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**The Spectrochemical Determination of
Beryllium and Lithium in Stream Sediments**

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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THE SPECTROCHEMICAL DETERMINATION OF BERYLLIUM AND LITHIUM IN STREAM SEDIMENTS

by

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ABSTRACT

A spectrochemical method was developed to analyze 200 or more samples of stream sediments per day for beryllium and lithium. One part of ground stream sediment is mixed with two parts graphite-SiO₂ buffer, packed into a graphite electrode, and excited in a direct-current arc. The resulting emission goes to a 3.4-m, direct-reading, Ebert spectrograph. A desk-top computer system is used to record and process the signals, and to report the beryllium and lithium concentrations. The limits of detection are 0.2 $\mu\text{g/g}$ for beryllium and 0.5 $\mu\text{g/g}$ for lithium. For analyses of prepared reference materials, the relative standard deviations were 16% for determining 0.2 to 100 $\mu\text{g/g}$ of beryllium and 15% for determining 0.5 to 500 $\mu\text{g/g}$ of lithium. A correction is made for vanadium interference.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) is engaged in the National Uranium Resource Evaluation (NURE) program of the Department of Energy (DOE) to assess more accurately our nation's mineral resources. LASL is responsible for determining the concentrations of 43 elements in water and stream sediment samples from the states of New Mexico, Colorado, Wyoming, Montana, and Alaska. We describe the method of arc-source emission spectroscopy to determine lithium and beryllium concentrations.

II. METHOD DEVELOPMENT

Our goal was to develop a method with a detection limit of 1 $\mu\text{g/g}$ for both beryllium and lithium, that

used a minimum of operator time, and that was relatively insensitive to variations in the sediment sample matrix. From previous experience it was known that certain materials would lower the detection limit, and that dilution of the sample with a common material would decrease the sensitivity to matrix differences. Many different buffer materials and mixtures were tried before a suitable one was found. Because beryllium and lithium do not volatilize from a carbon electrode at the same rate, time-resolved spectra were made and found to be valuable aids in these studies. A computer program was written to give a time history of the signal from each of the spectral lines set on the direct-reading Ebert spectrograph. Appendix A contains the computer program for the time-resolved plots. Typical plots for beryllium and lithium are shown in Figs. 1 and 2.

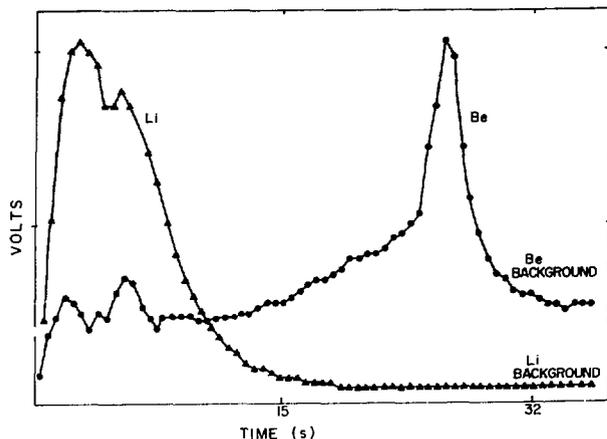


Fig. 1.
Typical time-resolved plots.

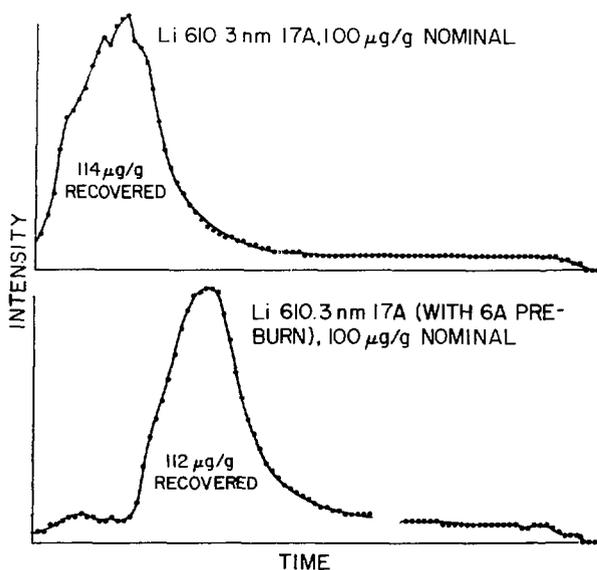


Fig. 2.
Effect of a change in arc current.

A. Spectrograph and Data Processing System

Studies were made using an existing photographic arc-source emission spectrochemical method. Then,

to reduce the operator time, the photographic measurement of line intensity on a 3.4-m Ebert spectrograph was replaced by a photoelectric system. The photographic plate holder was replaced with a sturdy box to hold the exit slits and photomultiplier tubes. To provide thermal stability to the spectrograph, an insulating cover was placed on the outside and the grating and the exit slits were separately regulated to a few degrees above room temperature with a heating tape and a precision thermostat. The spectrograph is shown in Fig. 3. A Hewlett Packard (HP) data processing system and a Texas Instruments (TI) 733 terminal were added to process and transmit the data.

The signals from the photomultiplier tubes are amplified by operational amplifiers in each circuit. The amplified signal for each channel then is read sequentially at the rate of about twice per second by an HP 3495A scanner and an HP 3455A digital voltmeter (DVM). The analog signal is converted by the DVM and stored in an HP 9825A calculator. When the calculator determines that the signal has reached the dark current level, it stops the scanning, compensates for fluctuation in the background, and determines the amount of interference due to vanadium on the beryllium signal. Then, using calibration data stored in memory, the concentrations of beryllium and lithium are determined and displayed. Along with the sample number, they are then transmitted to the data terminal, where the information is written onto cassette tape and printed on paper. (The hard copy is used to verify the correct

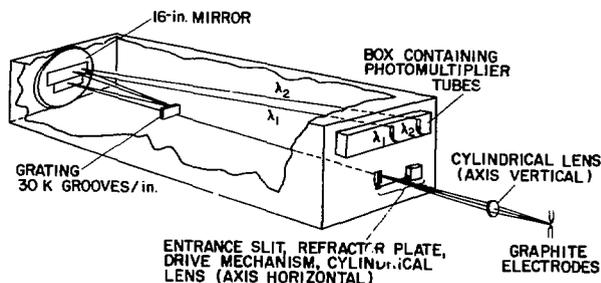


Fig. 3.

