption measurements	25
Photometric measurements for colorimetry	25
Determination of phosphorus	25
Determination of silica	25
Table 1. "Usable" values for international reference samples	4
2. Effect of time on silicomoybdate absorbance readings	7
3. Recovery of silica	8
4. Effect of titanium and phosphorus on silica results	8
5. Phosphorus recovery in a lithium-fluoborate solution	9
6. Recovery of manganese, chromium and nickel	10
7. Recovery of titanium	11
8. Recovery of barium and strontium	11
9. Operating parameters	13
10. Comparison with other atomic absorption methods – Sample USGS-AGV-1	14
11. Comparison .... – Sample USGS-BCR-1	14
12. Comparison .... – Sample CRPG-BR	15
13. Comparison .... – Sample USGS-DTS-1	15
14. Comparison .... – Sample USGS-G-2	16
15. Comparison .... – Sample CRPG-GA	16
16. Comparison .... – Sample CRPG-GH	17
17. Comparison .... – Sample USGS-GSP-1	17
18. Comparison .... – Sample USGS-PCC-1	18
19. Comparison .... – Sample USGS-W-1	18
20. Deviations from "expected" values	19

Illustration

Figure 1. Outline of lithium-fluoborate analytical scheme for silicate rocks and minerals	12

ABSTRACT

The "lithium-fluoborate" analytical scheme has been extended to cover fourteen elements. In the decomposition technique, fusion in platinum has been replaced by fusion in graphite. Silica determination has been improved by introducing a differential colorimetric procedure. Results obtained by the proposed method on international reference samples are compared with those reported in the literature, where similar methods were used. Possible further extension of the scheme is discussed.

RÉSUMÉ

On a étendu le système d'analyse "fluoborate-lithium" afin d'atteindre quatorze éléments. Dans la technique de décomposition, le creuset de platine servant à la fusion a été remplacé par un creuset de graphite. Le dosage de la silice a été amélioré en se servant d'une procédure de colorimétrie différentielle. On fait la comparaison entre les résultats obtenus avec des échantillons de référence internationaux par la méthode proposée, et avec ceux rapportés dans d'autres travaux où des méthodes similaires ont été utilisées. On discute la possibilité d'autres usages pour ce système.

ANALYSIS OF ROCKS AND MINERALS USING AN ATOMIC ABSORPTION SPECTROPHOTOMETER

PART 5. AN IMPROVED LITHIUM-FLUOBORATE SCHEME FOR FOURTEEN ELEMENTS

INTRODUCTION

Parts 1 and 2 of this series (Abbey, 1967, 1968) described the determination of several major, minor and trace elements by means of atomic absorption measurements, on solutions of rock samples prepared by hydrofluoric-perchloric acid decomposition. Part 3 (Abbey, 1970) introduced the lithium-fluoborate decomposition, and the determination of seven major elements by atomic absorption, in aliquots of the master solution. In Part 4 (Abbey, 1972a), emission methods were favoured for the minor alkali metals, and the words "... AND FLAME EMISSION ..." were added to the title of the series. In the present work, certain improvements are proposed in the lithium-fluoborate decomposition process, aliquots of the master solution are used for atomic absorption measurements on several additional elements, and colorimetric spectrophotometry is recommended for one major and one minor element, determined on aliquots of the same master solution, and using the same instrument (with slight modification). Hence, a further change was required in the title of the series, one reflecting the versatility of the instrumentation.

In the analytical scheme now proposed, the following changes have been made in the lithium-fluoborate scheme:

(1) Fusion of the sample in platinum is replaced by fusion in graphite.
(2) Silica is determined by differential colorimetry of the betamolybdosilicic acid complex.
(3) Manganese, chromium and nickel (where the latter two are present in greater than trace amounts) are determined by atomic absorption on the same aliquot as originally prepared for the determination of aluminum.
(4) Titanium is determined on an undiluted aliquot of the master solution, to which aluminum chloride is added to enhance the atomic absorption signal.
(5) Phosphorus is determined on another aliquot by conventional colorimetric spectrophotometry of a molybdenum blue complex.
(6) Barium and strontium (where present in greater than trace amounts) are determined by atomic absorption on a separate, undiluted aliquot, to which sodium chloride is added to suppress ionization in the nitrous-oxide-acetylene flame.

If the proposed scheme is combined with the automatic titration methods for ferrous iron, carbon dioxide, total carbon and total sulphur (Bouvier et al., 1972), a new general system of silicate analysis becomes possible. Such a system could yield precision and accuracy comparable to those of conventional methods (e.g. Maxwell, 1968, p. 536-539), for most elements, combined with simplicity comparable to so-called "rapid methods" (e.g. Maxwell, 1968, p. 540-543). Determination of "combined water" is the only normal component of silicate analysis not included in the proposed system, but work is now underway on a possible application of the Karl Fischer titration for that purpose.

Acknowledgments

The authors are indebted to Reiner Goguel (Department of Scientific and Industrial Research, Wellington, New Zealand) for providing working drawings of his water-cooled modified ridge-slot burner; to D.P. Sandoz (Varian-Techtron) for suggestions regarding cell corrections in spectrophotometric measurements; and to G.E.M. Aslin for critical reading of the manuscript.

APPARATUS

The instrument used, originally a Techtron AA-3 Atomic Absorption Spectrophotometer, has undergone considerable modification in this and earlier work, including:

(a) replacement of the original Techtron Gas Control Unit by the gas regulator unit from a Beckman Model 9200 Flame Photometry Accessory (to which a Techtron change-over valve was added for use with nitrous oxide);

Original manuscript submitted: November 26, 1973
Final version approved for publication: December 13, 1973

(b) replacement of the original Techtron glass spray chamber and burner mount with the Teflon chamber and more flexible burner mount normally supplied with the Techtron AA-5 instrument;
(c) introduction of a Goguel-type water-cooled ridge-slot burner head (details discussed below);
(d) installation of a Techtron burner shield and automatic flame igniter;
(e) adaptation of the absorption cell housing of a Beckman Model DU spectrophotometer for use on the Techtron instrument (details discussed below);
(f) replacement of the original Techtron readout and scale-expansion units with the corresponding module of the Techtron AA-5 instrument (including modification of the hollow-cathode power supply to provide 285-Hz modulation);
(g) addition of a Techtron beam-chopper and six-speed wavelength scanner, for emission measurements (not used in the work described in this paper); and
(h) addition of a Photovolt Varicord 43 recorder.

ASL-Techtron shielded hollow-cathode lamps were used for most measurements; similar Westinghouse lamps were used in some cases.

Some colorimetric measurements were also made with a Beckman Model B spectrophotometer.

For fusions in graphite, the crucibles were of a type commonly used for lithium tetraborate fusions in preparing samples for analysis by X-ray fluorescence or optical emission spectroscopy. Both Met Bay 1290 crucibles, made of high-purity graphite MB-100, and Ultra Carbon C-682-IB crucibles, made of UF 4S high-purity graphite, gave satisfactory results. In the former case, an inverted crucible of the same type was used as a cover during fusion; in the latter case, the cover was an Ultra Carbon A-6206 disc, also of UF 4S graphite.

The Goguel Burner

Goguel (1970, 1971a) reported on studies regarding the effect of burner head geometry on atomic absorption measurements. For the nitrous-oxide-acetylene flame (particularly for silicon determination), he recommended a ridge-slot titanium burner head, with slight tapers at the bottom and top of the slot, and provision for water-cooling. In the present work, the stainless steel top was removed from an old Techtron AB-40 head, and replaced with a new titanium top, machined to Goguel's specifications except where changes were required to fit the Techtron base instead of the Perkin-Elmer base used by Goguel. Goguel recommended that the cooling water be circulated from a reservoir, thermostatically controlled at 60°C. In this work, the reservoir was a 4-litre bottle, with no thermostat.

Among the advantages claimed for the Goguel burner was the more rapid attainment of a stable temperature in the burner head, resulting in more stable atomic absorption signals. That effect was observed in this work, but it did not result in significant improvement in the silica determination. However, the Goguel burner has proved to be useful in nearly all flame modes of operation. Although the slot length is only about 7.4 cm, sensitivities with the air-acetylene flame (both in absorption and emission) have been found to be essentially the same as with a conventional 10-cm slot. With the nitrous-oxide acetylene flame, sensitivities are equal or superior to those obtained with the more usual 5- or 6-cm slot. A marginal advantage is the fact that the burner head never becomes too hot to touch with the bare hand, thus simplifying removal for cleaning.

Colorimetric Measurements with an Atomic Absorption Instrument

Optical absorption spectrophotometry ("colorimetry"), flame emission spectrometry ("flame photometry") and atomic absorption spectrometry were developed separately as analytical tools, historically in the order mentioned. Instruments were designed specifically for use with one or another of those techniques. However, as more and more applications appeared it became increasingly evident that the ideal instrument would take advantage of the common components of the three schemes mentioned (and subsequently, of atomic fluorescence as well). Thus instruments designed for both colorimetry and flame photometry have been in use for some time. More recently, new commercial instruments for atomic absorption have been designed to be easily convertible for use in flame emission and atomic fluorescence.

If the burner of an atomic absorption spectrophotometer is replaced by an absorption-cell holder, the instrument becomes a spectrophotometer in the "colorimetric" sense, with the following advantages over a conventional spectrophotometer.

(1) Reproducibility of wavelength settings is much more certain with the discrete spectrum lines emitted by a hollow-cathode lamp than it is with a continuum source.
(2) Daylight or 60-Hz artificial room light do not interfere because the readout system responds only to the modulation frequency of the hollow-cathode lamp. There is no need for a light-tight cell housing.
(3) The controls available in the readout system of most modern atomic absorption instruments

(e.g. continuously variable gain, scale expansion, backing, damping, etc.) facilitate measurements by the differential technique (e.g. Meehan, 1964), where strongly absorbing solutions are used.

Possible disadvantages are as follows:

(1) The intensity of emission of a hollow-cathode lamp may not be quite as steady as that of a good continuum source.
(2) It may not always be possible to find a line at a suitable wavelength in the emission spectrum of available hollow-cathode lamps.

Hildon (1971), one of the first to adapt an atomic absorption instrument to colorimetry, used a vanadium hollow-cathode lamp to determine titanium as the hydrogen peroxide complex. Similarly, McKenzie (1972) determined manganese as the permanganate ion, using a continuum source, with a mechanical chopper to provide modulation. Thus McKenzie failed to use the wavelength precision of a line source, although he did suggest using a hollow-cathode source for work in the ultraviolet. Neither Hildon nor McKenzie used a differential colorimetry technique.

In this work, the burner head was removed from its mounting and the vertical adjustment mechanism retracted to its lowest position. A brass collar was attached to the bottom of the long-cell housing of a Beckman Model DU spectrophotometer, and the modified unit mounted on the burner mount of the atomic absorption instrument. The entire assembly was moved along the optical bar of the instrument to the point where the light from the source was focussed on the absorption cells in their holder. After rotational adjustment of the cell housing to give maximum light transmission, the housing was fixed in position by means of a set screw.

"STANDARD SAMPLES"

The use of international reference samples for calibration was introduced with the lithium-fluoborate scheme (Abbey, 1970). Advantages in the use of such samples include a reduction in the total number of standard solutions required, and the fact that knowns and unknowns are of similar composition and undergo identical chemical treatment. In developmental work, solutions prepared from samples of known composition are useful not only in studies of precision and accuracy, but also in checking for interferences.

