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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

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ABSTRACT

An analytical scheme is proposed for the determination of lithium, rubidium, cesium, barium and strontium in the concentration ranges where they occur in most silicate rocks. Where necessary, an aliquot of the same sample solution may also be used to determine total iron, magnesium, calcium, sodium and potassium by atomic absorption in the air-acetylene flame. The sample is decomposed by a conventional hydrofluoric-nitric-perchloric acid attack, and there are no chemical separations. Following the addition of potassium to suppress ionization, the three alkali metals are determined by emission in an air-acetylene flame. A standard-additon technique is sometimes required to overcome matrix effects. An aliquot is then diluted, more potassium is added, followed by lanthanum as releasing agent, and the two alkaline earths determined by atomic absorption in a nitrous oxide-acetylene flame.

RÉSUMÉ

On propose une méthode pour le dosage du lithium, du rubidium, du césium, du baryum et du strontium au niveau où chaque élément se trouve dans la plupart des roches silicatées. On peut aussi se servir d'un aliquot de la même solution de l'échantillon pour doser le fer total, le magnésium, le calcium, le sodium et le potassium au moyen de l'absorption atomique, en se servant de la flamme acétylène-air. L'échantillon est decomposé par le traitement conventionel avec les acides fluorhydrique, nitrique et perchlorique, en se servant d'aucune séparation chimique. Après avoir ajouté du potassium pour réduir l'ionisation, on peut doser les trois métaux alcalins par émission, en se servant d'une flamme acétylène-air. Il faut quelquefois se servir de la technique "addition-standard" pour combattre les effets de matrice. Enfin, on dilue un aliquot, on y ajoute encore de potassium, ainsi que du lanthane pour enlever l'interférence chimique, et on dose les alcalino-terreux par l'absorption atomique, en se servant de la flamme acétylène-protoxyde d'azote.

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PART 4. A COMPOSITE SCHEME FOR THE LESS COMMON ALKALI
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INTRODUCTION

Earlier papers (Abbey, 1967, 1968, 1970) outlined the principles of atomic absorption spectroscopy and its application to the determination of most of the major and minor elements (and some trace elements) in silicate rocks and minerals. It appeared that in combination with other modern analytical techniques, atomic absorption might well become the back-bone of an entirely new scheme of precise analysis of such materials. Recently, the need arose for a method for determining small amounts of lithium, rubidium and cesium (in the last case down to under 1 ppm) in rocks. After attempts at adapting various published methods, a relatively simple procedure was found to give the best results. With little modification, the method can also be adapted to the determination of at least five major elements, and to the determination of barium and strontium.

Acknowledgments

EARLIER WORK

The "ignition-and-leach" method (Abbey and Maxwell, 1960) for potassium in micas had been adapted for determining lithium, rubidium and cesium, using the Beckman DU Spectrophotometer with flame photometry attachment. More concentrated sample solutions were used because the amounts of the latter three elements present in most samples were much lower than the potassium content. Unfortunately, the lower limit of each element determinable under such conditions was about 100 ppm, and there was evidence that lithium recovery was not complete.

Horstman (1956) described a method in which the sample was decomposed with hydrofluoric and sulphuric acids, certain matrix elements were removed by precipitation with calcium carbonate, calcium was separated as the sulphate in alcoholic medium, and the three rarer alkali metals determined by flame photometry. Effects of the other alkalis and magnesium (which remained in the final solution) were compensated by adding similar amounts of those elements to the standard solutions. The lower limit for cesium in this method was too high for our needs, but it appeared to be possible to improve sensitivity with the instrumentation now available.

Ingamells (1962) modified the ignition-and-leach method to determine rubidium and cesium by means of a specially designed flame photometric system. His scheme required very carefully controlled additions of potassium, and a separate sample was required for lithium determination.

The lithium method described in Part 1 (Abbey, 1967) was not suitable for rubidium and cesium because the additional potassium required to suppress ionization would have led to an excessively high salt concentration in the final solution.

A series of Russian papers (Prudnikov, 1965, 1966; Prudnikov and Shapkina, 1970) described a simple flame photometric method for lithium, rubidium and cesium, for which extraordinarily high sensitivity is claimed - several orders of magnitude better than other references in the literature. Prudnikov attributes the improved sensitivity to the use of "monochromators of high linear dispersion and illumination, sensitive d.c. amplifiers and photomultipliers and more effective excitation sources" (Zacek, 1968). However, the most recent reference (Prudnikov and Shapkina, 1970) mentions use of the air-acetylene flame, hardly a "more effective excitation source". It is difficult to understand how so spectacular an increase in sensitivity can be brought about merely by means of higher spectral dispersion and more sensitive detectors, considering that the line-to-background ratio is the limiting parameter.

Other methods for lithium, rubidium and cesium in the literature are either insufficiently sensitive (Rubeska and Moldan, 1965) or involve chemical isolation of the alkali metals (Hara, 1959; Osterried, 1963; Pencheva and Stoyanova, 1965; Mountjoy and Wahlberg, 1968).

Strontium has on occasion been determined by flame photometry after isolation of the alkaline earth group. Calcium was similarly determined in the same solution, but barium sensitivity was generally inadequate. In an excellent review of methods for barium and strontium in rocks, Ingamells et al. (1971) describe a variety of methods. They report that strontium can be determined by atomic absorption in "whole-rock solutions" but mention difficulties in barium determination. They present evidence indicating that flame emission spectrometry and classical gravimetric methods are not satisfactory "as practicable routine methods" for these elements.

