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INVESTIGATION OF THERMIONIC EMISSION ION SOURCES FOR THE ISOTOPIC ANALYSIS OF LITHIUM

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ABSTRACT

A mass spectrometric procedure using a triple filament, thermal emission ion source for the analysis of lithium has been developed.

Five portions of an isotope reference sample No. 9 (NBS) of lithium carbonate were converted to the nitrate form and analyzed using two types of ion sources and two sample holders. It has been found that a triple filament ion source with a 0.005"-diameter tungsten wire as an ionizing filament and a 0.060" wide, 11/16" long, and 0.008" thick Nichrome sample holder is the most desirable. A steady ion current is achieved in about fifteen minutes.

The precision of the measured atom % Li^6 is 0.018 (Standard Deviation). The standard deviation between charges is 0.05.

INVESTIGATION OF THERMIONIC EMISSION ION SOURCES FOR THE ISOTOPIC ANALYSIS OF LITHIUM

H. O. Finley and J. J. Pucilowski, Jr.

Due to the increasing interest in the isotopic composition of lithium, a mass spectrometric procedure for the analysis of lithium was developed at the New Brunswick Laboratory (NBL). A lithium carbonate sample No. 9 distributed by the National Bureau of Standards (NBS) was used in the development of the present procedure. This material is not certified as to isotopic composition at the present time.

The isotopic composition of lithium has been examined by a great number of workers with a wide variety of results. The measured ratio (7/6) varies from 11.00 to 13.00.[1] The primary cause of this variation is that the Li^6 evaporates more quickly than the Li^7 by approximately $\sqrt{7/6}$.[2,5] The fractionation effect of the two isotopes of Masses 6 and 7, especially in the use of a single filament-type ion source, has been well documented. Fractionation is due to the formation of lithium ions directly from the solid.[1,2] The change in ratio does not produce a constant equilibrium of the two ion beams relative to each other, necessitating the integration of ion currents for the lifetime of the sample.[8]

The use of a furnace source to volatilize certain compounds of lithium and the ionization by electron impact has a low overall efficiency.[3] Also, this method has a general background of ions from the residual gases in the source region.[7] The background is especially troublesome when lithium iodide and lithium chloride are usedas charge materials. In addition, the method has certain disadvantages in that the chemical preparation and temperature used to volatilize the compound or the ion group measured may contribute to the absolute accuracy of a measurement.[6,8]

In order to avoid many of these problems a technique using a multiple-filament thermionic ion source has proved to be satisfactory.[2,4,6,7] Lithium nitrate has been chosen because it has the highest vapor pressure of the inorganic compounds.[7] The nitrate solution is placed on one of the side ribbons. This ribbon may be replaced by a larger piece of suitable metal, as no current is passed through the sample holder. Heating the center filament to a temperature of about 1000°C heats the sample sufficiently by radiation to sublime the nitrate. The lithium nitrate vapor impinges on the center tungsten filament producing Li^+ ions. Thus, the approximate fractionation error is a factor equal to $\sqrt{69/68}$; that is, the ratio of square roots of the masses of $Li^7 NO_3^0$ and $Li^6 NO_3^0$, or the isotopic ratio measurement, differs from the true ratio by approximately $\sqrt{69/68}$, which is much nearer to unity than $\sqrt{7/6}$.

The use of the vaporization and thermionic ionization technique reduces the background in the mass spectrometer to zero. This is due, in part, to the 4.6 electron volt work function of tungsten; thus, only those elements that have small enough ionization potentials give any appreciable ionization at the temperature used. Because of this selective vaporization and ionization there is no background in the mass spectrum and no need for long-time pump-down before measurements can be taken. The ratios are readily obtainable and do not alter appreciably as the sample is used up; therefore, this technique was chosen as the most desirable for the analysis of the isotopic ratio of lithium.

Five portions of NBS isotope reference sample No. 9 of lithium carbonate are converted to the nitrate form. Three charges from each container are analyzed. Two ion sources and two types of sample holders are compared. Due to the absence of a standard of known isotopic composition, no absolute value can be determined for the atom % Li^6; however, the overall reproducibility for an individual charge, expressed as a 95% confidence limit (C.L.), is 0.13. This confidence limit includes variability due to two ion sources, two sample holders, the amount of sample charged, and techniques of analysis.