Earlier work (Abbey, 1970) involved the use of six samples from the U.S. Geological Survey and three from the French Centre de Recherches Pétrographiques et Géochimiques. More recent studies (Abbey, 1972b, 1973) suggest that a number of additional samples can be used, but those listed in Table 1 are considered the best established. Compositional gaps can be bridged by using blends of solutions of two different reference samples. Similarly, the concentration range for any element can be extended upward by adding small amounts of a standard solution of that element to an aliquot of the solution of a reference sample, or downward by blending with a blank.

Because some of the samples listed in Table 1 are no longer available, it may be necessary to use additional "standard" samples (cf. Abbey, 1973). Details are given in the reference quoted.

DECOMPOSITION TECHNIQUE

In Part 3 of this series (Abbey, 1970), the sample was fused with a five-fold excess of lithium metaborate in a platinum crucible. Although the hot crucible was quenched in cold water to shatter the solidified fusion, the latter took the form of a paint-like coating on the inner surface of the crucible. Disintegration by magnetic stirring in an approximately 1.7 M solution of hydrofluoric acid was often a slow, tedious process, and it was sometimes difficult to tell when the disintegration was complete. Further, repeated quenching of hot platinum crucibles in a shallow pool of water caused considerable distortion of the crucibles.

Suhr and Ingamells (1966), and Van Loon and Parissis (1969) recommended that lithium metaborate fusions be done in graphite crucibles. If the crucible is pre-ignited and the resulting graphite dust on the inner surfaces left undisturbed, the subsequent lithium metaborate fusion will form a bead, which can readily be poured from the crucible, leaving little or no residual material. In the procedure now proposed, the molten bead is poured into about 40 ml of water, and the resulting shattered flakes are more readily attacked by dilute hydrofluoric acid.

In the scheme previously used (and also in some work with fusions performed in graphite crucibles), the disintegration of the solidified fusion was done by stirring with dilute hydrofluoric acid in a polypropylene beaker, with a loosely-fitting plastic watch-glass. Because of evidence of a small but significant possible loss of silicon as the volatile tetrafluoride during the disintegration step, it was decided to replace the polypropylene beaker with a screw-capped jar, made of transparent polymethylpentene. Possible volatilization when the jar is opened for the boric acid addition is minimized by chilling the jar and its contents in a refrigerator. Disintegration of the fusion is more rapid than it was with the fusions in platinum, but samples containing high concentrations of magnesium or calcium still require relatively long stirring periods.

Table 1

"Usable" Values for International Reference Samples
(per cent, dry basis)
(Ref. Abbey, 1973)

SiO_2	Sample	Al_2O_3	Sample	Fe_2O_3T	Sample	MgO	Sample
75.85	CRPG-GH	20.5	NBS-99A	13.52	USGS-BCR-1	49.83	USGS-DTS-1
69.96	CRPG-GA	19.8	BCS-375	12.98	CRPG-BR	43.63	USGS-PCC-1
69.19	USGS-G-2	17.9	NBS-70a	11.11	USGS-W-1	13.35	CRPG-BR
67.31	USGS-GSP-1	17.7	BCS-376	8.60	USGS-DTS-1	6.63	USGS-W-1
67.1	NBS-70a	17.22	USGS-AGV-1	8.28	USGS-PCC-1	3.49	USGS-BCR-1
67.1	BCS-375	15.35	USGS-G-2	6.84	USGS-AGV-1	1.55	USGS-AGV-1
67.1	BCS-376	15.19	USGS-GSP-1	4.33	USGS-GSP-1	0.96	USGS-GSP-1
65.2	NBS-99a	14.87	USGS-W-1	2.86	CRPG-GA	0.95	CRPG-GA
59.72	USGS-AGV-1	14.51	CRPG-GA	2.67	USGS-G-2	0.77	USGS-G-2
54.85	USGS-BCR-1	13.68	USGS-BCR-1	1.33	CRPG-GH	0.05	BCS-375
52.72	USGS-W-1	12.51	CRPG-GH	0.12	BCS-375	0.03	CRPG-GH
42.15	USGS-PCC-1	10.25	CRPG-BR	0.10	BCS-376	0.03	BCS-376
40.68	USGS-DTS-1	0.73	USGS-PCC-1	0.08	NBS-70a	0.02	NBS-99a
38.39	CRPG-BR	0.29	USGS-DTS-1	0.06	NBS-99a		

CaO	Sample	Na_2O	Sample	K_2O	Sample	TiO_2	Sample
13.87	CRPG-BR	10.4	BCS-375	11.8	NBS-70a	2.61	CRPG-BR
10.98	USGS-W-1	6.2	NBS-99a	11.2	BCS-376	2.22	USGS-BCR-1
6.98	USGS-BCR-1	4.31	USGS-AGV-1	5.53	USGS-GSP-1	1.07	USGS-W-1
5.00	USGS-AGV-1	4.06	USGS-G-2	5.2	NBS-99a	1.05	USGS-AGV-1
2.45	CRPG-GA	3.85	CRPG-GH	4.76	CRPG-GH	0.66	USGS-GSP-1
2.14	NBS-99a	3.55	CRPG-GA	4.50	USGS-G-2	0.50	USGS-G-2
2.02	USGS-GSP-1	3.29	USGS-BCR-1	4.03	CRPG-GA	0.38	CRPG-GA
1.98	USGS-G-2	3.07	CRPG-BR	2.93	USGS-AGV-1	0.38	BCS-375
0.89	BCS-375	2.83	BCS-376	1.68	USGS-BCR-1	0.08	CRPG-GH
0.69	CRPG-GH	2.80	USGS-GSP-1	1.41	CRPG-BR	0.01	USGS-DTS-1
0.54	BCS-376	2.55	NBS-70a	0.78	BCS-375	0.01	USGS-PCC-1
0.53	USGS-PCC-1	2.15	USGS-W-1	0.64	USGS-W-1	0.01	NBS-70a
0.15	USGS-DTS-1	0.01	USGS-DTS-1			0.01	NBS-99a
0.11	NBS-70a	0.01	USGS-PCC-1			0.01	BCS-376

MnO	Sample	BaO	Sample	SrO	Sample	P_2O_5	Sample
0.20	CRPG-BR	0.26	NBS-99a	0.16	CRPG-BR	1.05	CRPG-BR
0.19	USGS-BCR-1	0.21	USGS-G-2	0.08	USGS-AGV-1	0.50	USGS-AGV-1
0.17	USGS-W-1	0.15	USGS-GSP-1	0.06	USGS-G-2	0.33	USGS-BCR-1
0.12	USGS-PCC-1	0.14	USGS-AGV-1	0.04	USGS-BCR-1	0.28	USGS-GSP-1
0.11	USGS-DTS-1	0.11	CRPG-BR	0.04	CRPG-GA	0.14	USGS-G-2
0.10	USGS-AGV-1	0.10	CRPG-GA	0.03	USGS-GSP-1	0.14	USGS-W-1
0.09	CRPG-GA	0.08	USGS-BCR-1	0.02	USGS-W-1	0.12	CRPG-GA
0.05	CRPG-GH	0.02	USGS-W-1			0.01	CRPG-GH
0.04	USGS-G-2	0.02	NBS-70a				
0.04	USGS-GSP-1						

Cr_2O_3	Sample	NiO	Sample
0.64	USGS-DTS-1	0.32	USGS-PCC-1
0.44	USGS-PCC-1	0.31	USGS-DTS-1
0.06	CRPG-BR	0.03	CRPG-BR
0.02	USGS-W-1	0.01	USGS-W-1

Notes

BCS	British Chemical Standards
CRPG	Centre de Recherches Pétrographiques et Géochimiques
Fe_2O_3T	Total iron, expressed as Fe_2O_3
NBS	National Bureau of Standards
USGS	United States Geological Survey

After the addition of boric acid to complex excess fluoride and to dissolve precipitated fluorides, the resulting solution inevitably contains some suspended graphite. That can easily be removed by filtration through an open-textured paper, although the presence of graphite may be harmless for some purposes.

The solidified material after fusion in platinum was generally colourless, a slight yellow tint appearing where the sample contained more chromium than usual. The same yellow tint was evident in the final solution, probably being caused by the presence of chromate ions. Varying iron content produced no colour effect in the final solution, probably because ferric iron was complexed as the fluo-anion.

The beads from fusion in graphite show an increasing green coloration with increasing iron content, but the final fluoborate solutions are colourless, regardless of their chromium or iron contents. Evidently fusion in a covered graphite crucible provides sufficiently reducing conditions to keep both iron and chromium in their lower oxidation states. The change in oxidation state of iron and chromium shows no apparent effect on the atomic absorption sensitivities of those elements, nor on any interferences in the determination of the other elements.

DETERMINATION OF SILICA

Silica results obtained by atomic absorption measurements in a fluoborate solution are not sufficiently consistent for precise work (Abbey, 1970). After some attempts at improving reliability by changing to the Goguel burner and by using synthetic standard solutions, it was concluded that atomic absorption was not really suitable for the precise determination of a constituent which is present at such high concentration levels.

Colorimetric determination of silica is commonly used in "rapid" schemes of rock analysis, generally by means of a molybdenum blue reaction (e.g. Shapiro, 1967). The silicomolybdate yellow reaction is less frequently used in silicate analysis, although it has the advantage of being less sensitive, and is therefore applicable to larger sample aliquots. In a detailed study of the reactions involved, Strickland (1952) found the system to be complicated not only by the variety of monomeric and polymeric forms in which both silicate and molybdate anions can exist, but also by the existence of at least two forms of the silicomolybdate complex. The form which Strickland designated as "beta" apparently results on initial mixing of silicate and molybdate (under suitable conditions), but then the complex slowly changes to the "alpha" form, which is more stable. The relative sensitivities of the two forms (in terms of silica determination) vary with wavelength. Heating accelerates the conversion from beta to alpha form.

Ringbom et al. (1959) studied the effect of pH and adjusted conditions to favour the alpha form, probably because of its superior stability. Bloxam (1961) favoured a more restricted pH range and investigated interference effects from phosphorus. Bennett et al. (1962) applied the beta form for rapid routine control analysis of ceramic materials. Govett (1961) suggested that too much attention had been focussed on the pH of the final mixture, and not enough on such factors as the ionic state of the molybdenum in the reagent, the nature of the free acid present, the relative concentrations of free acid and free molybdate, etc. He recommended the addition of sodium hydroxide to the ammonium molybdate solution in order to stabilize the anion (presumably in the form of $MoO_4^{=}$), and the use of a controlled concentration of free sulphuric acid.

Although there were differences in details of the analytical procedures in the above applications, all involved decomposition of silicate samples by fusion with sodium hydroxide, followed by acidification. In the resulting solutions the silica likely existed as monomeric silicic acid. However, Langmyhr and Graff (1965) showed that molybdate will react with silica when the latter is present as fluo-silicic acid. In that case, the sample was decomposed by hydrofluoric acid under pressure, and the excess fluoride masked by the addition of aluminum. Possible interferences were eliminated by measuring absorbance against a blank solution of the same sample, from which silica had been volatilized with hydrofluoric acid.

Although many applications of the silicomolybdate reaction to the determination of major amounts of silica have appeared in the literature, no one, to our knowledge, has used differential spectrophotometry. In that technique, improved precision is possible by the measurement of the small difference in absorbance between a standard and the sample, rather than measurement of the sample absorbance relative to clear solvent or a blank. Meehan (1964) pointed out the factors that limit the potential increase in precision, but some of those limitations are minimized when a modified atomic absorption instrument is used instead of a conventional spectrophotometer. The light flux reaching the detector can be increased, either by increasing the current in the hollow-cathode lamp to the permissible maximum, or by widening the spectrometer slits to a maximum, with little loss in spectral selectivity. Increased amplifier gain and scale expansion can also be used, up to a point where damping can no longer overcome the increase in noise.