APPARATUS

The equipment used in this work was considerably modified from that described earlier. Of the original Techtron AA-3 Atomic Absorption Spectrophotometer, only the original monochromator, optical bar and hollow-cathode lamp mountings were retained unaltered. As mentioned earlier (Abbey, 1968), gas supplies were regulated by means of a Beckman unit intended for their Model 9200 Flame Photometer Attachment, and measurements were recorded on a Photovolt Varicord Linear/Log Model 43 recorder. Further (Abbey, 1970), a variable-flow nebulizer was installed and the Hamamatsu R-136 photomultiplier replaced by a R-213 tube.

Additional modifications installed since those listed above were as follows: The original "W.M.A." readout unit and the Techtron Scale Expansion Unit were replaced by the new solid-state readout unit designed for use as part of the Techtron AA-5 instrument. (This unit not only replaced the two older ones, but provided greater stability, more flexible scale expansion, improved damping control, automatic base line correction, linear absorbance readout and facility for connection to a digital readout system.) The glass spray-chamber and old burner mounting were replaced by the Teflon chamber and new burner mounting of the AA-5, providing finer control of burner settings. The Hollow-Cathode Lamp Power Supply was connected to the new readout unit, thereby converting its modulation frequency from 60 to 285 Hz. To provide facility for flame emission measurements, a 285-cycle chopper was installed between the second lens and the monochromator slit, and a six-speed wavelength-scanning

system attached to the monochromator. (A disadvantage of the latter unit is that maximum speed, 1000 angstroms per minute, is much slower than the old fast wavelength drive. Thus, changing the wavelength from, say Zn at 2139 to Cs at 8521, takes nearly 6.5 minutes.)

A conventional Perkin-Elmer hollow-cathode lamp was used for strontium, a conventional ASL hollow-cathode lamp for potassium, ASL shielded hollow-cathode lamps for barium, cesium and rubidium, and a Techtron shielded hollow-cathode lamp for lithium. A Hamamatsu R-406 photomultiplier was used at the longer wavelengths required for rubidium and cesium. The regular burner heads, designed for atomic absorption measurements with both air and nitrous oxide as support gases, were used both for absorption and emission, but some emission measurements were also made with a round Techtron emission burner.

Before this work was undertaken, cesium absorption measurements were attempted in another laboratory, using a Techtron AA-4 instrument and a cesium Osram lamp.

REAGENTS

As expected, difficulties were encountered with reagent impurities. Thus reagent grade potassium salts were found to contain small but significant amounts of rubidium, but no measurable cesium. C.P. grade cesium salts and "purified" rubidium salts contained enough of one another and of potassium to be useless. "Spectroscopically pure" (SPEX) cesium and rubidium chlorides proved satisfactory, although a correction was necessary for the slight cesium impurity in the rubidium salt. For the alkaline earths, Johnson-Matthey "Specpure" barium and strontium carbonates were used. The traces of strontium in the barium (and vice versa) were small enough to be insignificant in this work.

Standard solutions of cesium and rubidium, prepared by direct weighing of the chlorides, and of lithium, prepared by dissolving the carbonate (A.D. MacKay) in hydrochloric acid, were standardized by evaporating aliquots with sulphuric acid, igniting and weighing as sulphates. Slight departures from stoichiometry were observed, probably due to moisture. A large discrepancy was observed with "5-9's" lanthanum oxide (SPEX). Presence of carbon dioxide (and possibly of water) was indicated by the effervescence produced with hydrochloric acid, and a loss on ignition of 13.5 per cent, necessitating a correction in preparing solutions.

Other-alkali metal impurities in each of the alkali metal salts were determined, where necessary, by standard-addition tests, using atomic absorption or flame emission, where applicable.

EXPERIMENTAL

Earlier Work

It was recognized from the start that cesium and barium would present the greatest problems. A method for lithium (Abbey, 1967) was already in use. Medlin, Suhr and Bodkin (1969, 1970) had shown that rubidium and strontium were readily determinable in silicate rocks by using the dilute nitric acid solution derived from a lithium metaborate fusion. Some difficulty was expected with barium, because of its limited sensitivity in both the atomic absorption and flame emission techniques. Cesium suffers from the same limited sensitivity, further complicated by the facts that (a) the quantity present in most rocks is much lower than is the case with the other elements, and (b) the most sensitive cesium line is at 8521 angstroms, far above the normal working wavelength range of most photomultiplier tubes. In earlier work, the red-sensitive phototube of the Beckman DU Spectrophotometer was used for emission measurements, but sensitivity was poor. Further, the wide slit settings needed gave rather diffuse

peaks with the poor dispersion of the quartz monochromator at the far red end of the spectrum.

Because of the presumed advantages of atomic absorption and the superior dispersion of a grating monochromator at high wavelengths, an attempt was made several years ago to use that technique to determine cesium. Unfortunately, good hollow-cathode lamps were not available at the time, so a cesium Osram discharge lamp was used. On a Techtron AA-4 instrument, equipped with a Hamamatsu R-136 photomultiplier, it was easy to obtain an apparently strong emission signal from the lamp at the cesium wavelength. However, when a solution containing 10 micrograms of cesium per millilitre was sprayed into the flame, no absorption signal was observed. Variation of all flame parameters were to no avail.

At the time, there was no apparent explanation for this contradiction, but subsequently it was noticed that there is a strong argon line at 4259.36 angstroms (close enough to one half the wavelength of the cesium line at 8521.10 for the spectral band-pass used) and that argon was the filler gas in the Osram lamp. The R-136 photomultiplier, which is essentially blind at 8521, was apparently responding to the second order image of the 4259 line, a wavelength at which the R-136 is very sensitive. This explanation was confirmed by inserting an ultraviolet absorbing filter, which eliminated the argon line and reduced the photomultiplier response almost to zero.

