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ARTICLE *in* ANALYTICAL CHEMISTRY · DECEMBER 1966

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D.C. Arc Spectrographic Technique for Determination of Trace Amounts of Lithium, Rubidium, and Cesium in Silicate Rocks

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► A d.c. arc spectrographic technique has been developed for estimation of trace amounts of Rb, Cs, and Li in silicate rocks using a Jarrell-Ash 3.4-meter plane grating spectrograph and a red filter to remove 2nd- and 3rd-order interferences on the alkali element emission lines. The presence of calcium fluoride in the arc enhances the intensity of all the alkali metal lines, most markedly for lithium. Precautions must be taken to avoid cyanogen interference on the lines Cs 8521 Å. and Li 8126 Å. Determination of the optimum operating conditions has enabled a detection limit of 0.1 p.p.m. or less for each element. The accuracy and precision of the method appear satisfactory.

GEOCHEMICALLY, the determination of the trace alkali metals lithium, rubidium, and cesium has always been of great importance, and accurate values for certain types of naturally occurring basic silicate rocks are of especial interest at the present time. The data have relevance to problems concerning fractionation within the earth's crust and between the upper mantle and the crust. The distribution of lithium is almost entirely distinct from the other alkali metals on account of its small size (radius 0.68 Å.) and ability to replace Fe^{+2} and Mg^{+2} in certain ferromagnesian minerals. Rubidium has a very close relationship with potassium, which has been used, in terms of the K/Rb ratio, to follow processes of fractionation within a differentiated suite of samples. Cesium has a similar but less developed relationship with potassium, the difference being due to the larger size of the cesium ion compared with rubidium or potassium. A full review of the geochemistry of the alkalis has been given by Heier and Adams (8).

A comprehensive investigation has been carried out in order to develop a d.c. arc emission spectrographic procedure for the determination of these three trace elements in basic and ultrabasic rocks. The concentration ranges (p.p.m.) for which we required this method were:

Li	1-20
Rb	0.1-25
Cs	0.1-10

Previous work on these elements using the direct emission d.c. arc technique has usually been carried out using the glass optics of a prism spectrograph. The dispersion of a glass prism in the wavelength range of the spectrum in which the most sensitive alkali lines appear is extremely poor (40 Å. per mm.). The optical system also has other inherent defects. The net result is a procedure in which poor line shape, possible interferences, and bad background characteristics militate against obtaining accurate and precise results at low levels of concentration. The detection limits (1) quoted for instruments of this type are:

Li	0.5 p.p.m.
Rb	1.0 p.p.m.
Cs	2.0 p.p.m.

The quoted detection limit for Li would be satisfactory for our purposes were it not for the fact that the most sensitive line of lithium (6707 Å.) is liable to show self-absorption at concentrations greater than 5 p.p.m. The next most sensitive lithium line, Li 6103.6, is interfered with by Ca 6102.7 in a glass prism spectrograph. The only other lithium line in the red or infrared region of the spectrum, Li 8126, is normally too insensitive. The quoted detection limits for rubidium and cesium were clearly not satisfactory for our purposes.

DETAILS OF ANALYTICAL PROCEDURE

The method outlined here has been proved capable of determining lithium, rubidium, and cesium at concentrations as low as 0.1 p.p.m. The method is a d.c. arc technique involving no enrichment procedures. It is carried out on a Jarrell-Ash 3.4-meter plane grating spectrograph using the Spex Industries red filter (Catalog No. 9023 R) which eliminates possible second- and third-order interferences in the red and infrared regions.

Potassium is used as a variable internal standard, determined previously in each sample by a suitable method such as flame photometry or x-ray fluores-

cence. The spectral lines used are Li 8126 Å., Rb 7947 Å., Rb 7800 Å., and Cs 8521 Å. Li 6707 Å. can be used in samples containing extremely low concentrations of lithium. Previous work in this region on a grating spectrograph has been reported by Annell (5), who obtained a detection limit of 1 p.p.m. of cesium in tektites.

The optimum arcing conditions are summarized in Table I. However, several points are discussed here in some detail.