Experimental

Although Govett's (1961) technique was intended for use with small amounts of silica, it was decided to apply a modified version of his procedure to determine the major amounts of silica in fluoborate solutions of silicate rocks. As experimental work progressed, changes were made in details of the technique, as follows:

(a) Sample size

Initial tests with aliquots of the master solution containing 10 mg of sample gave some satisfactory results, but in general, it was found that the high absorbances involved resulted in too much noise in the highly amplified recorded signal. The aliquot was therefore reduced to half the former size.

(b) Volatilization losses

As pointed out above under "Decomposition Technique", possible loss of silica by volatization was reduced by doing the hydrofluoric digestion in a tightly capped plastic jar, and by chilling before opening the jar for the addition of boric acid.

(c) Contamination from glass

According to Bernas (1968), master solutions containing the appropriate concentrations of hydrofluoric and boric acids are inert toward glass for up to two hours. However, when the silica in a small aliquot reacts with molybdate, a corresponding quantity of free fluoride ion is released. Such fluoride could react with the glass of the volumetric flask or of the absorption cell, unless a sufficient excess of boric acid is present to prevent such action. To overcome this possible effect, the reaction of silicate and molybdate is carried out in a polyethylene bottle, and a large excess of boric acid is added to prevent reaction of the liberated fluoride with the glass walls of the absorption cell.

(d) Standard solutions

In the determination of most other elements, calibration is based on solutions of international reference samples. The slight uncertainty in the assigned values of the concentrations of most elements in such samples is not sufficient to cause significant errors, particularly where a calibration curve is drawn with four or more "standards". In the differential colorimetric determination of silica, however, it is more convenient to interpolate the readings on an unknown between two "bracketing" standards. Slight errors in the preparation of the master solution of a reference sample, which would normally be insignificant in determining other elements, could have more noticeable effect in determining silica. It was therefore decided to prepare a series of standard solutions of silica, from pure anhydrous material, and containing the same concentrations of lithium, borate and fluoride as in the sample solutions. These standards are used for the precise determination of silica, but solutions of the reference samples can still be used to obtain a first approximation on an unknown by atomic absorption, and hence to determine which standards to use for the final determination. Alternatively, a first approximation of the silica content can be found by difference, if all other elements are determined before silica.

(e) Colour stability

According to Ringbom et al. (1959), the spectral absorption curves of the beta and alpha forms of silicomolybdic acid intersect at about 330 nm. Thus absorbance measurements at that wavelength should remain unchanged with time, as the beta acid slowly changes to the alpha form. There are, however, several disadvantages in measuring absorbances at that wavelength. The most serious is that sensitivity is much too high for measurement by the differential technique. Secondly, other components of the solution are likely to show measurable absorbance.

The wavelength selected in this work is that of the iron line at 404.6 nm, which has a strong emission from an iron hollow-cathode lamp, when the latter is run at double the current ordinarily used for determination of iron by atomic absorption. At that wavelength, there is a slow change of absorbance with time, so measurements must be made on a rigorous time basis. The actual time at which absorbance is measured is not critical (15-25 minutes after mixing), provided sample and standards are measured after the same time interval. Table 2 shows the variation of absorbance with time, for three different samples. All were measured relative to a strongly-absorbing null.

(f) Photometric technique

The simplest technique for differential photometric measurements would involve the use of three absorption cells. The first cell would contain a standard solution with a slightly lower concentration of the analyte than expected in the sample; the second would contain the sample solution; and the third would contain another standard solution, slightly higher in analyte concentration than that in the sample. The spectrophotometer would be adjusted to read zero absorbance (or a small positive absorbance) on the "low" standard, and "relative" absorbance measurements would be made on the unknown and the "high" standard. Assuming Beer's Law to apply over the short concentration interval between the two standards, the concentration of the unknown could be calculated by linear interpolation of absorbances.

Table 2

Effect of Time on Silicomolybdate Absorbance Readings

Minutes after mixing	Absorbance		
	Sample 1	Sample 2	Sample 3
10	0.144	0.266	0.320
15	.137	.262	.315
20	.134	.257	.309
25	.129	.250	.305
30	.126	.248	.303
35	.121	.243	.294
40	.120	.241	.294
45	.115	.238	.287
50	.112	.235	.285

Slight differences in the absorption characteristics of individual cells are the main reason why the above technique is not suitable for high-precision differential measurements. In ordinary photometric measurements, "cell corrections" are derived by measuring absorbances with all cells filled with water. However, D.P. Sandoz has told us that such corrections are insufficient in measuring strongly-absorbing solutions. Differences between absorption cells can be traced to three causes:

(1) inadequate cleaning – therefore variable, and dependent on handling;
(2) optical imperfections in the glass – therefore constant, and easily allowed for by measurements with clear solvent; and
(3) differences in absorption-path length – therefore constant, but not eliminated by cell-correction measurements with a non-absorbing solvent.

Clearly, item (3) is a much more serious consideration in the differential measurement of highly-absorbing solutions than in conventional photometry of slightly-absorbing solutions. Item (1) suggests that for high-precision measurements, all cleaning procedures must be rigorous and consistent.

From the above considerations, it was concluded that optimum conditions would be attained if the absorbance of the sample solution were compared to those of bracketing standards in the same cell, and if the cell were subjected to a consistent cleaning treatment before each measurement. Because photometric measurements cannot be made on standards and samples at the same time, all measurements must be made against a stable, strongly-absorbing reference solution. In this case, solutions of potassium chromate were selected because their absorption characteristics are similar to those of silicomolybdic acid, except that they do not change with time.

The procedure finally adopted is designed to handle three samples simultaneously, the only limitation being that their concentrations must be sufficiently close together that they can be bracketed between standards over a range of not more than 15 per cent silica. The standard solutions are prepared at intervals equivalent to 5 per cent silica. The four absorption cells are individually identified and each is always oriented in the same direction, in the same position in the cell-holder.

The chemical preparations are first made for three solutions, representing the "low standards" for the three unknowns (L1, L2, L3). (These may differ, depending on the samples, by the equivalent of 0, 5 or 10 per cent silica. They should be arranged in ascending order of silica content.) The absorption cells are cleaned by a standardized procedure, and filled as follows:

Cell A: a chromate solution whose absorbance is close to (preferably slightly less than) that of L1,
Cell B: L1,
Cell C: L2, and
Cell D: L3.

The cells are placed in the spectrophotometer and the readout adjusted to give a transmittance of about 95 per cent for the lowest absorbing solution (generally the chromate, but sometimes L1). Experience has shown that all of these manipulations can be made in an interval of less than 15 minutes after mixing. A 20-minute interval may be used, but it must be the same for all sets of measurements for the group of three samples. Transmittance readings are then taken (preferably on a recorder) for all of the cells, in the sequence A-B-C-D-D-C-B-A. In measuring small absorbance differences, there is an advantage in using transmittance, rather than absorbance readings. The readout meter scale represents 0.0 to 100.0 per cent transmittance, or 0.000 to 1.000 absorbance. At the high-transmittance (low-absorbance) end of the scale, one unit in transmittance is equivalent to less than one half unit in absorbance. Thus transmittance readings are, in effect, equivalent to non-linearly scale-expanded absorbance readings. Such readings tend to be less noisy than those obtained by electronic scale expansion.

After the transmittance measurements have been made, the cells are emptied, rinsed and left immersed in water. The chemical preparations are then made for three solutions, representing the three unknowns (X1, X2, X3). The cells are cleaned by the same procedure as used for the readings on the low standards, and filled as follows:

Cell A: the same chromate solution as in the first set,
Cell B: X1,
Cell C: X2, and
Cell D: X3.

Transmittance readings are taken exactly as before, without changing any of the settings on the instrument.

Finally, the entire cycle is repeated for the three "high standards" (H1, H2, H3), the cells containing:

Cell A: the same chromate solution as before,
Cell B: H1,
Cell C: H2, and
Cell D: H3.

All transmittance readings are converted to absorbances (to four decimal places). The "net absorbance" is determined for each solution by subtracting the absorbance of the chromate solution from the same run. Finally, the concentration of each unknown is determined by interpolating net absorbance between those of the corresponding solutions, measured in the same absorption cell.

(g) Recoveries and interferences

Thirteen of the fourteen international reference samples listed in Table 1 were taken through the analytical procedure. Silica results are given in Table 3. With the exception of the abnormally high result for CRPG-BR, all "found" values are in acceptable agreement with the "expected".

Table 3
Recovery of Silica

Sample No.	SiO_2, per cent (dry basis) Expected*	Found
CRPG-GH	75.85	75.87
CRPG-GA	69.96	70.02
USGS-G-2	69.19	69.24
USGS-GSP-1	67.31	67.42
NBS-70a	67.1	67.05
BCS-375	67.1	67.02
NBS-99a	65.2	65.08
USGS-AGV-1	59.72	59.74
USGS-BCR-1	54.85	54.82
USGS-W-1	52.72	52.40
USGS-PCC-1	42.15	42.00
USGS-DTS-1	40.68	40.62
CRPG-BR	38.39	39.10

*Ref. Abbey (1973)

CRPG-BR differs from the other samples in that it contains much higher concentrations of titanium and phosphorus, two elements mentioned by Shell (1962) as possible interferences in the determination of silica as the silicomolybdate. Attempts were therefore made to establish correction factors for both interfering elements, but results were erratic. Addition of titanium and phosphorus to the standard solutions, in amounts approximating those in the sample, proved more satisfactory, as shown in Table 4. It appears that both elements cause some interference, but that the effects are not additive. Further evidence that the interference may be due to an interaction between the titanium and phosphorus is indicated by sample USGS-BCR-1, where the titanium content is almost as high as that of CRPG-BR, but the phosphorus content is much lower, and no interference was observed in the silica determination.

Arbitrarily, it appears that significant interference occurs only when the titanium dioxide content exceeds 2.5 per cent and the phosphorus pentoxide exceeds one per cent. In such cases, both interfering elements should be added in appropriate amounts to the standard solutions. Where the possibility of interference is uncertain, addition of the interfering elements to the standards is advisable. In any event, the silica determination should not be done before titanium and phosphorus have both been determined.

Table 4
Effect of Titanium and Phosphorus on Silica Results

(Sample CRPG-BR)

SiO_2 expected, per cent	38.39
Found, no additives in standards	39.10
Found, Ti added to standards	39.03
Found, P added to standards	38.89
Found, Ti and P added to standards	38.33

DETERMINATION OF PHOSPHORUS

Phosphorus determination by an established molybdenum-blue procedure (Maxwell, 1968, p. 394-396) was found to work well on aliquots of the lithium-fluoborate master solution. In Table 5, results for some of the samples were obtained by using the other samples as standards; for the other samples, a standard solution, prepared from ammonium phosphate, was used. In the latter case, a blank solution, containing the same concentrations of lithium, fluoride and borate as present in the sample aliquots, was added to the standard. For photometric measurements, the light source was an argon line at 826.5 nm, emitted by an argon-filled cesium hollow-cathode lamp with a glass end-window; the detector was a red-sensitive photomultiplier tube.