Mass Spectrometer

A six-inch radius, 60° mass spectrometer is used in conjunction with a thermionic emission ion source.[9] A vibrating reed electrometer (VRE) with a 5×10^{11} ohm input resistor is used to measure the ion currents. Magnetic scanning is employed with a fixed source voltage of 4.5 kv. The source slits are set at 0.006" and the collector slit is set at 0.040".

Two types of ionizing filaments and two types of sample holders are used and are shown in Figures 1A, 1B, and 1C. The dimensions of the ion source filaments are as follows:

Source 1: A tungsten ribbon 1/2" long, 0.030" wide, and 0.001" thick. (Ionizing filament)

Source 2: A 0.005"-diameter wire of tungsten, 1/2" long. (Ionizing filament)

The dimensions of the side ribbons (sample holders) are as follows:

Sample Holder 1: A rhenium ribbon 1" long, 0.030" wide, and 0.0015" thick.

Sample Holder 2: A Nichrome strip 11/16" long, 0.060" wide, and 0.008" thick.

Figure 1 A
Source 1, Sample Holder 1

Figure 1 C
Source 2, Sample Holder 2

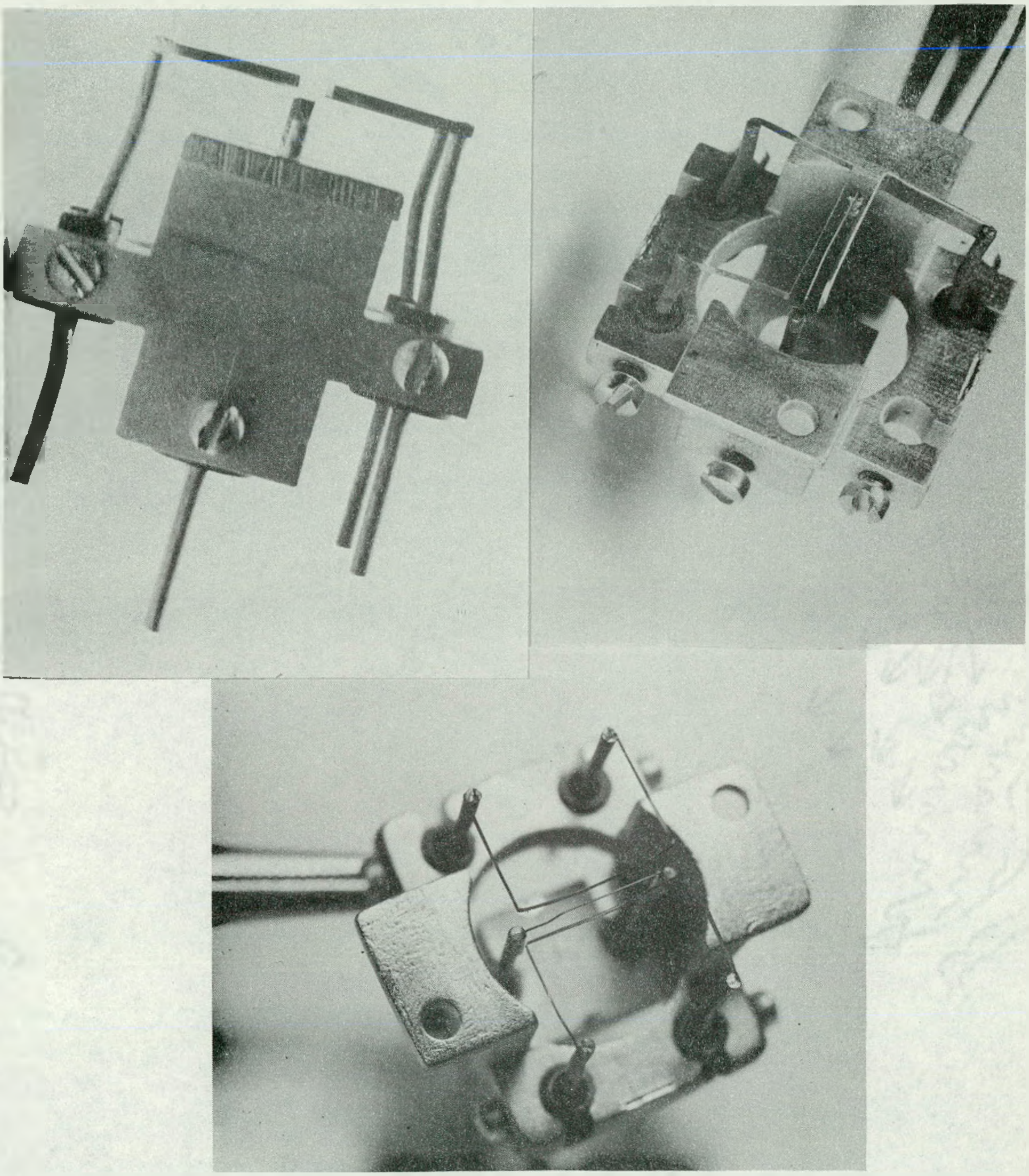

Figure 1 B
Source 2, Sample Holder 1

FIGURE 1. TYPES OF IONIZING FILAMENTS AND SAMPLE HOLDERS.

Sample Preparation

Lithium carbonate is treated with the stoichiometric amount of nitric acid and taken to dryness. A sufficient volume of distilled water is added to give a concentration of 5 µg. of lithium metal per µl. of solution. One µl. of solution is used for analysis.

Filament Preparation and Sample Loading

Two pieces of rhenium ribbon are placed in a jig and are spot-welded to the support rods (side filaments), Figure 1. The two side filaments are used for electrical symmetry; only one is charged with sample. The Nichrome sample holder is also used to replace one side filament. The center filament (ionizing filament), which may be either a ribbon or a wire of tungsten, is also spot-welded to the support rods.