Emission vs Absorption

Fassel (1969a, b) has repeatedly argued in favor of the advantages of flame emission over atomic absorption as an analytical technique. Among other advantages, he has emphasized the superior sensitivity and more flexible concentration working range. The former was thought to be of possible importance in this work because of the low cesium concentrations involved.

Upon receipt of a new cesium hollow-cathode lamp (also argon-filled), tests conducted with the R-213 photomultiplier revealed the same phenomenon as observed earlier with the Osram lamp and the R-136. Replacement of the R-213 with the red-sensitive R-406 eliminated the effect and confirmed published values for cesium sensitivity by atomic absorption (Varian Techtron, 1970), provided sufficient potassium was present to suppress ionization. However, that sensitivity did not appear quite adequate for rock samples, so emission measurements were made, using the emission chopper and the wavelength scanner. These tests revealed that at a sample concentration of 0.5 g per 50 ml, in the presence of about 800 micrograms of potassium per ml, cesium could probably be determined at a level corresponding to a fraction of 1 ppm in the original rock. On the other hand, attempts at improving sensitivity by the addition of methanol were unsuccessful (both in absorption and emission). It was also found that the 10-cm slot burner, designed for absorption work, gave an emission signal, other things being equal, that was 2.5 to 3 times as intense as that observed with the round burner, which was specifically designed for emission work.

A series of tests was then run with rubidium, with a view to comparing the advantages of emission and absorption, the performance of the two photomultipliers (both in emission and absorption) and the behaviour of the three types of burner heads in emission. Rubidium was chosen because its concentration range in rocks, the wavelengths of its most sensitive lines and its sensitivity in the flame were all such as to give some freedom of choice. All tests were performed in the presence of excess potassium, as had been done with cesium.

Results revealed that more stable and reproducible readings were possible by absorption. In using the 7800-angstrom line for rubidium in emission, there was considerable background effect from the "wing" of the nearby strong potassium line, but no such effect was observed with the 7948-angstrom rubidium line. A further disadvantage of the emission measurement is that in scanning across a peak, only an instantaneous reading is obtained, while in absorption it is possible to measure at a fixed wavelength for a finite time, and thereby

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correct for fluctuations. Fassel et al. (1971) remedied the problem by measure-
ing the emission signal of an alloying element in steel at the peak wavelength
for a finite time, and subtracting the "background" reading at the same wave-
length for an "alloy-free" steel - a procedure which is impractical with samples
as variable in composition as rocks. In spite of the general apparent superi-
ority of absorption, emission was favoured in this work because of the superior
sensitivity and the greater flexibility in changing concentration ranges. How-
ever, equally good results were obtained by absorption. Similar effects were
observed with lithium.

An apparent contradiction was observed in comparing the two photo-
multiplier tubes at 7800 angstroms. The R-213 gave a stronger response to
rubidium radiation for a given applied voltage, but the R-406 tube gave more
stable signals and less noise, even with a higher applied voltage. Although
the R-213 can be used, the R-406 gives much better results.

With the 10-cm slot "absorption" burner head in emission, any appar-
ent effect from self-absorption was apparently masked by the fact that emission
calibration curves are seldom straight lines, except at very low concentrations.

Potassium Anomaly

An even more striking effect was observed in comparing the two photo-
multiplier tubes at the potassium wavelength, 7665 angstroms. There, it
appeared that the R-213 tube was more sensitive to potassium emission than was
the R-406, but that the sensitivities were apparently reversed in absorption.
Further, the absorbance vs concentration curve was linear with the R-406 tube,
and curved with the R-213. Again, the apparent contradiction was traced to an
interfering argon line, whose wavelength is close to one half that of the potas-
sium line. Had the potassium lamp been filled with neon instead of argon, the
effect would probably not have been observed, and either tube would have been
satisfactory for atomic absorption measurements.

Chemical Tests for Lithium, Rubidium and Cesium

The aim of this investigation was to develop a chemical procedure
which would produce a solution suitable for the determination of lithium, rubid-
ium and cesium, preferably at the same sample dilution level. It was assumed
that the concentration ranges would be 0-50 ppm for lithium, 0-500 ppm for
rubidium and 0-5 ppm for cesium. However, it was realized that any of the con-
centration ranges could be extended upward, either by dilution, or by reducing
the sensitivity of instrumental response - a simple operation in emission
measurements.

Preliminary experiments indicated that matrix effects were inevitable,
but that there were no mutual interference effects between the three elements
under study as each was varied over the ranges indicated. The earlier lithium
method (Abbey, 1967) used a solution containing 0.5 g of sample per 25 ml to
provide sufficient sensitivity. At that concentration, there was evidence of
the existence of a "general matrix effect" - i.e. the total salt concentration
appeared to affect the atomization process, and a standard-addition technique
was used to overcome the effect. However, in the zinc method (Abbey, 1967),
the sample solution is only half as concentrated, and there appears to be little,
if any, such effect. With rubidium and cesium, addition of potassium (or some
other easily ionized cation) was known to be needed to suppress ionization, so
it was necessary to work at a lower sample concentration. However, by using
the superior sensitivity of the emission system, it was possible to retain ade-
quate sensitivity at the lower sample concentration.

The tendency of rubidium and cesium to ionize in the flame can be
affected by variation in the concentrations of other easily ionized metals in

the sample. Such elements and the others could affect the overall salt concentration, and possibly introduce additional interterences which are not readily explained. A few simple tests confirmed these effects. One test, using a solution containing, simultaneously, the expected maximum amounts of calcium, magnesium and iron, showed a drastic drop in sensitivity for the three rarer alkali metals, and gave very low and erratic readings. Increased viscosity, brought about by the high salt concentration, was the probable cause.