The LASL 3.4-m Ebert direct-reading spectrograph.

sample number and to ensure that the calibration ranges for beryllium and lithium have not been exceeded.) The computer program is described in Appendix B. Typical calibration curves are shown in Fig. 4.

The data are transferred at the convenience of the operator, via the tape cassette, to a main file on a CDC 6600 computer at the LASL Central Computer Facility (CCF) for final processing. The file can be edited to correct any errors.

One problem encountered with the 3.4-m Ebert spectrograph was a movement of the spectrum over a period of several hours. Exit slits and photomultiplier tubes were set at the edges of the mercury 546.1-nm and 579.1-nm lines, making the system very sensitive to movement of the spectrum. We designed the system to work essentially as a null detector. When the spectrum is properly aligned, the signals from the two photomultiplier tubes are balanced. A shift of the spectrum from point A to point B, as seen in Fig. 5, causes an imbalance in the signals that causes a motor to rotate the entrance refractor plate until the signals are again balanced. When the arcing stage of a sample analysis is completed, a mercury lamp is automatically moved in front of the entrance slit and the correction is carried out. When the arc is struck again for the next analysis, the mercury lamp moves to the side and the associated electronics are deactivated. A flow chart of the system in its final form is shown in Fig. 6.

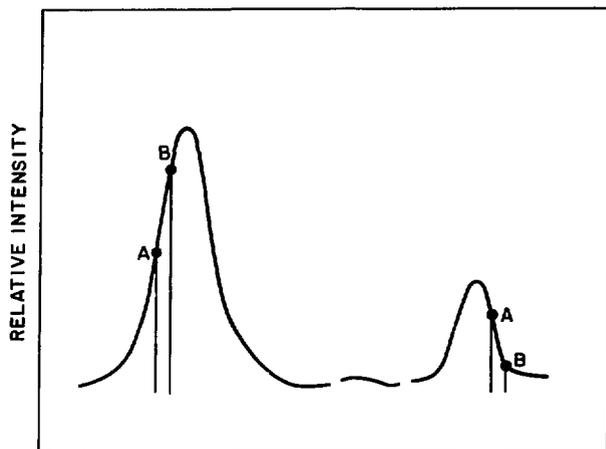


Fig. 5.
Mercury lines for corrector plate adjustment.

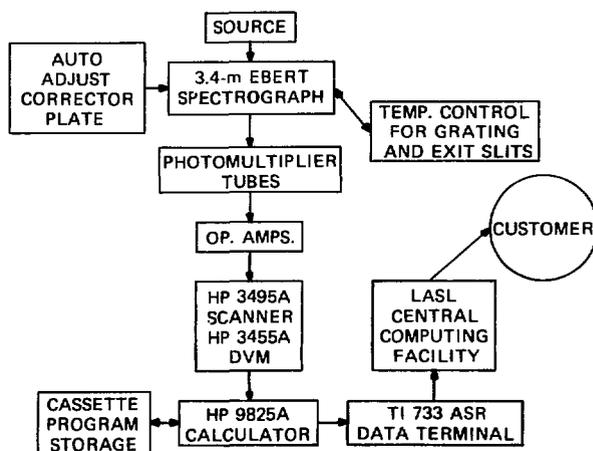


Fig. 6.
Flow chart of analytical system.

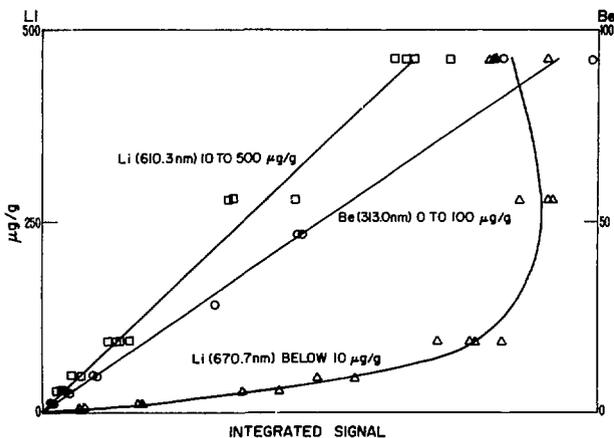


Fig. 4.
Typical calibration curves.

B. Selection of Spectrographic Lines

Because of self-reversal at higher lithium concentrations when using the lithium 670.7-nm line, the lithium 610.3-nm line also is used. The 670.7-nm line is used only for concentrations below 10 µg/g, and the 610.3-nm line is used for higher concentrations. (See Fig. 4.) These are both first-order lines. The second-order beryllium 313.0-nm line, and the second-order vanadium 327.6-nm line also are used.

A slit and photomultiplier tube are positioned near the lithium lines to provide a background signal. Filters are placed between the exit slits and the photomultiplier tubes so that only the orders of interest are passed to the photomultiplier tubes.

C. Selection of Buffer Material

Our initial studies started with the buffer recommended by Timperley.¹ With it the limits of detection were 1 $\mu\text{g/g}$ for lithium and 3 $\mu\text{g/g}$ for beryllium. Changes in sample size and in arcing and exposure conditions did not lower the detection limit for beryllium. The Timperley electrode charge was one part sample to four parts buffer, which was one part Na_2CO_3 to seven parts graphite powder. Several Na_2CO_3 -to-graphite ratios and sample-to-buffer ratios were tested, but no combination was found which improved the detectability of beryllium.

Other compounds were tested in combination with graphite powder in search of a buffer which would give a 1 $\mu\text{g/g}$ detectability for both beryllium and lithium. These were BaSO_4 , CaF_2 , CuO , Ga_2O_3 , GeO_2 , MgO , NaF , NaCl , and SiO_2 . The 1 $\mu\text{g/g}$ limit for lithium was reached with all nine compounds, but only the last two lowered the detection limit of beryllium to 1 $\mu\text{g/g}$. Interestingly, a mixture of NaCl and SiO_2 raised the detection limit of beryllium to 2 $\mu\text{g/g}$. A 1:1 mixture of SiO_2 and graphite was chosen as the buffer because most sediment samples have a high silica content, and the addition of SiO_2 to the sample would serve to make the composition of the sample mixture more nearly like the composition of the synthetic sediment matrix of the standards.²⁻⁴ All of these studies were made using photographic recordings of the spectra.