Table 5
Phosphorus Recovery in a
Lithium-Fluoborate Solution

Sample No.	P_2O_5, per cent, dry basis Expected*	Found
CRPG-BR	1.05	1.01
USGS-AGV-1	0.49	0.47
USGS-BCR-1	0.33	0.34
USGS-GSP-1	0.28	0.26
USGS-G-2	0.14	0.14
CRPG-GA	0.12	0.12
CRPG-GH	0.01	0.02

*Ref. Abbey (1973)

ATOMIC ABSORPTION MEASUREMENTS

In Part 3 (Abbey, 1970), determinations were done by interpolation between bracketing standards. That procedure is now changed as follows: after the first approximation of the concentration is found by comparison to any convenient standard, the samples are arranged in descending order of apparent concentration of the desired element. A group of at least four standards is selected, such that the concentration of the desired element in the lowest standard is lower than that in the sample with the lowest concentration, and similarly for the highest standard. Atomic absorption readings are then taken for both standards and samples, grouped together in descending order of concentration, and repeated in ascending order. Where readings are not sufficiently consistent, the entire cycle is repeated. For each set of readings in either direction, a curve of absorbance vs concentration is plotted from the readings on the standards (or, where possible, the best straight line is calculated), and results for the samples derived from the calibration for that set of readings. Final results are based on averaging two or more calculated values for each element in each sample.

Advantages of this measuring technique are that errors in the standards are "smoothed out" in plotting the curve, and instrumental drift is essentially compensated for by measuring samples and standards at the same time.

Where new hollow-cathode lamps are used operating currents and other parameters have been changed from those listed previously. The values used are generally those recommended by the manufacturer of the instrument, except where changes were necessary (as indicated for specific elements below).

The water-cooled Goguel burner was found suitable for all atomic absorption measurements, both with air and with nitrous oxide.

DETERMINATION OF MAGNESIUM AND CALCIUM

In Part 3 (Abbey, 1970) three different sample concentrations were recommended for magnesium determination, depending on the magnesium content. It has now been found possible to determine magnesium at levels as high as 50 per cent MgO, by using the nitrous-oxide flame and rotating the burner head at higher concentrations, without changing the aliquot size. Although most elements are more sensitive in the nitrous oxide flame, the reverse is true with magnesium. Addition of varying amounts of strontium (up to a 100-fold excess) was found to have no significant effect on the atomic absorption signal of magnesium, suggesting that ionization interference is not the cause. Woodward (1971) listed approximate percentages of ionization for 47 elements in both air-acetylene and nitrous-oxide-acetylene flames, but his list did not include magnesium.

With calcium, use of the larger sample aliquot suggested in Part 3 is generally not necessary. Using the air-supported flame at higher concentrations and that with nitrous oxide at lower concentrations, it is possible to determine calcium, over the entire range usually found in silicate rocks, in an aliquot containing 10 mg of sample in 100 ml.

DETERMINATION OF SODIUM AND POTASSIUM

The manufacturer's instructions for sodium determination with the combined sodium-potassium lamp call for a spectral bandpass of 6.6A (0.66 nm, or a slit width of 200 microns). Those conditions were found to allow too much light to reach the photomultiplier, the transmittance readout going off-scale at the lowest amplification. The spectral bandpass was therefore reduced to one quarter of that specified. Alternatively, the lamp current could have been reduced, although the very low current then required might have impaired the stability of the light emission.

Use of a more concentrated sample solution was recommended previously (Abbey, 1970) for determining relatively small concentrations of potassium. It now appears that the absorption sensitivity for potassium was limited by second-order interference from an argon line, originating in the filler gas of an old potassium hollow-cathode lamp. With the newer combined sodium-potassium lamp, which is helium-filled, potassium can be determined over the whole normal range on the aliquot containing 10 mg of sample per 100 ml of solution.

Table 6

Recovery of Manganese, Chromium and Nickel

Sample No.	Per cent, dry basis					
	MnO		Cr_2O_3		NiO	
	Expected*	Found	Expected	Found	Expected	Found
CRPG-BR	0.20	0.20	0.06	0.06	0.03	0.03
USGS-BCR-1	0.19	0.19				
USGS-PCC-1	0.12	0.12	0.44	0.43	0.32	0.32
USGS-DTS-1	0.11	0.13	0.64	0.64	0.31	0.31
USGS-AGV-1	0.10	0.10				
CRPG-GA	0.09	0.09				
CRPG-GH	0.04	0.04				
USGS-GSP-1	0.04	0.05				

*Ref. Abbey (1973)

DETERMINATION OF MANGANESE, CHROMIUM AND NICKEL

For each of these elements, the sample aliquots containing 50 mg of sample per 100 ml of solution for all available reference samples, were arranged in descending order of concentration of the desired element. Atomic absorption measurements were made for each sample, and the resulting absorbances plotted against the known concentrations. In all cases, either a straight line or a smooth curve was obtained, indicating that the element can be determined with no interference from any other element, at least in the concentration ranges covered by the available reference samples.

With chromium and nickel, the procedure proposed in this work is suitable only where those elements are present in more than traces (e.g. in ultrabasic rocks). Table 6 reports results on some reference samples.

DETERMINATION OF TITANIUM

In an addendum to Part 3 (Abbey, 1970), it was reported that the more concentrated sample aliquot, containing 50 mg of sample per 100 ml of solution, was still insufficiently concentrated for determination of titanium. It was therefore recommended that silicon, boron and fluorine be eliminated from a suitable aliquot by fuming with sulphuric acid, and titanium then be determined colorimetrically with Tiron (cf. Maxwell, 1968, p. 382-383). Results, while generally satisfactory, tended to run somewhat low. If the negative bias was caused by incomplete removal of fluoride, that effect could probably have been eliminated, if the solution had been fumed to dryness and then fused with potassium pyrosulphate. Attempts at determining titanium colorimetrically without separating boron and fluorine were unsuccessful.

Bernas (1968) and Langmyhr and Paus (1968) reported the determination of titanium by atomic absorption in fluoborate solutions. Bernas found no interferences, but Langmyhr and Paus observed that aluminum enhanced the titanium absorption, as was also reported by Van Loon and Parissis (1969), who used a solution prepared by dissolving a lithium metaborate fusion in nitric acid. In both cases, the effect reached a "plateau" at higher levels of aluminum concentration. Addition of excess aluminum could therefore overcome the interference.

The aluminum enhancement effect on titanium absorption was observed in this work when readings were taken on the undiluted master solution. Results were erratic, tending to increase with the aluminum content of the sample.

Addition of aluminum to bring all samples to a level equivalent to 20 per cent aluminum oxide proved ineffective. Increasing amounts of aluminum were then tried until a concentration was found at which the titanium absorbance of a sample becomes essentially constant. It appeared that the interference could thus be overcome by adding 2 mg of aluminum (as neutral aluminum nitrate solution) to 10 ml of the undiluted sample solution. However, the manufacturers of the instrument (Varian-Techtron, 1972) recommend about five times that concentration of aluminum,

in hydrochloric acid, without specifying acid concentration. Van Loon and Parissis (1969) also favoured the higher aluminum concentration, and a final acidity of 4 M.

In this work, it was not possible to bring the acidity to 4 M without excessively diluting the sample with hydrochloric acid. It is possible that Van Loon and Parissis favoured the high acidity to prevent hydrolysis of titanium, a hazard which does not apply in a fluoborate solution.

In the procedure finally adopted in this work, 10 mg of aluminum are added (as 1 ml of an aluminum chloride solution, approximately 1 M in hydrochloric acid) to 10 ml of the undiluted sample solutions. In such solutions, the titanium absorption signal was between five and ten per cent stronger than in solutions where only 2 mg of aluminum were added as the neutral nitrate. Scale expansion (ca 3-5X) was required.

Results obtained on some reference samples are given in Table 7. The results show no suggestion of ionization interference, although Woodward (1971) reported that titanium may be as much as 12 per cent ionized in a nitrous oxide-acetylene flame. Presumably the concentration of lithium derived from the fusion flux (about 650 micrograms per ml) was sufficient to suppress any titanium ionization.

Table 7
Recovery of Titanium

Sample No.	TiO_2, per cent, dry basis	
	Expected*	Found
CRPG-BR	2.61	2.57
USGS-BCR-1	2.22	2.28
USGS-AGV-1	1.05	1.11
USGS-GSP-1	0.66	0.66
USGS-G-2	0.50	0.46
CRPG-GA	0.38	0.38
CRPG-GH	0.08	0.06

*Ref. Abbey (1973)

The procedure is not recommended for samples containing less than 0.05 per cent titanium dioxide, because the scale expansion then required would yield very noisy signals. Two alternative procedures are then possible. Titanium could be determined photometrically with Tiron as mentioned above, or a larger sample aliquot could be concentrated by evaporation, as done by Van Loon and Parissis (1969), and the determination completed by atomic absorption. In the latter case, some additional steps might be necessary to assure a clear final solution. Details have not been investigated at this writing.

DETERMINATION OF BARIUM AND STRONTIUM

Part 4 (Abbey, 1972a) described the determination of barium and strontium as "traces", expressed in parts per million, in a sample solution derived from a hydrofluoric-perchloric acid decomposition. Potassium was added to suppress ionization and lanthanium was required as a releasing agent, even in the nitrous-oxide-acetylene flame.

These two elements occur in many rocks at higher concentration levels than such more "common" elements as manganese and phosphorus (see Table 1). They should therefore be considered as part of an analysis for major and minor elements. In a conventional analysis, barium would be weighed as part of several major components (Maxwell, 1968, p. 259), and if not determined as such, would have only a minor effect on the summation. Strontium, under those circumstances, would react mainly as calcium, but its concentration is generally so low as to have little effect on the accuracy of the complete analysis. Thus both elements could escape unnoticed, unless they are specifically sought by analyzing a separate portion of the sample for barium, or by examining the calcium precipitate for strontium.

Table 8
Recovery of Barium and Strontium

Sample No.	Per cent, dry basis			
	BaO		SrO	
	Expected*	Found	Expected	Found
USGS-G-2	0.21	0.20	0.06	0.05
USGS-GSP-1	0.15	0.14	0.03	0.03
USGS-AGV-1	0.14	0.14	0.08	0.08
CRPG-BR	0.11	0.13	0.16	0.16
CRPG-GA	0.10	0.09	0.04	0.04
USGS-W-1	0.02	0.02	0.02	0.02

*Ref. Abbey (1973)

There was some question whether barium and strontium could be determined as part of the present scheme. The master solution of the sample is only half as concentrated as the solution used in the acid-decomposition method, and barium needed scale expansion even in the latter case. Further, there was the question of how to overcome possible chemical interference from aluminum and silicon, because lanthanum forms a precipitate in a fluoborate solution at the concentration level of sample used. Similarly, potassium could not be used to overcome any ionization, as it also forms a precipitate with fluoborate.