An attempt was then made to apply Horstman's (1956) separation scheme, together with a modified version of Ingamells (1962) photometric technique, in which the effect of interferences from other elements is compensated by bringing them up to a fixed level. In Ingamells' work, magnesium is present in large excess, having been added in the chemical separation scheme, calcium and most other major rock components are absent, and sodium has little effect. In this work, following the Horstman separation, only the original magnesium, sodium and potassium contents of the sample would still be present. These can be determined on a small aliquot by atomic absorption.

Three of the U.S.G.S. reference rocks, basalt BCR-1, granite G-2 and granodiorite GSP-1, were carried through the Horstman separations. Sodium, potassium and magnesium were determined on aliquots of the final solutions by atomic absorption. Sufficient sodium, potassium and magnesium were then added to the sample solutions to bring their concentrations to the equivalent of 6 per cent Na_2O, 8 per cent K_2O and 10 per cent MgO in the original samples, and lithium, rubidium and cesium determined by flame emission, using standard solutions containing the same concentrations of the three major elements. Results, shown

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Table I

Horstman Separation and Modified Ingamells Photometry

Sample		Li, ppm	Rb, ppm	Cs, ppm
BCR-1	expected*	16	51	1.6
	found	9	28	0.3
G-2	expected	34	170	1.3
	found	29	121	1.4
GSP-1	expected	34	270	1.6
	found	22	202	1.2

*See text

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in Table I, were generally low, suggesting incomplete recovery of the "trace" alkali metals in one or both of the precipitation steps. The "expected" values in Table I were derived as follows: Using all of the data listed by Flanagan (1969) and as much additional material as possible from more recent publications, the mean value for each element in each sample was calculated. The 20 per cent of the available values for each component that were farthest removed from the mean were then rejected, new means calculated and these new means used as "expected" values.

The major elements separated in the Horstman scheme are aluminum, iron and calcium. The former two were thought to have little effect on the elements being determined, while calcium could readily be determined in the same way as were sodium, potassium and magnesium. It was then decided to eliminate the entire tedious chemical separation scheme, and to try to do the analysis on the "whole sample" solution. To further simplify the solution chemistry, perchloric acid was used instead of sulphuric, to take advantage of the generally higher solubilities of perchlorates (except in the cases of potassium, rubidium and cesium).

In this case, the three U.S.G.S. rocks were used again, but this time, as a further check on recovery and reproducibility, the samples were weighed out in duplicate and amounts of the three elements were added to some of the duplicates. After their sodium, potassium, calcium and magnesium contents were adjusted to match those of a set of standard solutions, the sample solutions were analyzed for lithium and cesium by flame emission, and for rubidium by flame emission and atomic absorption. The results, shown in Table II, are much better than those in Table I, but there is still a small but persistent negative bias. Perhaps more important is the fact that recoveries of the added amounts are low, with one exception (Cs in GSP-1), averaging 99 per cent for lithium, 94 per cent for rubidium and 97 per cent for cesium. If the recoveries of the added amounts are used to calculate correction factors, as in a standard-addition method, the rubidium results become more acceptable, but those for lithium and cesium are still not quite good enough.

Table II

No Chemical Separations - Modified Ingamells Photometry

Sample		Li, ppm FE*	Rb, ppm FE	Rb, ppm AA*	Cs, ppm FE
BCR-1 + 500 ppm Rb	expected*	16	549	549	1.7
	found	11	518	508	1.3
BCR-1 + 50 ppm Li + 5 ppm Cs	expected	66	49	49	6.2
	found	60	42	45	5.6
G-2 + 50 ppm Li	expected	84	170	170	1.5
	found	81	161	164	1.4
G-2 + 500 ppm Rb + 5 ppm Cs	expected	34	670	670	7.0
	found	31	626	649	6.6
GSP-1 + 5 ppm Cs	expected	34	260	260	6.4
	found	28	258	250	5.8
GSP-1 + 500 ppm Rb + 50 ppm Li	expected	84	760	760	1.9
	found	77	730	695	1.2

*"Expected" values have been corrected for impurities in the added salts.

FE - flame emission   AA - atomic absorption

The question is then: What is the cause of these discrepancies? Four major elements - sodium, potassium, magnesium and calcium - have been carefully matched between samples and standards. Of the remaining major elements, BCR-1 contains about five times as much iron as does G-2, and about three times as much as does GSP-1, yet there seems to be little difference in the negative bias between the three samples. Perhaps aluminum is causing the difficulty, because it is present to roughly the same extent in all three samples.

Three conclusions could now be drawn:
    (a) Potassium addition to sample and standards is essential to reduce ionization of rubidium and cesium.
    (b) Chemical separations are time-consuming and can lead to losses.
    (c) Matrix effects are unavoidable.

Rather than complicating the method further by introducing more deter-minations and additives, it was decided to fall back on the idea of standard-addition to overcome matrix effects, at the same time retaining the potassium

addition. The procedure which produced more acceptable results (given in Table III) was as follows: Duplicate half-gram samples were decomposed by hydrofluoric-nitric-perchloric treatment and the resulting solutions transferred to 50-ml volumetric flasks. To one of the duplicates were added sufficient standard solutions equivalent to an additional 50 ppm Li, 500 ppm Rb and 5 ppm Cs (in terms of the original sample weight), followed by a potassium addition equivalent to 8 per cent K in the sample. After dilution to volume, the solutions were analyzed for the three elements by comparison with standard solutions containing only varying amounts of the three elements being determined and the fixed quantity of potassium, equal to that added to the samples. Thus the sample solutions actually contain more potassium than do the standards, by the amount originally present. However, the error thereby introduced, if any, is apparently compensated in the standard-addition. In the final calculation, the apparent difference in concentration between the "spiked" and "unspiked" solutions for each element is used to calculate the correction factor to apply to the apparent concentration in the "unspiked" solution, to get the final results. In actual analysis of a series of samples of varying composition, the correction factors were essentially constant (±3 per cent of the amount present for rubidium, ±5 per cent for lithium and cesium). Concentration of major elements in those samples varied from 14 to 17 per cent Al_2O_3, 1 to 12.5 per cent Fe_2O_3 (including FeO, recalculated to Fe_2O_3), 0.5 to 6.5 per cent MgO, 1 to 10 per cent CaO, 0.5 to 4 per cent Na_2O and 0.5 to 4 per cent K_2O. Thus if correction factors can be established on a series of samples of known