Sometimes during the arcing of a sample, evolved gas ejects large chunks of the sample-buffer charge. This gas also forms gummy bubbles with the viscous, molten SiO_2 . To avoid this, MgO , CaO , and SrO were tried as a replacement for SiO_2 in the buffer mixture. Each compound decreased the apparent viscosity of the molten charge, but CaO and SrO gave low beryllium values. Although MgO gave a very smooth burn with no apparent loss of material, and satisfactory results for both beryllium and lithium, it occasionally gave erratic values. A SiO_2 - MgO -graphite buffer worked well, giving good results down to 0.2 $\mu\text{g/g}$ for beryllium, but the values

were not quite as good as those obtained with a SiO_2 -graphite buffer. With the SiO_2 -graphite buffer, the beryllium signal occurs over a period of about 24 s, as compared with about 20 s for the SiO_2 - MgO -graphite, and 12 s for the MgO -graphite buffer. Although the highest background signal and the roughest burn occurs with the SiO_2 -graphite buffer, the results for both beryllium and lithium are better than those obtained with the other buffers.

D. Mixing of Buffer and Sample

The electrode charge originally consisted of 50-mg weighed portions of the sample and buffer mixed in a plastic vial containing two plastic beads with a mechanical mixer (WIG-L-BUG, Crescent Dental Mfg. Co.). A 15-mg portion of this mixture was placed into the electrode cavity. Because this was a time-consuming operation, a study was made to determine if this amount of mixing was really necessary.

Six electrodes for each of four samples were prepared for analysis by mechanically mixing 50-mg portions of sample with buffer. Another six electrodes from each of the same samples were prepared by weighing 7.5 mg each of sample and buffer, mixing on the weighing pan with a platinum spatula, and transferring quantitatively to the electrode cavity. A third set of electrodes for each sample was prepared by weighing 7.5 mg of sample, transferring to the electrode, then weighing 7.5 mg of buffer, and adding this to the electrode, so that no mixing with the sample occurred. The results obtained with these electrodes after arcing are shown in Table I.

Because there appears to be no significant difference in the values obtained, the mechanical mixing was abandoned in favor of the pan-mixing technique. This resulted in a significant time saving.

E. Selection of Amounts of Sample and Buffer

Varying sample weight with constant buffer weight showed the signal per unit of beryllium increasing with decreasing sample weight, but no such effect was observed with lithium. The change in sample-to-buffer ratio is small compared with a variation in sample size.

TABLE I

EFFECT OF SAMPLE-BUFFER MIXING ON ANALYSIS RESULTS

<u>Sample No.</u>	<u>Be</u> <u>vial mix</u>	<u>Be</u> <u>pan mix</u>	<u>Be</u> <u>no mix</u>	<u>Li^b</u> <u>vial mix</u>	<u>Li^b</u> <u>pan mix</u>	<u>Li^b</u> <u>no mix</u>
417455						
Av ($\mu\text{g/g}$)	0.98	1.0	0.95	26.	25.	22.
S ($\mu\text{g/g}$)	0.04	0	0.05	1.9	1.0	1.7
RSD ^a	4.1%	0	5.8%	7.5%	4.0%	7.9%
417462						
Av ($\mu\text{g/g}$)	4.8	5.2	5.2	103.	122.	109.
S ($\mu\text{g/g}$)	0.98	1.2	0.98	6.8	12.3	6.6
RSD ^a	20.%	23.%	19.%	6.6%	10.%	5.6%
417463						
Av ($\mu\text{g/g}$)	3.3	3.8	3.0	97.	107.	85.
S ($\mu\text{g/g}$)	0.52	0.36	0	7.5	11.	5.3
RSD ^a	16.%	9.4%	0	7.8%	10.%	6.2%
417464						
Av ($\mu\text{g/g}$)	6.8 ^c	7.3	7.8	93. ^c	107.	98.
S ($\mu\text{g/g}$)	0.4	1.5	1.6	11.	13.	3.5
RSD ^a	6.6%	21.%	21.%	12.%	12.%	3.6%

^aRelative standard deviation.

^bThe lithium values were obtained from the 610.3-nm line.

^cThe concentration here is the average of five determinations. Each of the other concentrations is the average of six determinations.

A variation of 20% in the buffer weight caused no discernible difference in the observed values for either beryllium or lithium. Increasing the buffer-to-sample ratio to 2, but not exceeding 15 mg total electrode charge, resulted in a somewhat shorter integration time for the beryllium signal. No study was made of the effect of varying the ratio of SiO₂ to graphite in the buffer mixture.

Using time-resolved plots with a 17-A (short circuit) arc, we found that with 5 mg of sample plus 10 mg of buffer, the beryllium and lithium signals are complete in 30 to 40 s, whereas with 7.5 mg of sample and 7.5 mg of buffer, the beryllium signal takes as long as 53 s for completion. Although the buffer composition affects the length of time over which the beryllium signal appears, and the smoothness of the burn, it has less effect on the time required to receive the total beryllium signal, this being a function

primarily of the sample size. Typical time-resolved plots are shown in Figs. 1 and 2. In conclusion, we decided to use 5 mg of graphite and 10 mg of buffer.

F. Effect of Electrode Type and Packing

In an attempt to stabilize the arc, a center-post electrode was tried. In each of four attempts the beryllium value was acceptable, but the lithium value was very low, even though the arc was smooth and the rim burned evenly. The reason for the low lithium values is not known, but no further work was done with this electrode.

Three noncenter-post electrodes were prepared with standards, using a packing tool made to leave a vent hole in the center of the charge. These were compared with three similar electrodes packed with

a flat-end packing tool. No significant difference was observed, either in the burn or in the amount of beryllium and lithium found. Three other standards were prepared with varying amounts of pressure applied during the packing operation. Again, no significant difference was seen.