The supporting assembly and the filaments are placed in a vacuum system and out-gassed at about 1000°C. The center filament and one side filament are removed when loading the source, shown in Figures 1A and 1B. The remaining side strip is then charged with sample. The sample holder, shown in Figure 1C, is charged with material and then placed in position. The sample is dried under an infrared lamp at approximately 7" distance, and is dried for approximately 3 to 6 minutes. The sample is always placed on the bottom holder (in respect to gravity) of the ion source.*

Operating Procedure

The pump-down procedure is carried out until a pressure of 3×10^{-6} torr is reached. The instrument controls are set at the proper position. The filament is set at approximately 1.5 amp. and continues to out-gas until a pressure of 1 to 4×10^{-7} torr is reached. Approximately one hour is required. At no time is there current passing through the sample holders.

The $^{M}/e$-7 ion beam current is focused to an intensity of approximately 6×10^{-12} amp. The filament current required to produce this ion beam current is 1.8 to 2.0 amp. using the wire filament, and 2.8 to 3.2 amp. for the flat filament. The times required to stabilize the intensities are 30 to 45 minutes for the latter and 5 to 15 minutes for the former.

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* Note: The ionizing filament is protected when loading the sample holder to prevent contamination. If the ionizing filament is contaminated with sample, serious fractionation occurs. Also, the charged "hat" is placed into the mass spectrometer immediately since lithium nitrate is hygroscopic.

Magnetic scanning is used to drop the 6 and 7 ion beams alternately through a 0.040" defining slit into a Faraday cup which is the input to a vibrating reed electrometer. The output of the VRE is then displayed on a pen-recorder. The ion source voltage remains a constant 4.5 kv. for all measurements.