Table III

Standard Addition Method

Sample		Li, ppm	Rb, ppm	Cs, ppm
AGV-1	expected	14	70	1.2
	found	11	66	1.2
BCR-1	expected	16	49	1.0
	found	14	47	1.0
G-2	expected	34	170	1.3
	found	31	170	1.4
GSP-1	expected	34	260	1.0
	found	28	250	1.0

All measurements by flame emission in the presence of 800 micrograms of potassium per ml (or more).

composition, they can then be used on subsequent samples whose compositions fall within the same range, the standard-additions can be omitted, and the samples need no longer be weighed out in duplicate.

Determination of Some Major Elements

If necessary, determination of such major elements as total iron, magnesium, calcium, sodium and potassium can be incorporated in the analytical scheme as follows: The sample solutions are diluted to volume in their 50-ml volumetric flasks, without the potassium addition. A 1-ml pipette is rinsed by withdrawing about 1 ml of one sample solution and discarding it. A 1-ml aliquot of the duplicate sample solution is transferred with the same pipette to a 100-ml volumetric flask, strontium is added, the solution diluted to volume and any of the five major elements determined by atomic absorption (Abbey, 1968).

The potassium additive required for determination of the three minor alkalis is then introduced as 1 ml of solution, added to both of the original 50-ml volumetric flasks. A correction is applied for the 1 ml of sample solution removed, and for the fraction of standard addition also lost. The small error introduced, in that the volume of solution removed is not necessarily exactly 1 ml, may be ignored.

Determination of Barium and Strontium

These elements are generally present in rocks at a higher concentration than lithium, rubidium and cesium. Sensitivities of the two alkaline earth metals are high enough (Amos and Willis, 1966) in the nitrous oxide-acetylene flame to permit their determination in a diluted portion of the solution prepared for the three minor alkalis.

Increased sensitivity in the hotter nitrous oxide-acetylene flame (relative to the air-acetylene flame) is not a universal rule, nor is it always easily explained. Amos and Willis report a two-fold sensitivity decrease for magnesium, a four-fold increase for calcium, a three-fold increase for strontium and a twenty-five-fold increase for barium. Although temperature alone may account for much of the increased sensitivity for calcium and strontium, the very large increase for barium is more difficult to explain. Soanes (1967) reported that in the air-acetylene flame, barium absorption at its most sensitive wavelength, 5535.5 angstroms, may be masked by CaO bands, calcium normally being present where barium determination is required. In the hotter flame, oxides are more effectively decomposed, permitting more sensitive barium absorption. This explanation would not be valid where calcium is not present.

Table IV

Determination of Barium and Strontium

Sample		Ba, ppm	Sr, ppm
AGV-1	expected	1220	680
	found	1250	700
BCR-1	expected	710	330
	found	680	310
G-2	expected	1840	480
	found	1900	430
GSP-1	expected	1340	260
	found	1380	220

A major advantage of the nitrous oxide acetylene flame is its power to decompose the "inter-oxide" compounds which cause the "chemical interference" of aluminum, silicon, sulphur and phosphorus in the determination of magnesium and the alkaline earths. This advantage has been confirmed experimentally in this laboratory (Abbey, 1970) and elsewhere (Nesbitt, 1965) for calcium and magnesium. However, simple tests conducted here with synthetic solutions in the nitrous oxide-acetylene flame revealed that the equivalent of 20 per cent Al_2O_3 in a sample caused appreciable depression of both the strontium and barium absorption, a condition which could not be remedied by varying flame parameters. A similar effect was reported by Berthelay and Roubault (1969). Addition of lanthanum, equivalent to 1 gm of La_2O_3 per 100 ml, entirely eliminated the effect.

Ionization of strontium and barium in the nitrous oxide-acetylene flame may easily exceed 80 per cent (Amos and Willis, 1966). Thus additional potassium must be added on diluting the original sample solution before determining barium and strontium. The same amount of potassium is added to the standard solutions. The small additional amount of potassium carried over in the sample solution from the original solution for the three minor alkalis has no measurable effect on the alkaline earths. No other matrix effects were observed, hence standard additions were not required.

For the normal concentration ranges in rocks, barium and strontium can be determined in solutions containing 100 mg of sample per 50 ml. Barium requires a roughly three-fold scale expansion. Results are given in Table IV.

Some attempts were made to determine these elements by flame emission. Both showed improved sensitivity relative to atomic absorption, but background was high and noisy, and readings were erratic. Both effects were much more pronounced with barium than with strontium.

SUMMARY AND CONCLUSIONS

By utilizing both flame emission and atomic absorption, two types of photomultiplier tubes, and two different gas mixtures, it is possible to determine the three minor alkali metals, the two minor alkaline earths and five of the major elements on a solution prepared from a half-gram sample of most silicate rocks. In some cases, duplicate weighings and standard-additions are required for the alkali metals. The best results were obtained with the simplest procedure, involving no chemical separations. Satisfactory explanations were found for anomalous spectroscopic effects observed with potassium and cesium. A releasing agent was found to be necessary to overcome the unexpected chemical interference of aluminum in barium and strontium determinations in the nitrous oxide-acetylene flame.