G. Effect of Moisture on Sample Arcing

An explanation for the unreliability of the buffers containing MgO is moisture pickup from the air. Materials used in the preparation of electrode charges were initially dried for 2 h at 110°C, then weighed at intervals after exposure to 60% relative humidity laboratory atmosphere (RH) to determine the amount of moisture absorbed. An equilibrium was reached after 124 h. At this time powdered graphite showed no weight change, SiO₂ had increased by 5.5%, SiO₂-graphite buffer by 2%, synthetic sediment by 4%, and MgO-graphite by 6.5%. After 24-h exposure to anhydrous Mg(ClO₄)₂ in a desiccator, all except the MgO-graphite buffer were within 1% of their dry weights. (The SiO₂-graphite buffer reached its dry weight in about 10 h.) The MgO-graphite buffer was still 5.5% above its dry weight, and was 3% above its dry weight after being further dried at 110°C for 6 h. So MgO was not pursued as a buffer component.

In another study of the effect of moisture, three sets of electrodes containing SiO₂-graphite buffer were prepared. One set was dried by exposure to anhydrous Mg(ClO₄)₂, one set was exposed to the laboratory atmosphere at approximately 60% RH, and the other set was exposed to a 100% RH atmosphere in a closed container. The set exposed to 60% RH gave an average beryllium value which was 95% and an average lithium value which was 85% of the dry set. The set exposed to 100% RH gave 92% of the value for beryllium, and 64% for lithium.

After the moisture problem became apparent, a source of low-moisture, nonhygroscopic SiO₂ was found. This material is now used in the preparation of the buffer mixture. All samples and standards are now dried for at least 10 h before arcing.

H. Selection of Arcing Conditions

Our studies were made with a current of 12 A (short circuit) for 80 s. Other currents and times were tried, but the best conditions were achieved with currents of 6 A for 10 s, then 17 A for 50 s. The lower initial current slows gas evolution, thereby preventing loss of sample from the electrode, and it gives the arc a chance to stabilize before the higher current is applied. No loss of material from the electrode crater has been observed since this new procedure was used. Time-resolved plots (Fig. 2) were made to determine the effect of the change in arc current on the signal produced. A longer time is required to reach maximum signal intensity for both beryllium and lithium, but no detrimental effects have been observed when analyzing either samples or standards.

III. PROCEDURE

A. Apparatus

- **Balance**, analytical, with 0.1 mg sensitivity.
- **Calculator**, desk-top, HP 9825A, or equivalent, with appropriate software.
- **Data acquisition system**, HP 3052A with HP 3455A digital voltmeter and HP 3495A scanner, or equivalent.
- **Mixer**, mechanical, Spex Industries Spex mixer/mill, or equivalent.
- **Packing tool**, stainless steel. See Fig. 7.
- **Scoop**, calibrated to contain 10 mg of buffer. See Fig. 8. Drill cavity to contain slightly more than

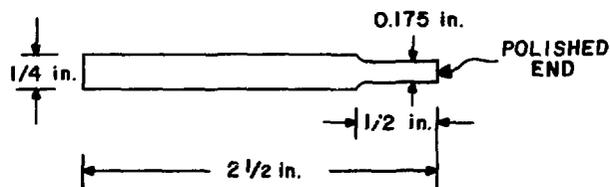


Fig. 7.
Packing tool.

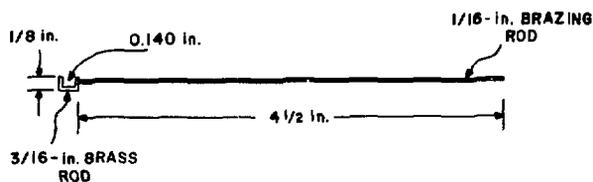


Fig. 8.
Buffer scoop.

10 mg of 1:1 SiO₂-to-graphite buffer. Adjust by filing top rim to contain exactly 10 mg of buffer.

- **Spatula**, platinum.
- **Spectrograph**, direct-reading 3.4-m Ebert, or equivalent, with exit slits at the second-order 313.0-nm line of beryllium, the first-order 670.7-nm and 610.3-nm lines of lithium, the background spectrum near these lines, and the second-order 327.6-nm line of vanadium, and the edges of the first-order 546.1- and 579.1-nm lines of mercury. See Fig. 3.
- **Terminal**, TI 733, or equivalent, with cassette tape output.
- **Weighing pan**, stainless steel.

B. Reagents and Materials

- **Buffer**, equal parts of SP-2 graphite powder and SiO₂ powder, mixed thoroughly.
- **Compounds**, for standards and matrix, the purest available, Al₂O₃, BeO, CaCO₃, Fe₂O₃, K₂CO₃, Li₂CO₃, MgO, Na₂CO₃, TiO₂, V₂O₅.
- **Electrodes**, graphite, National Carbon Co. (NCC) Grade AGKSP, or equivalent. The anode is NCC No. L4012, 1/4-in. diameter, and the cathode is NCC No. L4036.
- **Graphite**, powder, special spectroscopic, NCC Grade SP-2 high purity, or equivalent.
- **Mg(ClO₄)₂**, anhydrous.
- **SiO₂**, powder, Spex Industries, 6-9 s purity, or equivalent.
- **Standards**. Prepare a standard containing 10 000 μg/g of vanadium, 5 000 μg/g of lithium, and 500 μg/g of beryllium from V₂O₅, Li₂CO₃, and BeO in synthetic sediment. Mix thoroughly in the mixer/mill. From this master standard, prepare more dilute standards as needed by diluting with the synthetic sediment mixture.

• **Synthetic sediment**.⁴ Thoroughly mix the following compounds by grinding with a boron carbide mortar and pestle.

Compound	Weight (g)	Weight (% of total)
SiO ₂	7.240	72.4
Al ₂ O ₃	1.000	10.
CaCO ₃	0.500	5.
Fe ₂ O ₃	0.500	5.
K ₂ CO ₃	0.200	2.
MgO	0.300	3.
Na ₂ CO ₃	0.200	2.
TiO ₂	0.060	0.6

Heat the mixture to 850°C for 3 h, allow to cool in a desiccator, and again grind thoroughly with a boron carbide mortar and pestle.