Electrodes. Wide ranges of type and size of electrode were investigated in an attempt to improve sensitivity

Table I. Optimum Arcing Conditions

Spectrograph	Jaco 3.4-meter plane grating spectrograph. Dispersion 5 Å./mm.
Filter	Spex Industries filter 9023 R
Excitation Wavelength	Anode excitation 6400 to 8900 Å.
Lens system	Three lens system to give maximum intensity with uniform illumination
Current	7.5 amperes d.c.
Slit	30 microns
Plate	Kodak I - N plate, backed (plate cut in two pieces)
Electrodes	Anode, National Carbon Co. regular graphite (L 4306). Cavity 3.15 × 6 mm. Wall thickness 0.8 mm. Cathode, morganite carbon
Electrode packing	Sample depth 5 mm.
No. of superimposings	As required (Three superimposings will give a detection limit of 0.1 p.p.m. for all three elements)
Sectoring	Hilger 7 step sector with 2:1 ratio
Buffer/carrier	20% CaF_2 (B.D.H. extra pure)
Internal standard	K 6939 Å.
Analysis lines	Rb 7800, 7974 Å. Li 8126, 6707 Å. Cs 8521 Å.
Developer	Kodak D 19b developer (5 minutes)
Fixer	Amfix ultrarapid fixer (5 minutes)
Calibration	Self-calibration method (3)

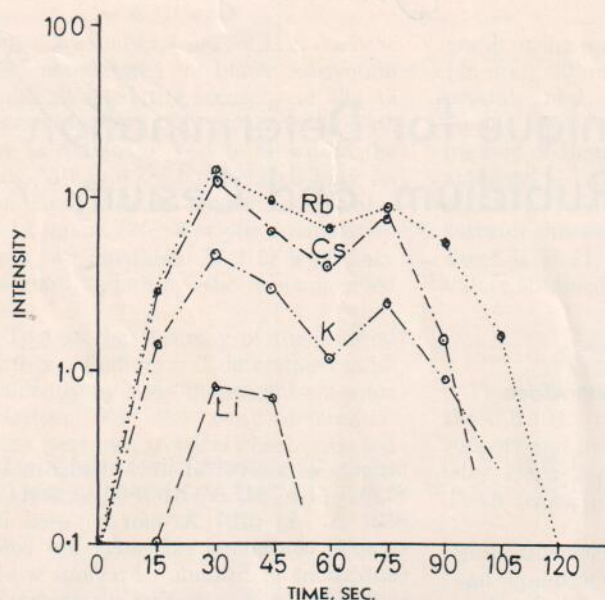


Figure 1. Moving plate study for pure sample

and precision. Electrodes with cavity sizes from 2.3×2.5 mm. to 4×8 mm. (carrier-type electrode) were used. Increase in capacity generally improved the line intensity of the alkalis. However, this was offset by a loss in precision when using the larger electrodes due to the erratic behavior of the arc. Scribner-Mullin carrier-type electrodes were more stable, but excessive cyanogen interference arising from burning of the walls of the electrode caused interference on Cs 8521 and Li 8126. Interference on Rb 7947 has been reported (4), but the other interferences have not been mentioned. The use of carbon electrodes as compared with graphite was unsuitable for the same reasons of cyanogen band production. Center post electrodes, undercutting, and varying wall thicknesses were all investigated. Ultimately it was found best to use a conventional type of electrode. Extra sensitivity could be obtained by exposing the photographic recording plate to two or more arcings of the sample—i.e., by superimposing.

The electrode selected had a 3.15×6 mm. cavity size with a wall thickness of 0.80 mm. packed to 1 mm. from the top of the crater. This electrode was large enough to give sensitivity and yet not so large as to introduce excessive arc wander. The superimposing gives added sensitivity when required and improves precision. The only limitation on the number of superimposings is the production of the interfering cyanogen bands with repeated arcings. A detection limit of 0.1 p.p.m. was obtained with three superimposings.

Carriers, Buffers, and Fluxes. A wide variety of buffers, carriers, and fluxes were investigated, with particular attention to their effect on the sensitivity, precision, and accuracy

of the alkali trace element determinations.

Of these two, CaF_2 and SrF_2 , gave encouraging results. Addition of CaF_2 was studied in detail. The presence of this substance in the arc brought about several desirable effects:

The period of distillation of the alkalis was appreciably shortened.

The intensities of all the alkali metal lines were enhanced.

The enhancement was greatest for lithium. This meant that the relatively insensitive line, Li 8126, became a usable analysis line at the concentration levels where the most sensitive line, Li 6707, is almost always self-absorbing.

Figure 1 is a moving plate study for the alkalis obtained for a pure sample. The time interval of the plotted points is 15 seconds. The alkali burn lasts for 2 minutes.

Figure 2 is a moving plate study for the alkalis obtained for the sample used in Figure 1 arced under identical conditions, but mixed with 20% CaF_2 . The time interval was not the same as in Figure 1 and this should be borne in mind when assessing the relative intensities of the lines in Figures 1 and 2. Nevertheless, it can clearly be seen that the distillation period is appreciably shortened, a factor of importance when superimposing several arcings on each other. Figure 2 also illustrates that the end of the alkali burn is followed by a short period in which calcium is the predominant cation distilling into the arc. This is distinguishable easily and is a convenient point at which to end the burn, preventing recording of excess cyanogen, the cyanogen emission being much greater after the end of the alkali phase.