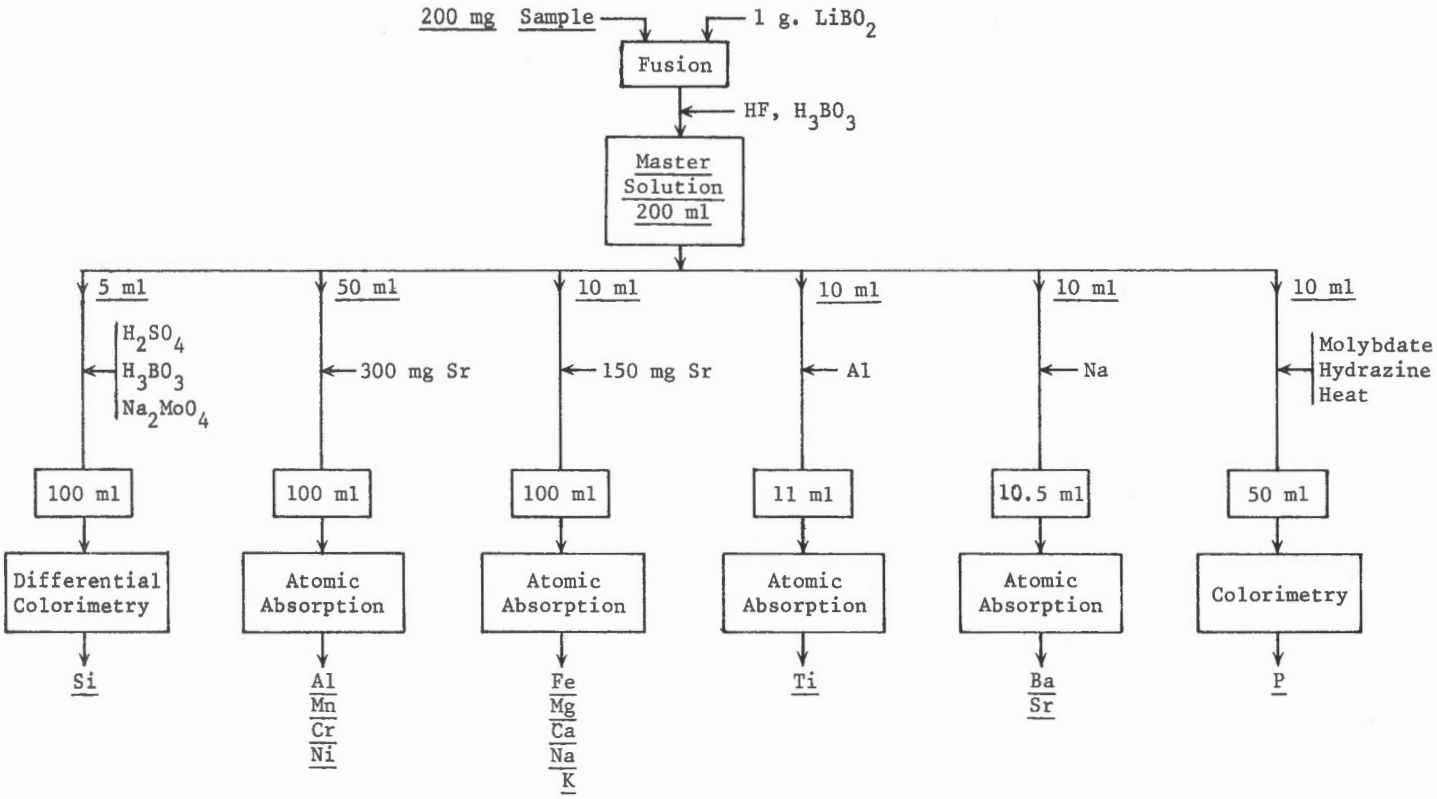

Figure 1. Outline of lithium-fluoborate analytical scheme for silicate rocks and minerals.

A few simple experiments easily overcame these doubts. Adequate sensitivity was attained for barium by means of scale expansion, without excessive noise. No chemical interference effects were observed, possibly because the potentially interfering elements were complexed as fluo-anions (Abbey, 1970). Ionization was overcome by the addition of a quantity of sodium somewhat greater than the potassium additive in the acid-decomposition method, and possibly also by the lithium derived from the fusion flux. The solution for analysis was prepared in much the same way as for titanium determination – i.e. 0.5 ml of a solution containing 50 mg of sodium chloride was added to 10 ml of the undiluted master solution. Results obtained on a number of reference samples are given in Table 8.

THE LITHIUM-FLUOBORATE SCHEME IN GENERAL

Supporting data are given in Tables 3 to 8 for those elements not previously determined (Abbey, 1970) and for those where major changes have been made. An outline of the entire scheme is presented in flow-sheet form in Figure 1, details being given in the APPENDIX. Recommended parameters for photometry are given in Table 9, but it must be emphasized that they represent conditions in our own laboratory at the time of writing. Changes are likely to be made at any time in order to improve performance, and the parameters would certainly require changes in adapting the method to other instruments.

COMPARISON WITH SIMILAR METHODS

In order to evaluate the revised lithium-fluoborate scheme as a whole, ten of the best-established international reference rocks were taken through the entire procedure, and the results compared with those obtained by similar methods as reported in the literature.

Many methods have appeared, in which major and minor elements have been determined by atomic absorption, but for purposes of comparison, selection was restricted to schemes in which silica, alumina and most of the other major and minor elements were reported, on at least several of the reference samples used in this work. Most methods differ from one another in the chemical pre-treatment of the sample. The methods considered are outlined below.

Buckley and Cranston (1971) decomposed the sample with hydrofluoric acid under pressure, complexed the excess fluoride with boric acid, and performed the analysis on the resulting solution without additives, using a combination of international reference rocks and successive dilutions of a synthetic solution, for standards. Foscolos and Barefoot (1970) fused the sample with a lithium carbonate-boric acid mixture, dissolved the fusion

Table 9

Operating Parameters

Component	In 100 ml: mg sample	In 100 ml: mg Sr	Range: per cent in sample	HC Lamp: Type	HC Lamp: mA	Support Gas*	Slit width: micron	Band pass: nm	Wave length: nm	Notes
SiO_2	50	300	30 - 80	Si-Al	15	N_2O	100	0.33	251.6	Approximate only
	5	0	30 - 80	Fe	10	Note	300	0.99	404.6	Differential colorimetry (molybdate)
Al_2O_3	50	300	0 - 25	Si-Al	15	N_2O	100	0.33	309.3	
Fe_2O_3T	10	150	1 - 30	Fe	5	Air	50	0.17	248.3	Total iron, expressed as Fe_2O_3
MgO	10	150	0 - 15	Ca-Mg	5	Air	100	0.33	285.2	*C_2H_2 fuel in all flames
	10	150	5 - 50	Ca-Mg	5	N_2O	100	0.33	285.2	5-mm aperture mask on 2nd lens with N_2O
										Burner angled where necessary
CaO	10	150	0 - 3	Ca-Mg	5	N_2O	100	0.33	422.7	Scale expanded where necessary
	10	150	2 - 20	Ca-Mg	5	Air	100	0.33	422.7	Flame parameters optimized
										HTV-R-213 photomultiplier (except for P)
Na_2O	10	150	0 - 10	Na-K	10	Air	50	0.17	589.0	
K_2O	10	150	0 - 10	Na-K	10	Air	100	0.33	766.5	
TiO_2	Note	0	0.05 - 10.0	Ti	20	N_2O	50	0.17	364.3	10 mg sample, 10 mg Al in 11 ml
MnO	50	300	0.01 - 1.0	Mn	5	Air	50	0.17	279.5	
BaO	Note	0	0.01 - 1.0	Ba	10	N_2O	100	0.33	553.6	10 mg sample, 50 mg NaCl in 10.5 ml
SrO	Note	0	0.01 - 1.0	Sr	10	N_2O	100	0.33	460.7	10 mg sample, 50 mg NaCl in 10.5 ml
Cr_2O_3	50	300	0.01 - 1.0	Cr-Ni	8	N_2O	100	0.33	357.9	
NiO	50	300	0.01 - 1.0	Ni	8	Air	50	0.17	232.0	
P_2O_5	Note	0	0.01 - 1.5	Cs(Ar)	20	Note	300	0.99	826.5	10 mg sample, 50 ml vol. Colorimetry (Mo-blue) Red-sensitive photomultiplier (HTV-R-406)

Table 10

Comparison with other atomic absorption methods - Sample U.S.G.S. - AGV-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	59.00	17.01	6.76	1.53	4.94	4.26	2.89	1.04	0.10	0.14	0.08
This work	58.99	17.35	6.81	1.55	5.04	4.29	2.87	1.10	0.10	0.13	0.08
Buckley & Cranston (1971)	63.32	17.33	6.56	1.59	5.40	4.25	2.78	1.02	0.10		0.07
Foscolos & Barefoot (1970)	59.20	17.38	6.80	1.48	4.93	4.37	2.88	1.17	0.08		
Goguel (1971b)	58.76	17.10	6.76	1.48	5.04	4.41	2.88	1.11	0.09		
Langmyhr & Paus (1969)	59.65	17.50	6.73	1.50	4.94	4.25	2.72	1.01	0.10		
Medlin et al. (1969)	58.7	16.60	6.88	1.50	5.00	4.20	2.90	1.02	0.10		0.08
Terashima (1972)	59.05	16.95		1.56	5.09			1.03	0.09	0.13	0.07
VanLoon & Parissis (1969)	59.1	16.9	6.69	1.43	4.87	4.28	2.85	1.02	0.08		
Yule & Swanson (1969)	59.6	17.6	6.60	1.58	4.99	4.36	3.08	1.14	0.09		

Table 11

Comparison with other atomic absorption methods - Sample U.S.G.S. - BCR-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	54.36	13.56	13.40	3.46	6.92	3.26	1.67	2.20	0.19	0.08	0.04
This work	54.33	13.50	13.57	3.46	6.87	3.30	1.69	2.26	0.19	0.07	0.04
Buckley & Cranston (1971)	53.70	13.70	12.92	3.48	7.09	2.93	1.55	2.17	0.18		0.04
Foscolos & Barefoot (1970)	53.60	13.98	13.67	3.17	6.86	3.29	1.61	2.34	0.17		
Goguel (1971b)	54.07	13.55	13.44	3.53	7.26	3.42	1.78	2.24	0.18		
Langmyhr & Paus (1969)	54.36	13.66	13.58	3.57	6.73	3.12	1.72	2.19	0.18		
Medlin et al. (1969)	53.6	13.60	13.60	3.50	7.10	3.15	1.70	2.22	0.18		0.04
Terashima (1972)	54.38	13.60		3.43	7.00			2.21		0.07	0.04
Van Loon & Parissis (1969)	54.5	13.4	13.40	3.40	6.94	3.26	1.73	2.23	0.19		
Yule & Swanson (1969)	56.4	14.0	12.72	3.54	6.89	3.38	1.73	2.40	0.19		

Table 12

Comparison with other atomic absorption methods - Sample C.R.P.G. - BR

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO	Cr_2O_3	NiO
Expected (Abbey, 1973) (per cent)	38.20	10.20	12.92	13.28	13.80	3.05	1.40	2.60	0.20	0.11	0.16	0.06	0.03
This work	38.14	10.01	13.04	13.26	13.84	3.07	1.39	2.66	0.22	0.12	0.17	0.06	0.04
Goguel (1971b)	38.33	10.31	12.95	13.21	13.86	3.14	1.45	2.61	0.19				
Langmyhr & Paus (1969)	38.85	10.28	12.78	13.43	13.42	3.08	1.50	2.69	0.19				
Medlin et al. (1969)	38.2	10.20	12.60	13.41	14.00	2.87	1.42		0.20			0.18	0.06
Van Loon & Parissis (1969)	38.5	10.3	12.86	13.3	14.0	3.07	1.26	2.59	0.19				