C. Preparation of Electrodes

- (1) Weigh 5 mg of sample (±0.1 mg), ground to -300 mesh, onto the balance pan. Close the balance door after the final adjustment, and wait 5 s to be sure the pointer doesn't drift.
- (2) Tap buffer from spatula into the scoop until it is full and slightly rounded on top. Scrape off excess with the edge of the spatula. The scoops have been adjusted to contain 10 mg of buffer. Occasionally weigh a scoop of buffer to verify that the scoop delivers 10 mg.
- (3) Transfer the scoop of buffer to the weighing pan and mix with the sample. Transfer the mixture to the electrode cavity and pack with the packing tool. *Replace cover on unused electrodes* when not in use to prevent contamination by airborne particles.
- (4) Store blocks of prepared sample electrodes in a cabinet containing desiccant and allow to dry at least 10 h. Place partially completed blocks in the cabinet when work is interrupted for an extended time, and always at the end of the shift.
- (5) Prepare calibration and control standards in the same manner as samples. Store the standards in the cabinet containing the desiccant.

D. Start-Up Procedure at the Spectrograph

- (1) Close breaker for power to the arc source.
- (2) Turn on the TI terminal.
 - (a) Turn on power switch.
 - (b) Set RECORD and PRINTER to LINE.
 - (c) Set the ON-LINE/OFF switch to ON-LINE.
 - (d) Place cassette tape in the cassette transport.
 - (e) Set RECORD CONTROL to OFF.
 - (f) Set Cassette to RECORD.
 - (g) Set the TAPE FORMAT switch to LINE.
 - (h) Set RECORD CONTROL to ON. The red light above this switch should light up. (The RECORD and READY lights for the cassette should also be lit at this time.)
- (3) Turn on the HP 9825A calculator power switch.
- (4) Turn on the HP 3455A digital voltmeter power switch and scanner switch.
- (5) With an old pair of electrodes in the electrode holders short out the arc gap. Press the START button on the arc source, and adjust the current to 17 A (after the first 10 s). The low current during the first 10 s will then be about 6 A.
- (6) Set the arc total-burn timer to 60 s and the low-current timer to 10 s.

E. Calibration

- (1) Prepare a series of standards, by making dilutions of the master standard with the synthetic sediment mixture to cover the range of beryllium and lithium values expected in the samples.
- (2) Prepare duplicate electrodes from each of the standards.
- (3) Prepare duplicate blank electrodes by substituting 5 mg of synthetic sediment for the standard.
- (4) Load a program into the calculator memory which will print out the integrated signals for lithium (670.7 nm), lithium (610.3 nm), beryllium (313.0 nm), vanadium (327.6 nm), and background.
- (5) Load a standard electrode and a new cathode into the electrode holders. Center the electrodes and set the standard electrode 2 mm from the center line.

(6) While pressing the START button on the arc source, momentarily touch the cathode to the edge of the standard electrode to start the arc, then move the cathode to its operating position 2 mm from the center line.

(7) During the arcing period, it is very important to keep each of the electrodes 2 mm from the center line to maintain a gap of 4 mm. See Fig. 9.

(8) Repeat from Step 5 for each standard and blank electrode.

(9) The net element signal NS is calculated using the element signal and the background signal from both the standard and the blank exposure.

$$NS = SS - BS (SB/BB)$$

where

SS = the element signal from the standard exposure,

BS = the background signal from the standard exposure,

SB = the element signal from the blank exposure, and

BB = the background signal from the blank exposure.

The net element signal is calculated for beryllium, vanadium, and both lithium lines. To correct for vanadium interference, use the data from all the standard exposures to calculate the constant KV so that the corrected net element signal for beryllium, CNSBe, is independent of the vanadium concentration.

$$CNSBe = NSBe - KV(NSV) ,$$

where NSBe = the net element signal for beryllium.

(10) Calculate the linear constant K for each element line so that the correct element concentration C is obtained from each standard.

$$C = K (NS) .$$

Use CNSBe for the net element signal for beryllium. The 670.7-nm lithium line is used only for concentrations below 10 $\mu\text{g/g}$. The 610.3-nm lithium line is used for concentrations above 10 $\mu\text{g/g}$. The 610.3-nm line is also used to determine whether the

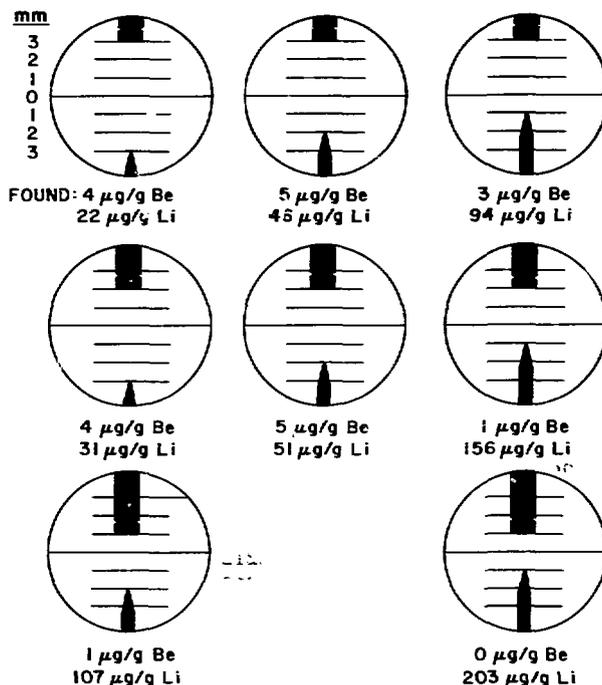


Fig. 9.

Effect of electrode position during arcing (upside down, as seen at the operator screen). The values below each picture are for the control standard (5 $\mu\text{g/g}$ beryllium, 50 $\mu\text{g/g}$ lithium). Note the incorrect values with the electrodes incorrectly positioned.

lithium concentration is high or low. Typical calibration curves are shown in Fig. 4.

(11) Enter the constants for the calibration data into the calculator SAMPLE ANALYSIS PROGRAM.

F. Analysis of Samples

(1) Load the SAMPLE ANALYSIS PROGRAM into the calculator memory.

(2) Analyze a CONTROL STANDARD as described for Calibration, steps 5-8.

(3) If the results obtained on the CONTROL STANDARD are acceptable, analyze the samples in the same manner.