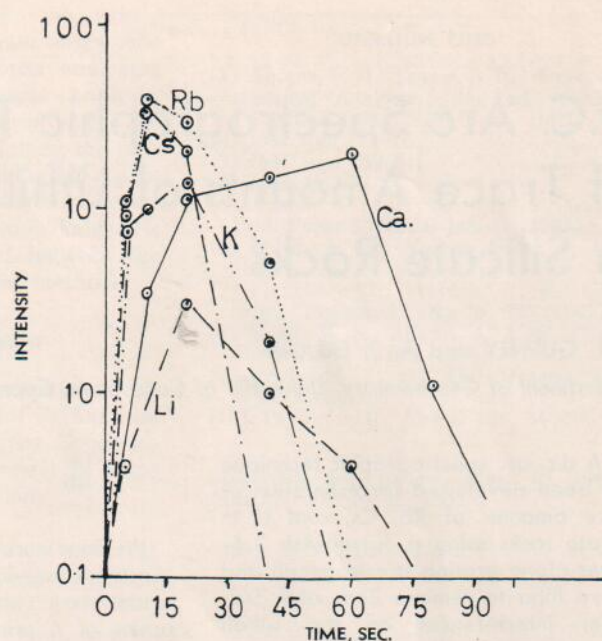


Figure 2. Moving plate study for sample mixed with 20% CaF_2

Figure 3 shows the intensity enhancement effect of calcium fluoride on the alkali metal lines. The diagram shows the relative intensities of the lines obtained when 5, 10, 15, 20, 25, and 50% CaF_2 are added to the sample. These intensities are normalized with respect to those obtained from arcing the pure sample, where the intensity of each line is taken as unity. From this figure the striking enhancement of lithium can be seen. Potassium, rubidium, and cesium are also enhanced by decreasing factors, in that order. The approximate figures for the enhancement are 4 to 5 for Li, 2 for K, and 1.5 for Rb and Cs.

It was decided to add 20% calcium fluoride to each sample. In addition to producing the enhancement effects shown in Figure 3, this amount was also sufficient to act as a conventional buffer in removing matrix effects. The mechanism of the enhancement effects obtained by the use of CaF_2 is not clear.

Cyanogen Interference. Cyanogen interference has been encountered on Cs 8521 and Li 8126 in particular. However, there are several lines in the cyanogen band spectrum close to and slightly greater in intensity than the interfering lines. These lines can be used to indicate whether or not a correction should be made for cyanogen interference.

An attempt was made to arc in an atmosphere free of nitrogen using a Stallwood jet. The only promising results were obtained with argon or argon-oxygen mixtures. However, as there is a line in the argon spectrum at 8521, this work was not pursued further. Helium or helium-oxygen atmospheres suppress the intensity of the alkali lines as well as reducing fractional distillation.

Table II. Experimental Precision

	Rb			Cs			Li		
	a	b	c	a	b	c	a	b	c
Concentration, p.p.m.	2-16	7.3	7.3	0.6-11	2.4	2.4	1-29	15	15
No. of samples	12	1	1	12	1	1	22	1	1
Rock type	Eclogite			Eclogite			Basalt		
Relative standard deviation, %	5.5	4.9	6.0	5.3	4.7	7.7	6.8	7.6	11.2

a = samples arced in duplicate, K internal standard

b = sample arced 12 times, K internal standard

c = sample arced 12 times, no internal standard

Table III. X-Ray and Spectrographic Determinations of Rubidium in Dolerites

Sample no.	Rb, p.p.m.	
	D.c. arc	X-ray
D/S 95	10.4	11
D/S 106	11.4	12
D/S 104	11.9	12
D/S 93	10.7	10
D/S 88	12.1	12
D/S 35	15.6	17
D/S 73	16.0	15
D/S 50	13.1	14
2	9.9	10
7028	13.0	16

The precision of the x-ray fluorescence technique at the concentration level of 10 to 15 p.p.m. Rb does not permit the quoting of a decimal place. The relative standard deviation is of the order of 10%. The emission spectrographic results are the means of replicate analyses.

Standards. Because of the lack of satisfactory natural rock standards at the concentration levels required, synthetic standards were utilized.

A basalt-eclogite base mix was prepared for specially purified natural quartz and Johnson Matthey Specpure chemicals. Oxides of the elements were used except for sodium and calcium, where carbonates were chosen on the grounds of purity, and potassium where the sulfate was added. The base was thoroughly mixed and sintered at 1000° C. for 12 hours to give a product approximating 48% SiO₂, 15% Al₂O₃, 12% Fe₂O₃, 12% MgO, 11% CaO, 1.5% Na₂O, and 0.5% K₂O. Standards were prepared by adding Jarrell-Ash S.Q. powder (containing 1.3% of 45 elements, including Li, Rb, and Cs) to the base mix to give a standard containing 1000 p.p.m. of Li, Rb, and Cs, followed by further dilution of this standard with the base mix, using $\sqrt{0.1}$ as a factor, to give standards containing 31.6, 10.0, 3.2, 1.0, 0.32, and 0.1 p.p.m. (2).