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.

Abbey, Sydney, and Maxwell, J.A.
    1960:   Determination of potassium in micas; *Chem. Can.*, vol. 12, No. 9,
             pp. 37-41.

Amos, M.D., and Willis, J.B.
    1966:   Use of high-temperature pre-mixed flames in atomic absorption
             spectroscopy; *Spectrochim. Acta*, vol. 22, pp. 1325-1343.

Berthelay, Jean-Claude, and Roubault, Marcel
    1969:   L'analyse des roches par spectrophotométrie de flamme (émission,
             absorption atomique); *C.R. Acad. Sc. Paris*, tome 269, série D,
             pp. 1807-1810.

Fassel, V.A.
    1969a: Atomic absorption spectroscopy - present status and future prospects; 52nd Can. Chem. Conf., Montreal.

    1969b: Critical evaluation of the analytical capabilities of flame atomic emission and absorption spectroscopy; Internat. Atom. Absorption Conf., Sheffield.

Fassel, V.A., Slack, R.W., and Knisely, R.N.
    1971:   Flame emission spectrometric determination of aluminum, cobalt, chromium, copper, manganese, niobium and vanadium in low and high alloy steels; *Anal. Chem.*, vol. 43, pp. 186-191.

Flanagan, F.J.
    1969:   U.S. Geological Survey standards - II. First compilation of data for the new U.S.G.S. rocks; *Geochim. Cosmochim. Acta*, vol. 33, pp. 81-120.

Hara, Tadashi
    1959:   Reagents for the separation and determination of potassium, rubidium and cesium; *Bull. Inst. Chem. Res. Kyoto Univ.*, vol. 37, pp. 112-119.

Horstman, E.L.
    1956:   Flame photometric determination of lithium, rubidium and cesium in silicate rocks; *Anal. Chem.*, vol. 48, pp. 1417-1418.

Ingamells, C.O.
    1962:   Determination of major and minor alkalies in silicates by differential flame spectrophotometry; *Talanta*, vol. 9, pp. 781-793.

Ingamells, C.O., Suhr, N.H., Tan, F.C., and Anderson, D.H.
    1971:   Barium and strontium in silicates. A study on the development of analytical methods; *Anal. Chim. Acta*, vol. 53, pp. 345-360.

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

    1970:   Determination of rubidium in silicate materials by atomic absorption spectrophotometry; *Chem. Geol.* vol. 6, pp. 143-148.

Mountjoy, W., and Wahlberg, J.S.
    1968:   Determination of micro amounts of cesium in geologic materials; *U.S. Geol. Surv.*, Prof. Paper 600B, pp. B119-B122.

Nesbitt, R.W.
    1966:   Determination of magnesium in silicates by atomic absorption spectroscopy; *Anal. Chim. Acta*, vol. 35, pp. 413-420.

Osterried, O.
    1963:   Flame-photometric determination of small amounts of cesium in silicates after concentration on zirconium phosphate ion-exchange material; *Z. Anal. Chem.*, vol. 199, pp. 260-270.

Pencheva, E.N., and Stoyanova, T.G.
    1965:   Spectrochemical determination of low contents of rubidium and cesium in rocks, minerals and natural water; *Revue roum. Chim.*, vol. 10, pp. 741-744.

Prudnikov, E.D.
    1965:   Flame-photometric determination of alkali metals; *Zh. analit. Khim.*,
             vol. 20, pp. 1248-1249.

    1966:   Determination, in a flame, of traces of lithium, rubidium and
             cesium; *Zh. analit. Khim.*, vol. 21, pp. 1015-1016.

Prudnikov, E.D., and Shapkina, Yu. S.
    1970:   Flame-spectrophotometric microdetermination of trace quantities
             of lithium, rubidium and cesium; *Zh. analit. Khim.*, vol. 25,
             pp. 250-252.

Rubeska, I., and Moldan, B.
    1965:   Rubidium- und Cësiumbestimmung in Silicaten mittels
             Flammenphotometrie; *Collection Czech. Chem. Commun.*, vol. 30,
             pp. 1731-1735.

Soanes, R.S.
    1967:   Personal communication.

Varian-Techtron Pty. Ltd.
    1970:   Hollow Cathode Lamp Data, p. 5.

Zacek, H.
    1968:   Abstract of Prudnikov (1966); *Anal. Abstr.*, vol. 15, abstr. 3164.

APPENDIX

Operating Procedures

Special Reagents

1. Standard Lithium (50 µg Li/ml)

    Dissolve sufficient lithium carbonate (A.D. MacKay or equivalent) in a
    slight excess of dilute HCl, evaporate to remove excess acid and dilute
    to an approximate concentration of 2500 µg Li/ml (Note a). Dilute a suffi-
    cient volume to a concentration of 250 µg/ml, and a portion of that solu-
    tion to 50 µg/ml.

2. Standard Rubidium (250 µg Rb/ml)

    Dissolve sufficient rubidium chloride (SPEX or equivalent) (Note b) in
    water and dilute to an approximate concentration of 2500 µg Rb/ml (Note a).
    Dilute a portion of the solution to 250 µg/ml.

3. Standard Cesium (5 µg Cs/ml)

    Prepare from cesium chloride (SPEX or equivalent) at an initial concentra-
    tion of approximately 2500 µg Cs/ml (Note a) and dilute successively to
    250 µg/ml, 25 µg/ml and 5 µg/ml.