IV. RELIABILITY

A series of standards prepared to contain varying amounts of beryllium and lithium in a simulated

sediment matrix was used to calibrate the system. The results are shown in Table II. Each reported value is the result of duplicate determinations. The average beryllium found was 98% with a standard deviation of 16%. The average lithium found was 97% with a standard deviation of 15%.

A random selection of samples that previously had been analyzed by a different direct-reading spectrochemical procedure was reanalyzed by the method described in this report. The results are shown in Table III.

The average difference between the reported values and the values obtained on the reruns was 0.17 $\mu\text{g/g}$ for beryllium, with a standard deviation of 0.8 $\mu\text{g/g}$, and 4.0 $\mu\text{g/g}$ for lithium, with a standard deviation of 11 $\mu\text{g/g}$.

Table IV shows the effect of the vanadium correction.

Eight United States Geological Survey (USGS) standards were analyzed to determine the reliability of the method with various types of material. The results are shown in Table V. The values listed under the heading "LASL" are averages of 10 analyses. The values listed under the heading "USGS" are averages of values obtained by several different methods, such as atomic absorption, fluorometry, and emission spectroscopy.⁵

TABLE II

CALIBRATION STANDARDS

Standard Value of Be ($\mu\text{g/g}$)	Be Found ($\mu\text{g/g}$)	Standard Value of Li ($\mu\text{g/g}$)	Li Found ($\mu\text{g/g}$)
0.2	0.20	0.5	0.44
0.3	0.30	1	0.8
0.5	0.48	2	2.0
1	1.1	3	3.1
2	1.8	5	4.2
3	2.9	10	10.3
5	5.4	30	26.0
10	10.1	50	47.6
3	2.7	100	99
5	4.9	300	348
10	10.0	500	524
30	31.9	100	114
50	47.3	300	258
100	93.0	500	502

TABLE III

ANALYSIS OF SAMPLES

Sample No.	Reported Be ($\mu\text{g/g}$)	Be Rerun ($\mu\text{g/g}$)	Reported Li ($\mu\text{g/g}$)	Li Rerun ($\mu\text{g/g}$)
314201	2	3	39	31
314220	1	2	18	36
314251	1	3	29	25
030380	2	2	26	61
030350	2	1	33	32
030209	2	2	22	40
030120	2	2	48	42
305322	1	2	30	43
305357	3	2	38	38
315901	1	2	22	22
315924	1	1	19	20
315960	2	1	35	25
316105	0	1	29	32
316145	1	1	25	20
316191	1	1	23	22
316200	2	3	27	37
221208	2	2	26	28
221245	2	2	21	32
221270	2	1	32	38
221281	2	2	29	33
404592	2	3	31	36
405213	2	2	33	35
405325	2	1	6	5
405350	2	2	33	37

TABLE IV

CORRECTION FOR VANADIUM

Nominal Be ($\mu\text{g/g}$)	V Added ($\mu\text{g/g}$)	Be Found Uncorrected ($\mu\text{g/g}$)	Be Found Corrected for V ($\mu\text{g/g}$)
3	120	3.5	2.5
3	120	4.6	2.9
5	200	7.1	4.9
5	200	6.1	4.9
10	400	13.0	10.0
30	1200	49.1	31.9
50	2000	61.7	47.5
50	2000	70.8	47.1

TABLE V
ANALYSIS OF USGS STANDARDS

Standard Material	Be USGS ($\mu\text{g/g}$)	Be LASL ($\mu\text{g/g}$)	Li USGS ($\mu\text{g/g}$)	Li LASL ($\mu\text{g/g}$)
Quartz Latite	1.9	2	23.8	30
Marine Mud	2.9	2	74.8	91
Hawaiian Basalt	1.	<1	4.6	4
Green River Shale	<1	<1	127	132
Nepheline Syenite	10.	7	30.6	44
Glass Mt. Rhyolite	2.5	3	53.6	66
Mica Schist	3.1	3	34.2	31
Cody Shale	1.5	2	42.9	45

V. CONCLUSIONS

We have developed a method and built new apparatus for the rapid determination of beryllium and lithium in stream sediment samples. The limit of detection is 0.2 $\mu\text{g/g}$ for beryllium and 0.5 $\mu\text{g/g}$ for lithium. We correct for vanadium, which is the only known element likely to be encountered that interferes with beryllium. It is possible to analyze more than 200 samples per 8-h day per spectrograph with about 30 samples per day per operator.

VI. FUTURE WORK

The addition of an automatic electrode changer and an automatic electrode gap controller would decrease the analysis time per sample and would improve the precision of the method.

Changes can be made in the computer program which would allow the operator to recalibrate by analyzing a series of standards.

More extensive studies are planned to determine the degree of interference by elements likely to be encountered in stream sediments.

The values obtained by the method described in this report should be compared with the values found on the same samples by an independent method. Such a method might be a spectrochemical analysis using an inductively coupled-plasma (ICP) source following a total dissolution of the sample.

New methods of excitation using an ICP, either by direct injection of the sample into the plasma or by following vaporization of the sample with a laser,

should be investigated. Measurement of the emission lines would be with a direct-reading spectrograph. This method has the potential of processing samples at a rate of 20 to 30 samples per hour per analyst. If successful, the method would give better limits of detection, and would permit the simultaneous determination of many more elements than is possible with the present method.