Measurement and Calculation

The ratio is calculated from measurements taken from the recorder chart by use of a linear scale. Lines are drawn from the up-scan peak deflection of Mass 7 to a down-scan of Mass 7, and a mid-point is taken. The same procedure is applied to Mass 6. This method is sufficient to take care of the fall-out-rate of intensity; however, a difference in up-scan peak height is observed as compared to the down-scan peak height of a pair of peaks.*

It is necessary, therefore, to allow for this time difference or apparent focusing effect. To compensate for this observed difference, a second line is drawn from the last Mass 6 peak of the first pair of peaks to the first Mass 6 peak of the second pair of peaks. Again, the same procedure is applied to the Mass 7 peaks. The mid-point of these lines are now used for a second ratio calculation. Eight ratios are taken and averaged for a measurement. An analysis is complete with the average of four or more measurements taken on different scales and ion intensities making a total of twenty-four individual peak deflections. Confidence limits (C.L.) are determined solely for the individual peak-to-peak ratio in order to determine the internal precision, degree of fractionation with time, and any non-linearity of the measuring circuit. Only the four averages are used to determine the reproducility, not 24 averages. However, there is no apparent difference in the 95% C.L. of the two methods. Due to the lack of a known standard to determine the accuracy, only precision can be determined.

Experimental

Five equal portions of the lithium carbonate were treated with the stoichiometric amount of nitric acid. The five resulting solutions were then analyzed several times to see if any difference due to chemical treatment was observed. Two ion sources were also used to determine their difference when using Sample Holder 1. The data are shown in Table 1 and are shown by graphical form in Figure 2.

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* Note: This is especially noticeable when the magnet current is varied in a large-radius (12") magnet.[10] This effect in peak heights is caused, in part, by the difference in slope in the hysteresis loop of the magnet.[7] This appears to give a different image width or scan speed.

TABLE 1

MEAN VALUE USING ION SOURCE 1 AND SAMPLE HOLDER 1

Portion	Atom % Li^6	Charge No.	Standard Deviation		N**
			Individual	Mean	
1	7.531	1	0.010	0.005	4
	7.478	2	0.042	0.021	4
	7.531	3	0.014	0.007	4
Average	7.513		0.030	0.018	3
2	7.516	1	0.048	0.021	5
	7.526	2	0.014	0.006	5
	7.596	3	0.015	0.007	5
Average	7.546		0.044	0.026	3
3	7.568	1	0.013	0.006	5
	7.516	2	0.019	0.008	5
	7.555	3	0.004	0.002	5
Average	7.546		0.027	0.016	3
4	7.513	1	0.032	0.014	5
	7.502	2	0.024	0.011	5
	7.493	3	0.025	0.011	5
Average	7.502		0.010	0.006	3
5	7.550	1	0.028	0.012	5
	7.556	2	0.027	0.012	5
	7.537	3	0.030	0.013	5
Average	7.548		0.010	0.006	3
Average of 5 portions of $LiCO_3$	7.531		0.022	0.010	5
Corrected Value*	7.480				

* On the assumption that $LiNO_3$ is sublimed from the side filament.

** N = Number of measurements.

The above data show no variances between portions. However, portions 1, 2, and 3 show variance between charges over and above the measurement variance. Portions 3 and 4 show no variance between charges. As noted, the standard deviation (S.D.), Figure 2, of the measurements for each charge is high and the difference between charges may be contributed, in part, to the technique of charging that may contaminate the ionizing filament.

Another ion source was tested in an effort to improve this effect.