    Note   a   The above solutions must be standardized by evaporating a small por-
                 tion of the approximately 2500 µg/ml solution with a slight excess
                 of sulphuric acid, fuming to dryness and igniting to constant weight
                 at 800°C. The weight of sulphate found is used to calculate how much
                 of the "2500 µg/ml" solution to use to produce the 250 µg/ml solution.

    Note   b   The cesium impurity in the rubidum chloride may be high enough to
                 affect the actual cesium contents of the mixed standards described
                 below. The cesium in the rubidium solution may be determined by
                 running a standard-addition series under the conditions of actual
                 analysis (see below) keeping rubidium concentration fixed at the
                 maximum value and potassium at the same concentration as used in
                 analysis. This test should be repeated for every new bottle of
                 rubidium chloride. (SPEX rubidium chloride was found to have a
                 Cs:Rb ratio of 1:1000, and this correction has been applied in
                 Table V.)

4. Standard Barium (100 µg Ba/ml)

    Prepare by dissolving sufficient barium carbonate (Johnson-Matthey or
    equivalent)(Note c) in a small excess of HCl, evaporate to remove excess
    acid and dilute to a concentration of 100 µg Ba/ml.

5. Standard Strontium (100 µg Sr/ml)

    Prepare in the same way as for barium, using strontium carbonate (Johnson-
    Matthey or equivalent)(Note c), with the final concentration 100 µg Sr/ml.

    Note   c   With "spectroscopically pure" barium and strontium carbonates, there
                 is no need for standardization, nor for corrections for impurities.

6. Potassium Buffer

    Dissolve 7.63g KCl in water and dilute to 100 ml (Note d).

    Note   d   Reagent grade KCl may contain traces of rubidium, but their effect
                 is compensated by adding the same quantity of KCl to both sample and
                 standard solution. Barium and strontium impurities in KCl are
                 generally too low to have any effect.

7. **Mixed Standard Solutions** (Li–Rb–Cs)

Into six 250-ml volumetric flasks, measure 5 ml of potassium buffer solution. Then add:

Volumetric Flask No.	Standard Li (Soln. 1) ml	Standard Rb (Soln. 2) ml	Standard Cs (Soln. 3) ml
1	5.0	2.0	3.0
2	4.0	6.0	0.0
3	3.0	10.0	4.0
4	2.0	0.0	1.0
5	1.0	4.0	5.0
6	0.0	8.0	2.0

Finally, add 10 ml concentrated HCl to each and dilute to volume. Resulting concentrations are given in Table V.

8. **Lanthanum Buffer**

From a well-mixed bottle of lanthanum oxide, weight 30 g into a 400-ml beaker and 0.5 g (accurately weighed) into a 30-ml platinum crucible. Ignite the 0.5 g portion to constant weight at 800°C and use the weight loss to determine the true La_2O_3 content of the 30 g portion. Cover the 30 g with water, add 50 ml HCl, in small portions, to dissolve the lanthanum oxide. Finally dilute to a concentration of 5 g La_2O_3 per 100 ml.

9. **Mixed Standard Solutions** (Ba–Sr)

Into six 250-ml volumetric flasks, measure 10 ml potassium buffer solution, then add:

Volumetric Flask No.	Standard Ba (Soln. 4) ml	Standard Sr (Soln. 5) ml
1	15.0	5.0
2	12.0	12.5
3	9.0	2.5
4	6.0	0.0
5	3.0	7.5
6	0.0	10.0

Finally, add 50 ml lanthanum buffer solution to each and dilute to volume. Resulting concentrations are given in Table VI.

Sample Treatment

Weigh 0.5 g sample into a 100-ml platinum dish (in duplicate if standard-addition method is to be used). Add 5 ml nitric acid, 2 ml perchloric acid and 5 ml HF. Evaporate to perchloric fumes.

Cool, rinse down the dish walls with a little water and evaporate until no further perchloric fumes are produced. Cool, add 2 ml HCl, rinse down the dish walls with a little water, swirl to dissolve and evaporate to dryness. (Note e)

Table V

Mixed Standards for Lithium, Rubidium and Cesium

Flask No.	µg/ml solution			ppm in sample (0.5 g in 50 ml)		
	Li	Rb	Cs*	Li	Rb	Cs*
1	1.0	2.0	0.062	100	200	6.2
2	0.8	6.0	.006	80	600	0.6
3	0.6	10.0	.090	60	1000	9.0
4	0.4	0.0	.020	40	0	2.0
5	0.2	4.0	.104	20	400	10.4
6	0.0	8.0	.048	0	800	4.8

*Corrected for Cs impurity in SPEX RbCl. See text.

Table VI

Mixed Standards for Barium and Strontium

Flask No.	µg/ml solution		ppm in sample (0.1 g in 50 ml)	
	Ba	Sr	Ba	Sr
1	6.0	2.0	3000	1000
2	4.8	5.0	2400	2500
3	3.6	1.0	1800	500
4	2.4	0.0	1200	0
5	1.2	3.0	600	1500
6	0.0	4.0	0	2000

Note e   A white residue after sample decomposition suggests the presence of
barium sulphate. In that case it should be removed by filtration
and washed with warm dilute HCl (ca. 1 N), before the evaporation
to dryness with HCl. If barium is not to be determined, the residue
may be discarded. Otherwise it must be fused with about four times
its weight of sodium carbonate. The cooled fusion is leached with
warm water, filtered on a small, fine-porosity paper, and washed with
hot sodium carbonate solution. The sulphate-bearing leachate is
discarded, and the barium carbonate residue on the filter dissolved
by passing through successive small portions of warm HCl (ca. 1 N).
The resulting solution is combined with the main solution, and all
evaporated to dryness. Further modification of the sample decomposi-
tion technique may be necessary with samples containing unusual con-
centrations of other components.