Table 13

Comparison with other atomic absorption methods - Sample U.S.G.S. - DTS-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO	Cr_2O_3	NiO
Expected (Abbey, 1973) (per cent)	40.66	0.29	8.59	49.80	0.15	0.01	0.00	0.01	0.11	0.00	0.00	0.64	0.31
This work	40.60	0.28	8.82	49.84	0.13				0.13			0.65	0.31
Foscolos & Barefoot (1970)	40.80	0.38	8.98	49.41	0.11	0.01	0.06	0.00	0.13				
Goguel (1971b)	41.10	0.19	8.58	49.39	0.15	0.02	0.00	0.03	0.12				
Langmyhr & Paus (1969)	40.47		8.43	49.82	0.05	0.07			0.11				
Medlin et al. (1969)	39.8	0.22	8.70	51.70	0.16	0.00	0.00	0.00	0.12			0.61	
Terashima (1972)	40.42	0.24		49.80	0.14					0.00	0.00		
Van Loon & Parissis (1969)	40.4		8.73	49.8	0.18			<0.01	0.11				

Table 14

Comparison with other atomic absorption methods – Sample U.S.G.S. – G-2

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	69.11	15.33	2.67	0.77	1.98	4.06	4.51	0.48	0.04	0.21	0.06
This work	69.16	15.29	2.56	0.76	2.00	4.03	4.36	0.48	0.04	0.21	0.05
Buckley & Cranston (1971)	65.46	15.97	2.59	0.69	2.77	4.08	4.47	0.50	0.03		0.06
Foscolos & Barefoot (1970)	68.80	15.48	2.63	0.80	1.92	4.16	4.28	0.50	0.02		
Langmyhr & Paus (1968)	69.10	15.60	2.70	0.75	1.83	4.00	4.45	0.46	0.03		
Medlin et al. (1969)	69.0	15.10	2.62	0.72	2.10	4.15	4.50	0.46	0.03		0.06
Terashima (1972)	69.13	15.27		0.75	1.91			0.51		0.20	0.05
Van Loon & Parissis (1969)	69.4	15.1	2.90	0.74	2.02	4.10	4.56	0.46	0.03		
Yule & Swanson (1969)	70.1	15.4	2.66	0.76	1.83	3.93	4.52	0.50	0.03		

Table 15

Comparison with other atomic absorption methods – Sample C.R.P.G. – GA

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	69.90	14.50	2.86	0.95	2.45	3.55	4.03	0.38	0.09	0.10	0.04
This work	69.96	14.66	2.76	0.93	2.42	3.54	4.01	0.36	0.08	0.09	0.04
Langmyhr & Paus (1969)	69.70	14.65	2.71	0.90	2.31	3.63	4.26	0.36	0.08		
Van Loon & Parissis (1969)	69.6	14.5	2.66	0.96	2.44	3.45	4.12	0.37	0.07		

Table 16

Comparison with other atomic absorption methods - Sample C.R.P.G. - GH

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	75.80	12.50	1.33	0.03	0.69	3.85	4.76	0.08	0.05	0.00	0.00
This work	75.83	12.64	1.28	0.03	0.70	3.82	4.74	0.09	0.05		
Goguel (1971b)	75.82	12.30	1.39	0.00	0.64	3.84	4.75	0.04	0.04		
Langmyhr & Paus (1969)	75.15	12.75	1.39	0.03	0.63	3.79	5.01	0.08	0.05		
Medlin et al. (1969)	74.8	12.3	1.35	0.00	0.75	3.77	4.86	0.05	0.05		0.00
Van Loon & Parissis (1969)	75.6	12.6	1.27		0.66	3.87	4.75		0.04		

Table 17

Comparison with other atomic absorption methods - Sample U.S.G.S. - GSP-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO
Expected (Abbey, 1973) (per cent)	67.27	15.18	4.33	0.96	2.02	2.80	5.53	0.66	0.04	0.15	0.03
This work	67.38	15.06	4.20	0.98	2.06	2.82	5.42	0.67	0.04	0.14	0.02
Buckley & Cranston (1971)	67.60	15.12	4.29	0.91	2.21	2.62	5.66	0.70	0.04		0.03
Foscolos & Barefoot (1971)	67.20	15.12	4.29	0.93	1.93	2.86	5.60	0.67	0.03		
Goguel (1971b)	67.40	15.18	4.30	0.93	1.96	2.84	5.50	0.65	0.04		
Langmyhr & Paus (1969)	67.07	15.49	4.29	0.97	1.94	2.86	5.56	0.64	0.04		
Medlin et al. (1969)	67.2	14.85	4.40	0.95	2.05	2.63	5.52	0.65	0.04		0.03
Terashima (1972)	67.38	15.00		0.97	2.00			0.68		0.14	0.03
Van Loon & Parissis (1969)	67.2	14.9	4.16	0.96	2.10	2.80	5.43	0.63	0.03		
Yule & Swanson (1969)	67.3	15.0	4.29	0.98	2.28	2.84	5.84	0.68	0.04		

Table 18

Comparison with other atomic absorption methods – Sample U.S.G.S. – PCC-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO	Cr_2O_3	NiO
Expected (Abbey, 1973) (per cent)	41.90	0.73	8.23	43.37	0.53	0.01	0.00	0.01	0.12	0.00	0.00	0.44	0.32
This work	41.75	0.72	8.28	43.42	0.51				0.12			0.41	0.32
Foscolos & Barefoot (1970)	42.40	0.94	8.52	42.78	0.52	0.03	0.00	0.00	0.12				
Medlin et al. (1969)	41.8	0.67	8.30	45.65	0.66	0.00	0.00	0.00	0.12			0.42	
Terashima (1972)	41.94	0.79		43.43	0.55			<0.01		0.00	0.00		
Van Loon & Parissis (1969)	41.9		8.23	42.9	0.54				0.12				

Table 19

Comparison with other atomic absorption methods – Sample U.S.G.S. – W-1

	SiO_2	Al_2O_3	Fe_2O_3T	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	BaO	SrO	Cr_2O_3	NiO
Expected (Abbey, 1973) (per cent)	52.64	14.85	11.09	6.62	10.96	2.15	0.64	1.07	0.17	0.02	0.02	0.02	0.01
This work	52.32	14.88	11.13	6.60	10.80	2.36	0.66	1.12	0.18	0.02	0.02	0.02	0.01
Buckley & Cranston (1971)	48.13	15.49	10.95	6.81	11.25	2.04	0.64	1.13	0.17		0.02	0.03	0.01
Langmyhr & Paus (1968)	52.65	15.27	11.20	6.59	10.83	2.11	0.60	1.08	0.17				
Van Loon & Parissis (1969)	52.7	14.9	11.12	6.56	10.8	2.10	0.64	1.07	0.16				

in dilute nitric acid, and used a lanthanum buffer and standard additions to overcome interferences. Goguel (pers. comm., 1971) used a flux mixture containing lithium tetraborate, lithium carbonate and rubidium iodide, dissolved the fusion in dilute perchloric acid containing a little hydrazine, and compared the absorbances of the sample solution with similarly-prepared solutions of international reference rocks. Langmyhr et al. (1965, 1968, 1969) pioneered in the use of pressure vessels for decompositions with hydrofluoric acid. Their decomposition temperature was higher than that of Buckley and Cranston, and they used lanthanum, potassium and cesium additives to overcome various interferences. Medlin et al. (1969) used a lithium metaborate fusion, dissolution of the fusion in dilute nitric acid, and a lanthanum buffer, also including some international reference rocks among their standards. Terashima (1972) concluded that atomic absorption determinations of silica were inadequate. He therefore decomposed a portion of the sample by fusion with sodium carbonate and boric acid, dissolved in hydrochloric acid, coagulated the bulk of the silica with polyethylene oxide and determined it gravimetrically. Only the silica remaining in the filtrate was determined by atomic absorption. Two additional portions were decomposed by acid treatments, one being used to determine barium, the other for aluminum, magnesium, calcium, titanium and strontium. All of Terashima's determinations were done in a nitrous oxide-acetylene flame, generally with potassium addition to overcome ionization effects. His earlier work (Terashima, 1970), using an air-acetylene flame for iron, sodium, potassium and manganese, did not report results on any of the international reference samples listed in this paper. Van Loon and Parissis (1969) used a scheme much like that of Medlin et al. (1969), but they made a detailed study of interference effects. Yule and Swanson (1969) used a similar system, but dissolved their fusion in hydrochloric, instead of nitric acid.

Tables 10 to 19 inclusive compare the results reported by the above authors with those obtained by the method now proposed. Although it was not always clear, the evidence suggests that most of the other authors did not report their results on the "dry basis". For that reason, our own results in Tables 10 to 19 are given on the "as received" basis, and do not agree exactly with our results in Tables 3 to 8 because they were obtained as separate analyses. "Expected" values were also converted to the "as received" basis by utilizing the H_2O^- figures reported earlier (Abbey, 1972b).

In Table 20, average deviation per determination is used as a measure for comparing this work with that of others. Although those figures show the present work to advantage, they should not be taken as a quantitative measure of precision and accuracy, for several reasons:

(1) The "expected" values used were derived by one of us (Abbey, 1972b, 1973) from published analytical data, although in most cases they do not differ greatly from those listed in other compilations.
(2) Some of the other authors also reported results on reference samples not used in this work, and it was therefore not possible to include them in the comparison.
(3) Some of the other authors may have improved their methods since they were published.

In connection with (3), it is interesting that only the most recent work (Terashima, 1972) gave a lower average deviation than did our work. Further, Terashima's work resembles our own also in that he did not use atomic absorption for determining the major portion of the silica.

Table 20
Deviations from "Expected" Values
This Work vs Other Methods

Method	*Samples Analyzed	Determinations	Average Deviation**
This work	10	102	0.05
Buckley & Cranston (1971)	5	52	0.38
Foscolos & Barefoot (1970)	6	54	0.13
Goguel (1971b)	6	54	0.08
Langmyhr & Paus (1969)	8	78	0.11
Medlin et al. (1969)	8	80	0.15
Terashima (1972)	6	41	0.04
Van Loon & Parissis (1969)	8	81	0.08
Yule & Swanson (1969)	4	36	0.16

* In common with the present work
**Per cent (absolute) – see text

POSSIBLE FURTHER WORK

As in many other analytical schemes silica determination remains the weakest link in the analytical method described in this paper. Before the present work on silica could be completed, the need arose here for accurate analysis of a number of rock samples to be used as calibration standards in X-ray fluorescence spectroscopy. An

alternative method, tentatively named "neo-classical" was introduced, and it produced some satisfactory results, although some problems remain to be resolved.

In the "neo-classical" system, a 500-mg sample is fused in graphite with 1.5 g of lithium metaborate and the bead poured into water in a Teflon dish. The shattered bead is dissolved by digestion in hydrochloric acid, methanol is added and the solution is evaporated to volatilize the boron and to dehydrate the bulk of the silica. The silica is then determined gravimetrically in the conventional manner (Maxwell, 1968, p. 327-328). After the silica has been volatilized with hydrofluoric acid, any remaining residue is fused with a little more lithium metaborate, dissolved in hydrochloric acid and combined with the filtrate from the silica separation. The filtrate is diluted to 250 ml and aliquots taken for the colorimetric determination of unprecipitated silica and of phosphorus, both as molybdenum blue, and for the determination of aluminum, total iron, magnesium, calcium, sodium, potassium, titanium, manganese, and possibly also barium, strontium, chromium and nickel, all by atomic absorption.

Aside from the more reliable gravimetric silica determination, the neo-classical system has the advantage of producing a master solution at double the sample concentration as that in the lithium fluoborate scheme, thus permitting such determinations as that of titanium to be extended to lower levels. However, the silica determination can also be considered a disadvantage, as it requires greater manipulative skill and decidedly more time than that required in the differential colorimetric method.