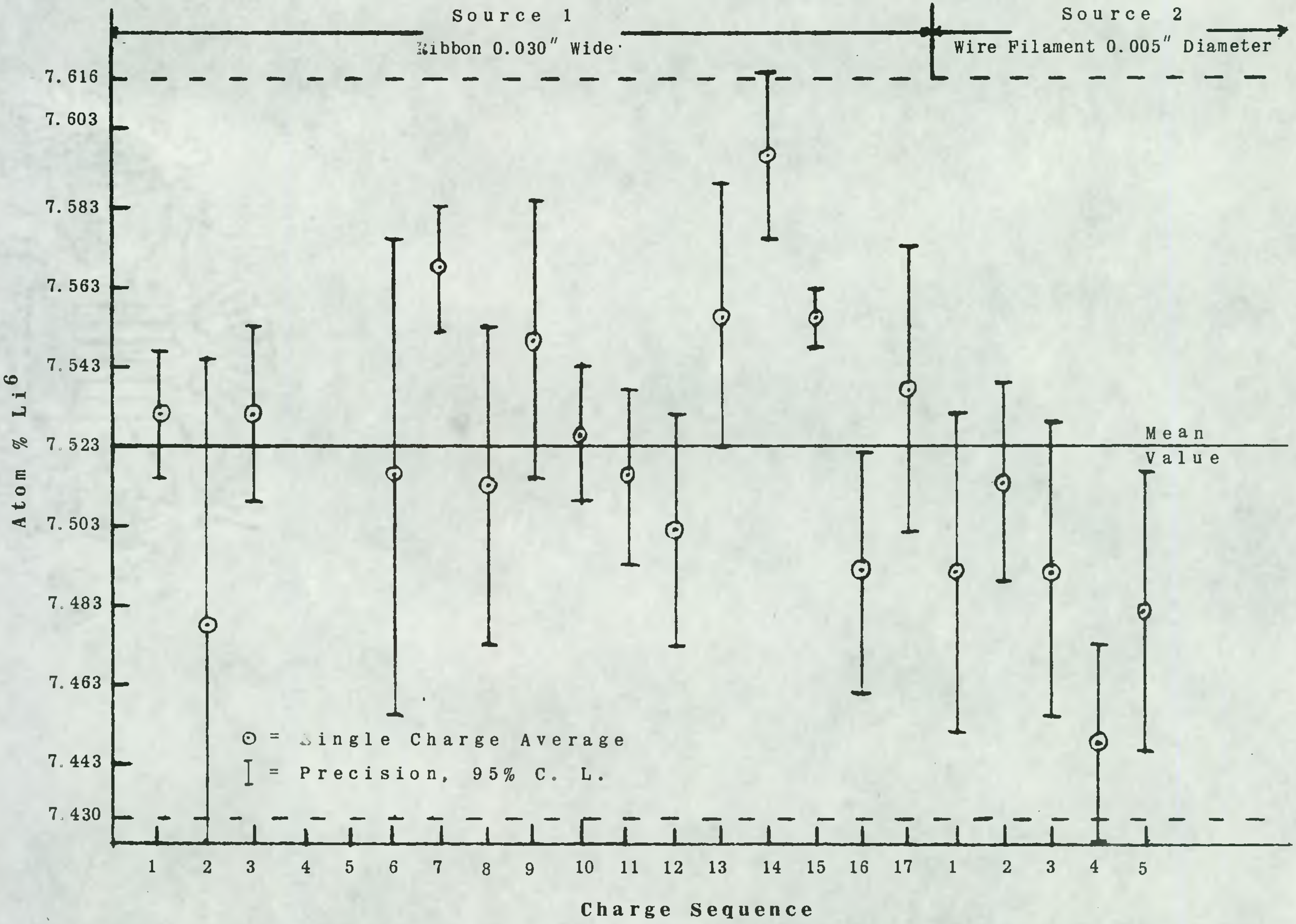

FIGURE 2. MEAN VALUES AND PRECISION FOR SOURCE 1 AND SOURCE 2 WITH RHENIUM SAMPLE HOLDER.

The suspicious step in the above technique, using the 0.030" flat ionizing filament, is the high probability that a very small amount of the sample from the side filament may condense on the center filament during the pumping and out-gassing period, regardless of the care taken. The small surface of Source 2 using a 0.005"-diameter wire should reduce this probability.

One charge from each portion was analyzed using Source 2. The data are shown in Table 2 and a comparison of the two sets of data is shown in Figure 2.

TABLE 2

MEAN VALUES USING ION SOURCE 2 AND SAMPLE HOLDER 1

Portion	Charge	Atom % Li^6	Standard Deviation Individual	Standard Deviation Mean	N
1	1	7.465	0.028	0.012	5
2	1	7.491	0.033	0.015	5
3	1	7.514	0.021	0.009	5
4	1	7.491	0.031	0.014	5
5	1	7.449	0.020	0.009	5
Average 5 portions		7.482	0.025	0.011	5
Corrected Value*		7.431			

* On the assumption that $LiNO_3$ is sublimed from the side filament.

Discussion of Data Using Source 1 and 2 (Sample Holder 1)

There is a significant difference between the two ion sources. Source 2 averages 0.014 lower than Source 1. Source variability for an individual analysis is 0.029 (S.D.). The charge variability, over and above the measurement variability, is 0.026 (S.D.) and there is no significant difference between the five portions of lithium carbonate.