Add 2 ml HCl (pipette), rinse the dish walls with 20-30 ml water, swirl
to dissolve (warm if necessary) and transfer to a 50-ml volumetric flask.

If the standard-addition is to be used, add to one of the duplicate
solutions: 0.5 ml standard Li (50 µg/ml), 1.0 ml standard Rb (250 µg/ml) and
0.5 ml standard Cs (5 µg/ml). If the Cs:Rb ratio in the rubidium solution is
1:1000, these correspond to an additional concentration, in the final 50-ml

volume, of 0.50 µg Li/ml, 5.0 µg Rb/ml and 0.055 µg Cs/ml. On a 0.5-g sample, these additions correspond to an additional 50 ppm Li, 500 ppm Rb and 5.5 ppm Cs.

Add 1 ml potassium buffer solution (pipette) to both "spiked" and "unspiked" sample solutions and dilute to volume. (Note f)

Note f   If determination of such major elements as Fe, Mg, Ca, Na and/or K is required, dilute the sample solutions to volume without adding the potassium buffer. Using a clean 1-ml pipette (as dry as conveniently possible), withdraw 1 ml of the solution of the first duplicate sample and discard that 1 ml as a pipette rinse. Without further rinsing of the pipette, withdraw 1 ml of the second duplicate solution and transfer to a 100-ml volumetric flask. To that flask, add 10 ml of a solution containing 15000 µgm Sr per ml in 1.2N HCl, dilute to volume and determine the required major elements by atomic absorption, using standard solutions prepared from pure reagents (Abbey, 1968) or from international reference samples (Abbey, 1970). To each remaining sample solution in the 50-ml volumetric flasks, add 1 ml potassium buffer solution. In the final calculations, a correction must be made, each "spike" having been reduced by 2 per cent, as has the weight of sample being analyzed.

If barium and strontium are to be determined, pipette 10 ml of one of the duplicate sample solutions into another 50-ml volumetric flask. Add 2 ml potassium buffer solution, 10 ml lanthanum buffer solution and dilute to volume.

Flame Measurements

Operating parameters are given in Table VII. The usual precautions are necessary in using the nitrous oxide-acetylene flame. Details are given in Part 3 of this series (Abbey, 1970), for use with the equipment used in developing these methods. Modifications will be required for other types of equipment.

In all emission measurements, use a wavelength scan speed of 40 A/minute, starting the scan at 8-10 angstroms above the expected peak, and stopping when the recorder returns to a stable base line (or a minimum). All emission readings should be made with a recorder. Damping and "backing" may be used, as required, to provide a readable signal. If automatic base-line correction is used in atomic absorption measurements, occasional checks must be made to detect wavelength drift.

In determining each element, leave air pressure constant at 18 psi (or nitrous oxide at 15 psi), but vary the acetylene pressure and the burner position to provide maximum signal (remembering that the red "feather" must never be allowed to disappear from the nitrous oxide-acetylene flame). These adjustments are made with a "high" standard solution in the flame.

In emission measurements (except for cesium), amplifier gain should be adjusted to give a signal of 80-90 scale divisions for the highest standard. For cesium, the HIGH GAIN range is used, together with full COARSE GAIN and full FINE GAIN, except for samples containing abnormally high cesium concentrations.

For barium measurements by atomic absorption, scale expansion is necessary, except where abnormally high concentrations are present.

For samples falling outside the concentration ranges of the mixed standards, corresponding new mixed standards should be prepared.

If potassium is determined by atomic absorption, readings should be made with the R-406 photomultiplier tube.

In determining lithium, rubidium, cesium, barium and strontium, readings are taken in the following sequence: For each element, the mixed standard

solutions are read in order of descending concentration of the element being determined. Sample solutions are interspersed among the standards, close to those of similar concentration (if known approximately). The operation is then repeated, but this time each sample solution is read between the two standard solutions containing a little more and little less of the element being determined. Calibration curves are plotted for both runs, and values for the sample solutions derived from the curve plotted on the same run.

Where the standard-addition method is used, determine the mean apparent concentration of the element concerned, treating "spiked" and "unspiked" sample solutions as separate samples. Divide the actual concentration difference between "spiked" and "unspiked" by the apparent concentration difference, to get the correction factor. Multiply the apparent concentration of the "unspiked" sample solution by the corresponding correction factor to get the final result.

Table VII

Operating Parameters

Element	Absorb. or Emis.	Lamp Current mA	Range* ppm/sample	Sample mg/50ml	K µg/50ml	La_2O_3 mg/50ml	Flame**	Slit µ	Wave-length Å	Photo-multiplier
Rb	A	15	0-500	500	800	0	Air-C_2H_2	200	7800	R-406
	E	--	0-500	500	800	0	Air-C_2H_2	200	7948	R-406
Li	A	5	5-150	500	800	0	Air-C_2H_2	200	6708	R-213
	E	--	0-50	500	800	0	Air-C_2H_2	200	6708	R-213
Cs	E	--	0-5	500	800	0	Air-C_2H_2	300	8521	R-406
Ba	A	10	0-3000[o]	100	1600+	500	N_2O-C_2H_2	100	5536	R-213
Sr	A	8	0-2500	100	1600+	500	N_2O-C_2H_2	100	4607	R-213

* Burner may be angled where required to reduce sensitivity. Amplification may be varied to extend range (emission only).

** Lens mask used with N_2O-C_2H_2 flame.
[o] Scale expansion (about 3X) required.