A persistent problem in the neo-classical method has been the difficulty in obtaining a clear acid solution after lithium metaborate fusion of the residue from the volatilization of the silica, particularly with samples of relatively high titanium content. Spectrographic examination has shown that residue to be composed mainly of titanium dioxide. The residue can readily be dissolved by fusion with potassium pyrosulphate, but the resulting solution cannot then be combined with the main filtrate, in which the alkali metals must also be determined. Titanium has been determined colorimetrically in the solution from the pyrosulphate fusion, but the bulk of that element must also be determined in the main solution.

Thus far, synthetic solutions have been used as standards for the neo-classical system, but it should be possible to simplify the preparation of standards by using solutions prepared from international reference rocks.

It may be possible to extend the lithium fluoborate or the neo-classical method to the determination of some additional elements which are normally present as traces, but can occur at concentrations exceeding 100 ppm in some rocks. Published sensitivities suggest cobalt, copper, lithium, lead, rubidium and zinc as possibilities.

REFERENCES

Abbey, Sydney

1967: Analysis of rocks and minerals by atomic absorption spectroscopy; Part 1: Determination of magnesium, lithium, zinc and iron; Geol. Surv. Can., Paper 67-37.

1968: Analysis of rocks and minerals by atomic absorption spectroscopy; Part 2: Determination of total iron, magnesium, calcium, sodium and potassium; Geol. Surv. Can., Paper 68-20.

1970: Analysis of rocks and minerals by atomic absorption spectroscopy; Part 3: A lithium-fluoborate scheme for seven major elements; Geol. Surv. Can., Paper 70-23.

1972a: Analysis of rocks and minerals by atomic absorption and flame emission spectroscopy; Part 4: A composite scheme for the less common alkali and alkaline-earth elements; Geol. Surv. Can., Paper 71-50.

1972b: "Standard samples" of silicate rocks and minerals – A review and compilation; Geol. Surv. Can., Paper 72-30.

1973: Studies in "standard samples" of silicate rocks and minerals; Part 3: 1973 extension and revision of "usable" values; Geol. Surv. Can., Paper 73-36.

Bennett, H., Eardley, R.P., Hawley, W.G., and Twaites, I.

1962: Routine control analysis of high silica and aluminosilicate materials; Brit. Ceram. Soc. Trans., v. 61, p. 636-666.

Bernas, Bedrich

1968: A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry; Anal. Chem., v. 40, p. 1682-1686.

Bloxam, T.W.

1961: The photometric determination of silica in rocks and refractory minerals; Analyst, v. 86, p. 420-422.

Bouvier, J.-L., Sen Gupta, J.G., and Abbey, S.
1972: Use of an "automatic sulphur titrator" in rock and mineral analysis; Determination of sulphur, total carbon, carbonate and ferrous iron; Geol. Surv. Can., Paper 72-31.

Buckley, D.E., and Cranston, R.E.
1971: Atomic absorption analyses of 18 elements from a single decomposition of aluminosilicate; Chem. Geol., v. 7, p. 273-284.

Foscolos, A.E., and Barefoot, R.R.
1970: A buffering and standard addition technique as an aid in the comprehensive analysis of silicates by atomic absorption spectroscopy; Geol. Surv. Can., Paper 70-16.

Goguel, Reiner
1970: An improved nitrous oxide burner for atomic absorption spectroscopy; N.Z. J. Sci., v. 13, p. 603-609.

1971a: The effects of burner temperature on atomic absorption spectroscopy with the nitrous oxide-acetylene flame; Spectrochim. Acta, v. 26B, p. 313-330.

1971b: Private communication.

Govett, G.J.S.
1961: Critical factors in the colorimetric determination of silica; Anal. Chim. Acta, v. 25, p. 69-80.

Hildon, M.A.
1971: Use of an atomic absorption spectrophotometer for colorimetric analysis; Anal. Chem., v. 43, p. 973-974.

Langmyhr, F.J., and Graff, P.R.
1965: A contribution to the analytical chemistry of silicate rocks; A scheme of analysis for eleven main constituents based on decomposition by hydrofluoric acid; Norg. Geol. Unders., Nr. 230, p. 53-61.

Langmyhr, F.J., and Paus, P.E.
1968: The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part 1: The analysis of silicate rocks; Anal. Chim. Acta, v. 43, p. 397-408.

1969: Hydrofluoric acid decomposition-atomic absorption analysis of nine silicate mineral and rock reference samples; Anal. Chim. Acta, v. 47, p. 371-373.

Maxwell, J.A.
1968: Rock and Mineral Analysis (Interscience).

McKenzie, R.M.
1972: Conversion of an atomic absorption spectrophotometer to measure absorption in solution; Lab. Practice, v. 21, p. 494.

Medlin, J.H., Suhr, N.H., and Bodkin, J.B.
1969: Atomic absorption analysis of silicates employing $LiBO_2$ fusion; Atom. Absorpt. Newsletter, v. 8, p. 25-29.

Meehan, E.J.
1964: Fundamentals of spectrophotometry; in Treatise on Analytical Chemistry (Interscience) (I.M. Kolthoff and P.J. Elving, eds.), Part 1, v. 5, p. 2784-2788.

Ringbom, Anders, Ahlers, P.E., and Siitonen, Soini
1959: The photometric determination of silicon as alpha-silicomolybdic acid; Anal. Chim. Acta, v. 20, p. 78-83.

Shapiro, Leonard
1967: Rapid analysis of rocks and minerals by a single dilution method; U.S. Geol. Surv., Prof. Paper 575-B, p. B-187-B-191.

Shell, H.R.
1962: Silicon; in Treatise on Analytical Chemistry (Interscience) (I.M. Kolthoff and P.J. Elving, eds.), Part II, v. 2, p. 165.

Strickland, J.D.H.
1952: The preparation and properties of silicomolybdic acid; J. Amer. Chem. Soc., v. 74, p. 862-876.

Suhr, N.H., and Ingamells, C.O.
1966: Solution technique for analysis of silicates; Anal. Chem., v. 38, p. 730-734.

Terashima, Shigeru
1970: Quantitative analyses of sodium, potassium, magnesium, calcium, manganese and iron in silicate rocks; Bull. Geol. Surv. Japan, v. 21, p. 693-707.

1972: Analyses of silicates by atomic absorption spectrophotometry in a nitrous oxide-acetylene flame; Bull. Geol. Surv. Japan, v. 23, p. 287-304.

Van Loon, J.C., and Parissis, C.M.
1969: Rapid scheme of silicate analysis based on the lithium metaborate fusion followed by atomic absorption spectrophotometry; Analyst, v. 94, p. 1057-1062.

Varian-Techtron
1972: Analytical methods for flame spectroscopy.

Woodward, Colin
1971: Ionization of metal atoms in flames; Spectrosc. Letters, v. 4, p. 191-193.

Yule, John W., and Swanson, Glenda
1969: A rapid method for decomposition and the analysis of silicates and carbonates by atomic absorption spectroscopy; Atom. Absorpt. Newsletter, v. 8, p. 30-33.

APPENDIX - Operating Procedures

Special Reagents

1. Hydrofluoric Acid (6:19)
   Mix 120 ml of concentrated hydrofluoric acid with 380 ml of water. Store in a plastic bottle.

2. Boric Acid, 50 g per l
   Dissolve 50 g of boric acid crystals in about 400 ml of boiling water in a silica or Vycor beaker, with magnetic stirring. Pour into about 500 ml of cold water in a 1000-ml polyethylene graduate cylinder. Stir to mix and dilute to volume. Store in a plastic bottle. Because this solution is used in large quantities, several litres should be prepared at the same time.

3. Strontium Nitrate, 15000 micrograms Sr per ml
   Dissolve 72 g of strontium nitrate in about one litre of water and dilute to two litres. Store in a plastic bottle.

4. Blank Solutions
   Stir 1.0 g of lithium metaborate in 50 ml of water in a 400-ml plastic beaker, and add 25 ml of HF (6:19). Add 100 ml of boric acid solution (50 g per l), stir to complete solution and dilute to 200 ml. Store in a plastic bottle. For each size of aliquot of sample solution required for analysis, a corresponding blank solution may be prepared from the master blank solution, including the same additives. Large quantities of the master blank solution are required in preparing standard silica solutions, so it may be necessary to prepare a larger volume of the former.

5. Standard Solutions
   Prepare by processing international reference rock samples in exactly the same way as the unknown samples. After a complete set of standard solutions has been prepared, a different international reference rock should be processed with groups of unknowns at regular intervals, and the old solutions of that reference sample should be discarded. Such a procedure provides for continuous renewal of all of the standard solutions.
   Recommended international reference rocks are listed in Table 1. For information on possible additional reference samples, see Abbey (1973). Blended aliquots of two reference rocks may be used to bridge compositional gaps. Standard solutions of individual elements, prepared as described earlier (Abbey, 1968, 1970), may also be needed to extend the upper limit of concentration.

   To prepare standard silica solutions, weigh 1.00-1.01 g of pure silica (e.g. SPEX) into a porcelain crucible and ignite, under a cover at 800°C. The final weight, after ignition, must be known correct to 0.1 mg. Transfer the ignited silica by rinsing with a minimum volume of water, through a polyethylene funnel, into a 250-ml Teflon bottle, containing a small Teflon-coated magnetic stirring bar. Add 30 ml of hydrofluoric acid, tighten the bottle cap immediately and stir until the silica is dissolved. Chill the bottle and contents thoroughly in a refrigerator. Add, through a plastic funnel, 5 g of lithium metaborate, rinsed in with about 100 ml of water. Again cap, stir and chill. Pour the chilled solution into 500 ml of boric acid solution (50 g per l) and stir to dissolve. Transfer to a 1-litre volumetric flask, dilute to the mark and add n ml of water, where (1000 + n) mg is the weight of silica. Mix well and transfer to a polyethylene bottle. The resulting solution corresponds to that of a sample containing 100 per cent silica.
   Into a series of 120-ml polyethylene bottles, pipette 30, 35, 40 .... 80 ml of the "100 per cent silica" solution. To the same bottles, then pipette 70, 65, 60 .... 20 ml of the blank master solution (solution no. 4). The resulting solutions then correspond to master solutions of samples containing 30, 35, 40 .... 80 per cent silica.

6. Aluminum Buffer (for titanium)
   Dissolve 14 g of Al $(NO_3)_3$ $9H_2O$ in a minimum volume of water (25-30 ml) in a 400-ml beaker. Add 100 ml concentrated HCl, cover and boil until no further gases are evolved. Evaporate to dryness overnight on a steam bath. Add 25 ml of concentrated HCl and just enough water to provide a clear solution. Repeat the boiling and evaporation to dryness. Add 10 ml of concentrated HCl, about 50 ml of water and warm to dissolve. Dilute to 100 ml.

7. Sodium Buffer (for barium and strontium)
   Dissolve 10 g of sodium chloride in water and dilute to 100 ml.

8. Sulphuric Acid, 5 M
   Mix 555 ml of sulphuric acid (1:1) with 445 ml of water.

9. Ammonium Molybdate (acid, for phosphorus)
   Dissolve 5 g of $(NH_4)_6$ Mo_7 $O_{24}.4H_2O$ in about 200 ml of 5 M sulphuric acid and dilute to 250 ml with the same acid.

10. Hydrazine Sulphate (for phosphorus)
Dissolve 0.15 g in water and dilute to 100 ml.

11. Sulphuric Acid, 0.5 M
Dilute 100 ml of sulphuric acid, 5 M, to 1 litre with water.

12. Sodium Hydroxide, 10 M
Carefully dissolve 40 g of NaOH in about 60 ml of water in a plastic beaker, with magnetic stirring. Dilute to 100 ml and store in a plastic bottle.