Traces of lithium were present in the quartz used in the base mix and although a blank determination was carried out, difficulty has been experienced in establishing the accuracy of the lithium determinations. Standards and unknown

samples are arced under identical conditions with the same number of superimposings per exposure.

PRECISION AND ACCURACY

The method has been used to determine the Li, Rb, and Cs contents of a variety of eclogites, basalts, and dolerites. Precision, expressed as the relative standard deviation, is indicated in Table II, using data derived by arcing one sample 12 times and by arcing a series of samples in duplicate. Also shown are precision data calculated without the use of K as internal standard, as it is possible to use the method without internal standardization by simply plotting intensity against concentration if the K contents of the samples are not known. The differences in precision between columns *b* and *c* in Table II provide a direct indication of

the efficiency of K as an internal standard. The level of precision obtained by the proposed method may be considered satisfactory and is attributed to the use of K as internal standard, the technique of superimposing three arcings per exposure, the use of an electrode packing machine (Elpac) for filling the electrodes, and the addition of CaF₂ to the sample to promote a more effective distillation of the alkali metals into the arc.

To assess the accuracy of the method, the U. S. Geological Survey standard diabase rock W-1 (7) was analyzed as an unknown sample. Values of 22.8 p.p.m. Rb and 0.8 p.p.m. Cs were obtained. The Rb figure is close to the recommended value of 22 p.p.m., while the Cs figure, although lower than the recommended value (7), agrees with the most recent determination (10) by spark source mass spectrometry. As men-

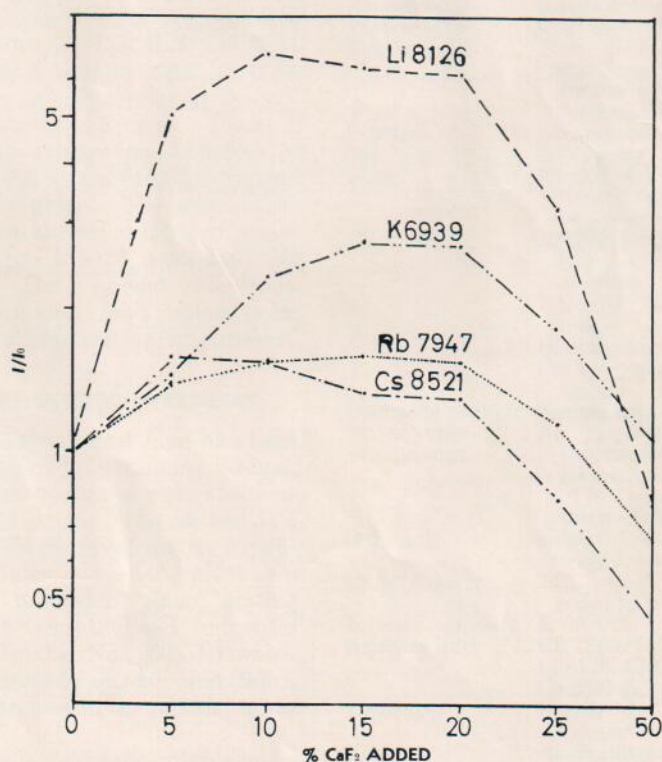


Figure 3. Intensities of alkali lines with increasing addition of calcium fluoride relative to intensities of same lines obtained from pure sample

tioned previously, traces of Li in the base mix necessitated a blank correction which affected the accuracy of the Li determinations. Our analyses indicate the Li content of W-1 to be within the range 10 to 12 p.p.m., which may be compared with the recommended value of 12 p.p.m. (7). For our quantitative work, we have used W-1 as a primary standard, adopting the recommended value.

To test the accuracy of the method further, rubidium was determined independently by x-ray fluorescence in some dolerites. For the x-ray determinations, pure rock powders were briquetted as described by Baird (6) and analyzed in a Phillips PW 1540 vacuum spectro-

graph, using a molybdenum target tube (48 kv., 20 ma.), a topaz analyzing crystal, and pulse height analysis. Results were calculated according to the method of Reynolds (9), using the rock standard G-1 (7), containing 220 p.p.m. of Rb, as reference standard. The results for this test are listed in Table III; there is good agreement between the values obtained by the two methods.

ACKNOWLEDGMENT

The authors express their gratitude to the C.S.I.R. (Pretoria) for its financial support and to L. H. Ahrens, Geochemistry Department, University of Cape Town, for helpful discussions.

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RECEIVED for review May 9, 1966.
Accepted August 29, 1966.