It is not an easy matter to define source variability using this type of technique because the ionization processes are not clearly understood.[11,7] Ion source 1 showed fractionation from the beginning to the end of an analysis but eventually came to some type of equilibrium as the data indicates; whereas Source 2 reached an equilibrium within 15 minutes giving acceptable ratios for several hours without any measurable change. If source variability can be eliminated, the standard error for a charge of five measurements is 0.027. Due to the fractionation effects associated with Source 1, it was decided to eliminate it and accept Source 2 as the most reliable.

The approximate 95% confidence limits for a single charge of five measurements are 0.1 absolute or about 0.06 after the source variability is eliminated. As shown in Figure 2, the precision within a single analysis is also large for Ion Source 2 and Sample Holder 1. This lack of precision is due to the inability of the analyst to control the intensity of the ion beams. To improve this condition, a second sample holder of greater mass was used and is shown in Figure 1C. This holder functions as a "heat-sink"; accordingly, the analyst has excellent control of the intensity.

The data are shown in Table 3. A comparison of data between the two sample holders using Source 2 is shown graphically in Figure 3.

TABLE 3

MEAN VALUES USING ION SOURCE 2 AND SAMPLE HOLDER 2

Portion	Charge	Atom % Li^6	Standard Deviation Individual	Standard Deviation Mean
1	1	7.420	0.012	0.005
1	2	7.533	0.018	0.006
1	3	7.542	0.019	0.006
1	4	7.534	0.014	0.006
1	5	7.484	0.017	0.007
1	6	7.438	0.024	0.008
1	7	7.481	0.013	0.006
Average 7 charges		7.496	0.050	0.019
Corrected Value*		7.444		

* On the assumption that $LiNO_3$ is sublimed from the side filament.

The precision of the measurements using Sample Holder 2 shows a definite improvement over Sample Holder 1; however, the charge variability is greater for Sample Holder 2. This difference is due, in part, to the routine method used to analyze the samples; i.e., two analysts charged and operated the instrument with little consideration to sample size and temperature of the ionizing filament. However, the advantages outweigh the disadvantages; therefore, Source 2, Sample Holder 2, is more acceptable.