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APPENDIX A

PROGRAM FOR TIME-RESOLVED PLOTS USING HP 9825A CALCULATOR

This program was originally written in BASIC language by Charles T. Apel for use on a DEC PDP-11/20 using a DEC VT55 terminal for output. The program was modified and translated to HPL language by David Gallimore for use on an HP 9825A desk-top calculator using a TI 733 ASR data terminal for output.

```

0:  "PLOT -- THIS PROGRAM GIVES TIME RESOLVED PLOTS FOR BE 310 NM SECOND
    ORDER, V 328 NM SECOND ORDER, BACKGROUND, LI 671 AND 610 NM.":
1:  WTI 0,10; WTI 6,1; WTC 10,1; WTB 10,39; WTC 10,0
2:  DIM SS[10],R[5,130],E[5,4],Q[4,4],B[5,5]
3:  "BE"→E[1]; "LILD"→E[2]; "BK6"→E[3]; "V"→E[4]; "LIHI"→E[5];
    " "→B[1]
4:  REM 7; FMT F3.0; WRT 709,0; WRT 722, "F1 R7 A0 H0 M3 T1 DO"
5:  "NEXT": ENT "SAMPLE NUMBER?",S
6:  IF LEN(SS) >= 8; JMP 2
7:  SS&" "→SS; GTO -1
8:  "WAIT": FMT ; RED 722,R[1,1]; IF R[1,1] > .05; GTO "INIT"
9:  GTO "WAIT"
10: "INIT": 0→J; 1→K; 1→L
11: "READ": FMT F3.0; WRT 709,J; WRT 722, "T1"
12: FMT ; RED 722,R[K,L]; IF J > 0; JMP 2
13: IF R[K,L] < .05; GTO "HALT"
14: K+1→K; IF K > 5; 1→K; L+1→L; 0→J; GTO "READ"
15: J+1→J; GTO "READ"
16: "HALT": ENT "INTEGRATED READING - YES OR NO",Q[1]
17: IF Q[1,1,3] = "YES"; GSB "INTGR"
18: ENT "GRAPHIC DISPLAY - YES OR NO",Q[2]
19: IF Q[2,1,2] = "NO"; GTO "NEXT"
20: "GRAPH": ENT "BE,LILD,LIHI,BK6,V, DR STOP?",Q[3]
21: IF Q[3,1,2] = "BE"; 1→K; GTO "TI"
22: IF Q[3,1,4] = "LILD"; 2→K; GTO "TI"
23: IF Q[3,1,4] = "LIHI"; 5→K; GTO "TI"
24: IF Q[3,1,3] = "BK6"; 3→K; GTO "TI"
25: IF Q[3,1,1] = "V"; 4→K; GTO "TI"
26: IF Q[3,1,4] = "STOP"; GTO "NEXT"
27: GTO "GRAPH"
28: "TI": R[K,1]→T; R[K,1]→B
29: FOR I = 2 TO L-1
30: IF T < R[K,I]; R[K,I]→T; JMP 2
31: IF B > R[K,I]; R[K,I]→B
32: NEXT I
33: "SCALE": (B+T)/2→H; T-B→S; 69/S→C
34: FMT 1,12X,C4,20X,C10
35: FOR I = 1 TO 5; WTB 10,10; NEXT I
36: "RDG. #"→B[2]; "VOLTS"→B[3]
37: WRT 10.1,E[K],SS; WTB 10,10,13
38: FMT 2,2X,C5,30X,C5; WRT 10.2,B[2],B[3]
39: FMT 3,7X,F6.3,28X,F6.3,28X,F6.3
40: WRT 10.3,B,H,T
41: FOR I = 1 TO 9; WTB 10,45; NEXT I; WTB 10,73
42: FOR I = 1 TO 33; WTB 10,45; NEXT I; WTB 10,73
43: FOR I = 1 TO 33; WTB 10,45; NEXT I; WTB 10,73
44: WTB 10,10,13
45: "PLOT": FOR I = 1 TO L-1
46: FOR J = 1 TO 10; WTB 10,32; NEXT J
47: C←(R[K,I]-B)→P; INT(P+.5)→P
48: IF P = 0; WTB 10,42; WTB 10,10,13; JMP 4
49: WTB 10,73
50: FOR G = 1 TO P; WTB 10,32; NEXT G
51: WTB 10,42; WTB 10,10,13
52: NEXT I

```

```

53: GTD "GRAPH"
54: "INTGR": ENT "BE,LIL0,LIH.,BKG,V, DR STOP?";QS[4]
55: IF QS[4,1,2] = "BE"; 1→K; GTD "SUM"
56: IF QS[4,1,4] = "LIL0"; 2→K; GTD "SUM"
57: IF QS[4,1,4] = "LIHI"; 5→K; GTD "SUM"
58: IF QS[4,1,3] = "BKG"; 3→K; GTD "SUM"
59: IF QS[4,1,1] = "V"; 4→K; GTD "SUM"
60: IF QS[4,1,4] = "STOP"; GTD "ENUF"
61: GTD "INTGR"
62: "SUM": 0→F
63: FOR T = 1 TO L-1
64: R[K,T]+F→F
65: NEXT T
66: PRT "CHANNEL READING"; FMT 5,C4,2X,E10.3
67: WRT 16.5,E$(K),F; GTD "INTGR"
68: "ENUF": RET
69: END

```

Explanation of Program Statements

- Line 0 PLOT produces time-resolved plots of line intensity for any of the following analytical lines: beryllium 313.0 nm (second-order), lithium 670.7 nm, lithium 610.3 nm, vanadium 327.6 nm, and background.
- Line 1 Outputs information to interface cards.
- Line 2 Dimensions all simple and array variables to be used.
- Line 3 Assigns values to string variable array E\$.
- Line 4 Sets the scanner to channel 0 (beryllium). Sets parameters of digital voltmeter.
- Lines 5-7 Enters sample number (S\$) and checks to see if it has the correct number of characters.
- Line 8 Begins reading the signal of channel 0. If the signal is >0.05 V (dark current of photomultiplier tube) program execution is continued.
- Line 10 Sets subscripts of array R to 1,1 (first element of array to contain first reading on channel 0). K = 1, beryllium; K = 2, lithium 670.7; K = 3, background; K = 4, vanadium; K = 5, lithium 610.3.
- Lines 11-15 Sequentially reads the five channels and stores the readings in array R. Each time channel 0 (beryllium) is read, the calculator determines if the reading has reached dark current level. If this test is true, the calculator stops reading the channels.
- Lines 16-17 Inquires if the user wants to integrate the readings for the individual channels. If response is yes, program execution branches to subroutine INTGR.

- Lines 18-19 Inquires if user wants graphic display of time-resolved analytical line intensity. If response is yes, program then inquires which analytical line user wants displayed. If response is no, program branches to line with label NEXT, which is prompt for next sample number.
- Lines 20-27 Prompts for channel that the user wants plotted.
- Lines 28-32 Finds highest and lowest readings.
- Line 33 Determines middle reading and scaling factor. Scales each channel so that the highest reading is at the top of the plotting paper. The plots are, therefore, not on the same scale.
- Lines 34-44 Prints heading for the plot. This includes the channel, sample number, lowest, middle, and highest voltage readings. The y (voltage) axis is also printed.
- Lines 45-53 Determines where the individual point (P) should be, spaces over to that position and prints a (*) for P and (-) on the x (time) axis.
- Lines 54-67 Subroutine INTGR calculates the integrated reading for the channel of interest. The channel (beryllium, low lithium, high lithium, background, or vanadium) and the reading are printed on the HP 9825A thermal printer. When the user types STOP, after being asked which channel is to be integrated, this subroutine is stopped and the program execution returns to line 18.