13. Ammonium Molybdate ("neutral", for silica)
Dissolve 53 g of $(NH_4)_6\ Mo_7\ O_{24}.4H_2O$ in water in a plastic container and dilute to about 900 ml. Add 36 ml of 10 M NaOH, mix well and dilute to 1 litre.

14. Chromate Reference Solutions (for silica)
Dissolve approximately 0.135 g of potassium chromate and dilute to 500 ml. Into a series of 120-ml polyethylene bottles, measure 30, 35, 40 .... 75 ml of the chromate solution and add to them 70, 65, 60 .... 25 ml of water. The colours of the resulting solutions should give absorbances close to those of the final silicomolybdate complexes of the corresponding equivalent percentage of silica. After a number of silica determinations have been done, it may be found necessary to readjust the concentrations of the chromate solutions.

Sample Decomposition

All "standard" samples and other samples which are to be analyzed on the "dry basis" should be weighed into small porcelain crucibles and dried at 110°C. The sample weight (after drying, where that is done) should be between 200 and 205 mg, weighed to the nearest 0.1 mg. For some samples, decomposition will be facilitated if the sample is pre-ignited at 600-700°C, preferably overnight. Samples may be conveniently analyzed in groups of six.

Pre-ignite the covered graphite crucibles at about 1000°C for 15-20 minutes. Allow to cool. Without disturbing the graphite dust in the crucible, add 1.0 g of lithium metaborate. Carefully brush the weighed sample on to the lithium metaborate and mix lightly with a small spatula. Place the covered crucible in a preheated muffle furnace and hold at 950-1000°C for fifteen minutes. Quickly but carefully move the crucible to the front of the furnace, remove the lid and take the crucible out of the furnace. Immediately rotate the molten bead to pick up any unattacked sample and allow to cool until the crucible no longer glows. Return the covered crucible to the furnace (reversing positions where a group is involved) and heat for five minutes more.

While the fusion is going on, remove the screw-cap from a 250-ml transparent plastic (e.g. trimethylpentene) jar and place 40 ml of water in the jar. Remove the crucible from the furnace as done before, but this time pour the hot, molten fusion into the water in the plastic jar. After the crucible has cooled to room temperature, examine it carefully for any retained material from the fusion. If any is found, use a small spatula and a brush to transfer it to the plastic jar.

Add a Teflon-coated stirring bar to the jar, followed by 25 ml of HF (6:19) and immediately cap the jar tightly. Stir the contents until the shattered fusion bead is completely disintegrated, then chill thoroughly in a refrigerator.

Open the chilled jar, immediately add 100 ml of boric acid solution (50 g per 1), cover again and stir until a clear solution is obtained. Filter through a rapid filter paper (e.g. Whatman no. 541) in a plastic funnel, receiving the filtrate in a 200-ml volumetric flask. Wash the jar and the filter several times with water.

Dilute the filtrate to the mark, add m ml of water, where (200 + m) mg is the sample weight. Mix well and transfer to a polyethylene bottle. (Teflon bottles are recommended for the "standard samples".) The final solution then contains 200 mg of sample per 200 ml of solution, and the bottle should be labelled with the sample number and date.

Solution for Al, Mn, Cr, Ni and approximate Si

Pipette 20 ml of strontium solution (15000 micrograms per ml) into a 100-ml volumetric flask. Add, with a pipette, 50 ml of sample solution. Dilute to the mark, mix and transfer to a polyethylene bottle. The solution contains 50 mg of sample per 100 ml of solution, and the bottle should be labelled with the sample number, followed by "-50", and the date.

Solution for Mg, Ca, Na, K and total Fe

Pipette 10 ml of strontium solution (15000 micrograms per ml) into a 100-ml volumetric flask. Add, with a pipette, 10 ml of sample solution. Dilute to the mark, mix and transfer to a polyethylene bottle. The solution contains 10 mg of sample per 100 ml of solution, and the bottle should be labelled with the sample number, followed by "-10", and the date.

Solution for Ti

Pipette 1 ml of the aluminum buffer solution into a clean, dry plastic vial of about 15 ml capacity. Add, with a pipette, 10 ml of sample solution. Without further dilution, cap the vial and mix well.

Solution for Ba and Sr

Pipette 0.5 ml of the sodium buffer solution into a clean, dry plastic vial of about 15 ml

capacity. Add, with a pipette, 10 ml of sample solution. Without further dilution, cap the vial and mix well.

Atomic Absorption Measurements

After sufficient warm-up, adjust the parameters for the determination of each element as listed in Table 9. Aspirate a standard solution and optimize other parameters (gas controls, burner position, damping, scale expansion) for each element.

For each element, obtain a first approximation of its concentration by comparison with any convenient standard. Select at least four standards, covering a concentration range slightly greater than that of the samples. Arrange samples and standards together in a series of progressively decreasing concentration of the desired element. Measure the absorbance of all of the solutions in order (preferably with a recorder), then repeat the readings in the reverse order. For elements whose oxides are present to the extent of 10 per cent or more, the entire sequence of measurements should be repeated. This should also be done where there are apparent discrepancies between the two sets of readings.

For each set of readings, plot a curve (or calculate the best straight line) from the absorbances and known concentrations of the standards, and read values for the samples from the curve. Calculate the mean of all values for a given element in a given sample, rejecting any questionable readings. If there is any doubt about the acceptability of a particular reading, additional measurements should be made.

Photometric Measurements for Colorimetry

When not in use, absorption cells should be stored totally immersed in water. Immediately before use, each cell should be immersed several times in:

(1) dilute HCl (about 1:10),
(2) warm, running tap water, and
(3) hot, freshly boiled, distilled water.

They should then be placed, vertically and inverted, on a clean, dry tissue and allowed to drain dry.

Immediately after use, the cells should be emptied, rinsed several times in running water, and totally immersed in a dilute solution of a laboratory detergent (e.g. Alconox), preferably overnight. If the cells are to be used early in the next morning, they should first be immersed several times in warm, running tap water, then treated as above. Otherwise, they should be:

(1) immersed in dilute HCl,
(2) immersed in warm, running tap water,
(3) rinsed thoroughly in distilled water, and
(4) stored, totally immersed in distilled water.

Occasionally, where necessary, the cells should be given a more drastic treatment, such as soaking overnight in a cleaning solution, such as chromic acid or Nochromix.

For phosphorus determination, adequate precision can be attained by making cell corrections in the conventional way. For silica determination, samples and standards are compared in the same cell, so no cell correction is necessary.

In all photometric measurements, adjust instrument response to give a small positive absorbance (or transmittance a little below 100 per cent) for the reference solution, and take all readings without changing settings. Any variations in the reading on the reference solution can be used as a correction on the other readings. For every set of measurements, read all four cells in the sequence A-B-C-D-D-C-B-A, preferably with the recorder.

Determination of Phosphorus

Into 50-ml volumetric flasks, pipette 10-ml aliquots of the master solution of each sample, a 10-ml aliquot of the master blank solution, and a 10-ml aliquot of one or two master standard solutions (preferably containing more phosphorus than expected in the samples).

Add 5 ml of the acid molybdate solution and mix. Add 2 ml of the hydrazine solution and mix. Dilute to within 1 cm of the base of the neck of each flask, and mix well. Cap each flask loosely with an inverted 5-ml glass beaker and immerse the flask in boiling water for 20-30 minutes. Allow to cool to room temperature.

Dilute each flask to the mark and mix well. Place each solution in a freshly-cleaned absorption cell and measure absorbance. After applying cell corrections, calculate phosphorus content of each sample, assuming absorbance to be directly proportional to concentration. Details of operating conditions are given in Table 9.

Determination of Silica

A first approximation of the silica content is obtained either by atomic absorption measurements or by difference, after all other components have been determined.

The following procedure is applicable to groups of one, two, or three samples. Within each group, the range of expected silica contents must be such as can be bracketed by standards differing by no more than 15 per cent silica. The procedure is written for a group of three samples that meet these requirements.

Into a set of nine clean, dry 120-ml polyethylene bottles, pipette 5 ml of the following:

Bottle	Solution
1	L1 (standard slightly lower than X1)
2	L2 (" " " " X2)
3	L3 (" " " " X3)
4	X1 (sample with lowest expected silica)
5	X2 (sample with intermediate silica)
6	X3 (sample with highest expected silica)
7	H1 (standard slightly higher than X1)
8	H2 (" " " " X2)
9	H3 (" " " " X3)

Any two or all three of L1, L2 and L3 may be the same, depending on the samples, and similarly with the high standards. Each H standard contains the equivalent of 5 per cent silica more than the corresponding L. If the titanium and phosphorus contents of any sample are sufficient to cause possible interference, standard titanium and phosphorus solutions should be added to both standards that bracket that sample. The concentrations of the standard titanium and phosphorus used should be such that the volumes added do not total more than 5 ml, and an exactly equal volume of water should be added to the sample aliquot.

Before the next step, the stability of the output of the iron hollow-cathode lamp should be checked. Generally 30-60 minutes' warm-up, with the modulated current in the operational mode, will produce a steady signal. Into bottles 1, 2 and 3, pipette:

(a) 20 ml of sulphuric acid, 0.5 M,
(b) 50 ml of boric acid (50 g/l), and
(c) 25 ml of ammonium molybdate ("neutral").

Immediately after the addition of molybdate to bottle 1, start a timer, which is set to ring a bell after 15 minutes.

Mix the contents of each bottle by inverting a number of times.

Clean four absorption cells, as described above, under "immediately before use". The cells should be marked in such a way that each one always goes into the same location in the cell holder, and always facing in the same direction.

Rinse and fill cell A with the chromate solution corresponding to L1, cell B with L1, cell C with L2 and cell D with L3. Place the cells in the spectrophotometer and adjust GAIN to give a transmittance reading of about 95 on the cell with the least absorption.

As soon as the bell rings, take a series of transmittance readings on all of the cells, in the sequence A-B-C-D-D-C-B-A, without changing any instrumental settings. These readings are best made with a recorder.

Before removing the cells from the instrument, reduce COARSE GAIN to a point where the meter will not go off scale, but leave FINE GAIN and all other controls as they are.

Empty the four cells, rinse with tap water and distilled water, and immerse in distilled water.

Proceed with bottles 4, 5 and 6 in exactly the same manner as with 1, 2 and 3, and clean the cells in the same way.

Rinse and fill cell A with the same chromate solution as before, cell B with X1, cell C with X2 and cell D with X3. Place the cells in the spectrophotometer and re-set COARSE GAIN to the point where it was for the first series of readings, but leave all other controls unchanged.

Take a series of timed readings, exactly as before.

Repeat the entire cycle with H1, H2 and H3, always using the same chromate solution in cell A.

Convert all transmittance readings to absorbances (to four decimal places). Subtract the absorbance of the chromate solution from the absorbance of every other solution in the same series, giving "net absorbance". Calculate the concentration of the X solution by linear interpolation of the absorbances between the corresponding L and H.

Example: L: 50 per cent SiO_2

H: 55 per cent SiO_2

	Transmittance	Absorbance	Net Absorbance	Absorbance Difference
Chromate	95.0	0.0223		
L	71.3	0.1469	0.1246	0.0000
Chromate	95.1	0.0218		
X	65.5	0.1838	0.1620	0.0374
Chromate	95.1	0.0218		
H	59.7	0.2240	0.2022	0.0776

Interpolation: $x = 50 + 5\left(\frac{0.0374}{0.0776}\right)$

$= \underline{52.41}$