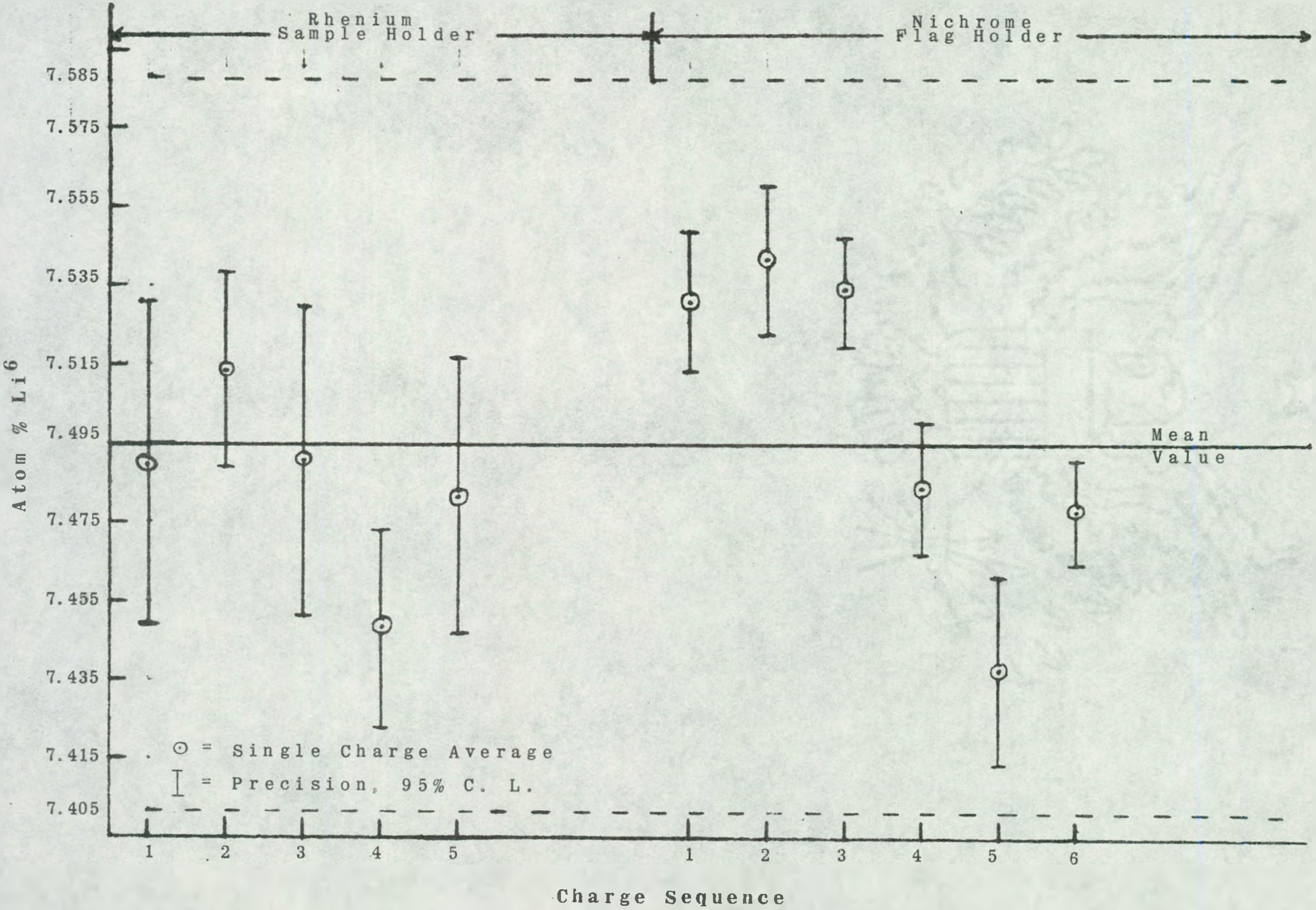

FIGURE 3. DATA FOR TWO TYPES OF SAMPLE HOLDERS USING ION SOURCE 2.

Summary of Data

The summary of the data for the two ion sources and two sample holders is shown in Table 4.

TABLE 4

SUMMARY OF DATA (ATOM % Li^6)

	Ion Source 1 Sample Holder 1	Ion Source 2 Sample Holder 1	Ion Source 2 Sample Holder 2
Mean Values (Not Corrected)	7.532	7.482	7.496
Corrected $\sqrt{69/68}$	7.480	7.431	7.444
Standard Deviation Individual Charge	0.025	0.019	0.048
Standard Deviation Individual Measurement	0.026	0.028	0.015
Standard Deviation - Mean	0.010	0.010	0.019

Differences in Variability

1. The between-charge variability is greater for Source 2 and Sample Holder 2 than for Source 2 and Sample Holder 1.

2. The measurement error for Source 2 and Sample Holder 2 is significantly lower than for the other two combinations.

3. The only significant difference is between Source 1 and Source 2 when using Sample Holder 1.

Conclusion

1. Significant differences have been determined between two thermionic emission ion sources used in the isotopic analysis of a lithium nitrate charge material.

2. An ion source composed of a 0.005"-diameter ionizing filament of tungsten and sample holder of Nichrome, 0.060" wide, 11/16" long, and 0.008" thick, is proven to be the most desirable, based on the following:

   a. An equilibrium between the sublimation of the lithium nitrate and the ionization processes is reached, yielding a steady ion current within 15 minutes. Due to the assumed sublimation process, a correction, $\sqrt{69/68}$, is applied to the measurements, but no change in ratio is observed due to the ionization processes on the surface of the ionizing filament; thus the correction $\sqrt{7/6}$ is not applied.

b. The precision of the measurements within an analysis has improved from a standard deviation of 0.028 to 0.018. The standard deviation for a single analysis is 0.05.

c. The large standard deviation shown for a single charge is believed to be due to a relationship between sample sizes, methods of sample loading, and analysts' techniques.

3. No experimentation was carried out in order to observe effects of the magnetic analyzer and ion source optics associated with this method of analysis, and, if present, these effects are included in the total error.

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