APPENDIX B

PROGRAM FOR SAMPLE CALCULATION USING HP 9825A CALCULATOR

```

0: "SAMPLE":
1: WTI 0,10
2: WTI 6,1
3: WTC 10,1; WTB 10,39; WTC 10,0
4: WTB 10,18
5: DIM S[6,6],DS[10],T[10],ES[6,4],SS[10],C[5],A[6],QS[1,3],NS[10],AS[2]
6: TRK 1
7: LDF 4,S[*]; LDF 5,A[*]; LDK 8
8: REM 7
9: FMT F3.0; WRT 709,0
10: WRT 722, "F1 R7 A0 H0 M3 T1 D0"
11: ENT "SAMPLE NUMBER?",SS
12: "NXT": 64→L; STR(VAL(SS[1,6])+1)→SS; SS[2,7]→SS; DSP SS
13: "WAIT":
14: FMT ; RED 722,A
15: A→R
16: IF R > .05; GTD "INIT"
17: GTD "WAIT"
18: "INIT": 1→I; 0→J
19: FOR K = 1 TO 10

```

```

20: 0→T[K]
21: NEXT K
22: "READ":
23: J+1→J
24: FMT F3.0; WRT .709,J-1
25: WRT 722, "T1"
26: FMT ; RED 722,A
27: A→R
28: IF J > 1; JMP 2
29: IF R < .04; GTD "HALT"
30: T[J]+R→T[J]
31: IF J < 5; GTD "READ"
32: 0→J
33: I+1→I
34: GTD "READ"
35: "HALT":
36: IF LEN(SS) >= 8; GTD "SM1"
37: SS&" "→SS; GTD -1
38: "SM1": FOR I = 1 TO 5
39: IF I=1; T[1]-A[1]+T[3]-A[6]+T[4]+A[6]+A[4]+T[3]→T[1]; GTD "IT"
40: IF I=3; 5→I
41: T[1]-A[1]+T[3]→T[1]
42: "IT": NEXT I
43: FOR I = 1 TO 5
44: IF I=3; 5→I
45: S[1,1]→C[1]
46: T[1]+S[1,2]+T[1]^2+S[1,3]+C[1]→C[1]
47: NEXT I
48: "TI": IF C[1] < 1; 0→C[1]
49: INT(C[1]+.5)→C[1]
50: FMT 2,C8,F8.0,F8.0
51: IF C[2] < 1; 0→C[2]; WRT 10.2,SS,C[1],C[2]; GTD "NEXT"
52: IF C[2] <= 10; INT(C[2]+.5)→C[2]; WRT 10.2,SS,C[1],C[2]; GTD "NEXT"
53: INT(C[5]+.5)→C[5]; WRT 10.2,SS,C[1],C[5]; C[5]→C[2]
54: "NEXT": BEEP; DSP "BE",C[1],"LI",C[2]; WAIT 5000
55: IF SS[1,7] = "CONTROL"; NS→SS
56: GTD "NXT"
57: END

```

SPECIAL FUNCTION KEYS

```

F0: ♦STR(VAL(SS[1,6])+1)→SS; SS[2,7]→SS; DSP SS
F1: ♦STR(VAL(SS[1,6])-1)→SS; SS[2,7]→SS; DSP SS
F2: ♦VAL(SS)-1→X; STR(X)→NS; NS[2,7]→NS; "CONTROL"→SS; DSP SS
F3: ♦L+1→L; CHAR(L)→AS; AS→SS[7,8]; DSP SS
F4: ♦DSP SS
F5: ♦DSP "BE",C[1],"LI",C[2]; WAIT 1000; DSP SS

```

Explanation of Program Statements

- Lines 1-4 Outputs information to the interface cards.
- Lines 5-10 Dimensions variables, loads calibration coefficients and values of special function keys into memory. Sets parameters of the digital voltmeter, and sets scanner to channel 0 (beryllium).
- Lines 11-12 Sample number is entered, incremented by 1, and displayed.
- Lines 13-17 Begins reading channel 0 (beryllium). Waits for signal >0.05 V (dark current of photomultiplier tube).

- Lines 18-34 A signal on channel 0 > 0.05 V has been reached. Sets variables for storage of readings to zero. The system now begins reading the channels sequentially and summing the values in T[J]. Each time channel 0 is read, it is checked to see if it has reached dark current level of photomultiplier tube. If it has, the arc has stopped and scanning is stopped.
- Lines 35-37 Determines if sample number (S\$) has the proper number of characters.
- Lines 38-42 Corrects the integrated readings for each element for background fluctuations. The beryllium signal is also corrected for vanadium interference.
- Lines 43-47 Calculates the concentrations of beryllium and lithium using the calibration coefficients stored in memory.
- Lines 48-49 If the concentration of beryllium found is <1 μg/g, enters a zero for beryllium concentration. Otherwise, rounds the number.
- Lines 50-51 If the concentration of lithium found is <1 μg/g, enters a zero. The sample number and concentrations of beryllium and lithium are now written on cassette tape and printed on paper.
- Line 52 If the lithium concentration is ≤ 10 μg/g, the lithium 670.8-nm line is used. Rounds the concentration. Sample number, beryllium and lithium concentrations are printed on paper and written on cassette tape.
- Line 53 If the above conditions for lithium are not met, uses the lithium 610.3-nm line. This information is then printed on paper and written on cassette tape.
- Lines 54-56 Displays concentrations of beryllium and lithium found. The system is now ready to analyze another sample.

Explanation of Special Function Keys

- Key** (All are defined as immediate execute.)
- f0 Increments and displays sample number.
- f1 Decrements and displays sample number.
- f2 Stores existing sample number so that a "control" can be analyzed.
- f3 Adds a letter character to the sample number.
- f4 Displays sample number.
- f5 Displays results obtained for last sample.