

# Lithium Isotopic Analysis Using ERIAD (Electrospray with in-source collisional atomization)

Artyem Dyachenko<sup>1</sup>, Natalia Samsonova<sup>2</sup>, and Nikolay Gall<sup>2\*</sup>

<sup>1</sup>IAI RAS, 31-33, Lit. A, Ivan Chernykh St., St. Petersburg, Russia

<sup>2</sup>Ioffe Institute, 26, Polytechnicheskaya, St. Petersburg, Russia

**Abstract.** The paper considers a number of physical processes occurring during electrospraying of analytical solution, ion transport in the ERIAD interface (electrospraying with atomization in the ion source) and in a specialized mass analyzer, and providing analytical characteristics of the device required for lithium isotope analysis. Registration of lithium isotope signals (<sup>6</sup>Li and <sup>7</sup>Li), is carried out simultaneously on a two-channel receiver based on a doublet of microchannel plates. The gas-dynamic interface is constructed according to the Kontorowitz-Gray type scheme; it is gas-dynamically "long", i.e. the distance between the nozzle and the skimmer is ~4 times larger than the size of the "Mach barrel" at operating pressure (200 Pa). It is shown that the achieved accuracy of analysis in determining the fraction of <sup>7</sup>Li isotope in the mixture is 0.03%, which corresponds to the requirements of technological control in lithium isotope enrichment by homogeneous sorption methods.

## 1 Introduction

Lithium is one of the elements demanded by modern high-tech industry. It is used to create compact batteries and capacitors, and is also used in electronics, ceramics and metallurgy. Of great importance is the use of various lithium isotopes in nuclear technology, for example, to improve the stability of nuclear reactors [1]. For this purpose it is necessary to carry out isotopic enrichment of lithium and measure its isotopic composition, for this purpose mass spectrometry is usually used. In nature, lithium is represented by two isotopes <sup>6</sup>Li (~6%) and <sup>7</sup>Li (~94%); the former is a strong neutron absorber, the latter, on the contrary, absorbs neutrons weakly and selectively [2]. These differences in properties determine both the differences in application and the requirements for the degree of isotopic enrichment, and hence the accuracy of isotopic ratio measurements. The present work is devoted to the description of the measurement of lithium isotopic composition using the ERIAD method.

---

\* Corresponding author: [gall@ms.ioffe.ru](mailto:gall@ms.ioffe.ru)

## 2 Methods

ERIAD is a modern method for measuring the isotopic and elemental composition of substances based on electrospraying of highly dilute solutions of salts of the target element at atmospheric pressure, introduction of the resulting ions into vacuum through a gas-dynamic interface with simultaneous collision atomization. It is suitable for the vast majority of elements, the method has a high absolute sensitivity, allows analysis in a time of about 180-300 seconds and does not require evacuation of the device for sample change. All these characteristics make this method valuable, especially for solving technological problems or scientific tasks on the development of isotope separation technology, where it is necessary to make more measurements in short time intervals.

The specificity of lithium isotope measurements is a significant contribution of ion scattering on the residual gas, since the mass of lithium ions is much lower than the mass of atmospheric gas molecules. Therefore, for lithium measurements it is desirable to create specialized mass spectrometers with a short ion-optical path, which is possible because of the small mass number of lithium isotopes [3].

The measurements were performed on a compact specialized mass spectrometer MI-20 LowMass, based on a magnetic mass analyzer with a double-focusing Mattauch-Herzog-type geometry with a constant magnet. The instrument used an inverted power supply scheme: the skimmer, i.e., the ion birth region, was under the Earth potential, while the mass analyzer elements, including the dispersing magnet, were under the accelerating potential. The ERIAD source described in [4] was used as an ion source. The ion guide was not used: the skimmer was opened directly into high vacuum, while the double-focusing mass analyzer allowed the use of an ion beam with a large energy spread, and the wide slits of the source reduced the losses caused by chromatic aberration of electrostatic lenses.

The signal was recorded using a receiver on a doublet microchannel plate with two detectors located behind the second plate. In front of the first plate, a metal diaphragm closed with a grid was installed at a distance of 2 mm from it. Both lithium isotopes were registered simultaneously each on its collector, and the value of the supply voltage of the secondary electron multiplier was adjusted simultaneously with respect to the discriminators of the ion counters of both channels, which made it possible to achieve practically the same level of discrimination. In this way it is possible to achieve maximum sample utilization, and at the same time to level out possible instabilities in the operation of the ion source, power electronics and recording system, since they simultaneously affect both measured isotopes. The instrument itself and its analytical characteristics are described in [5].

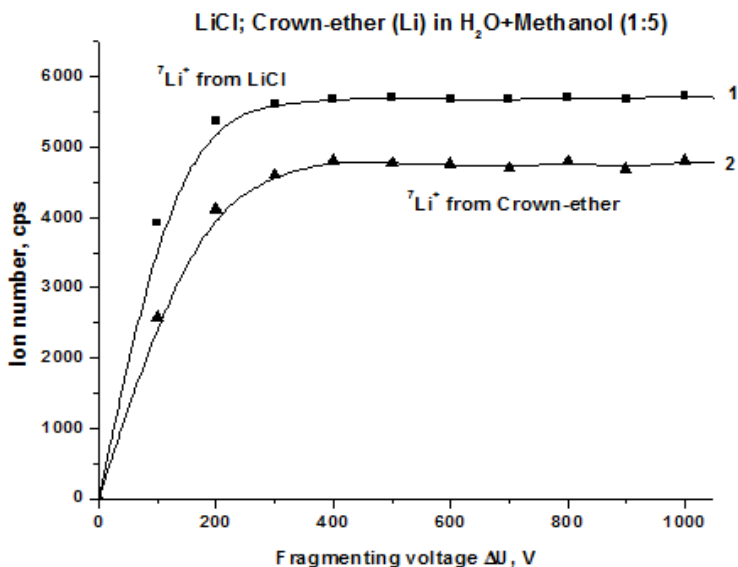
Electrospraying was carried out at atmospheric pressure in atmospheric air. The sample was supplied by a syringe pump from a disposable syringe through a polypropylene capillary. The interface was constructed using a Contorowitz Gray-type scheme in which the axes of the nozzle and skimmer, are offset by 1 mm to prevent unevaporated droplets from entering the skimmer orifice. From the gas dynamic point of view, the interface was built according to the "long" scheme, when its length is several times longer than the length of the "Mach barrel", which is formed behind the nozzle. Such an interface is technological and provides a stable mode of ion transportation [6].

## 3 Results and discussion

The operating pressure in the interface was  $\sim 200$  Pa. By adjusting the pumping speed of the forevacuum pump using the valve installed on it, it was possible to vary this pressure up to  $\sim 1000$  Pa. The pressure in the main chamber was  $2 \cdot 10^{-4}$  Pa at  $\sim 200$  Pa in the interface and dropped to  $7 \cdot 10^{-4}$  Pa at  $\sim 1000$  Pa. The accelerating voltage was 2300 V

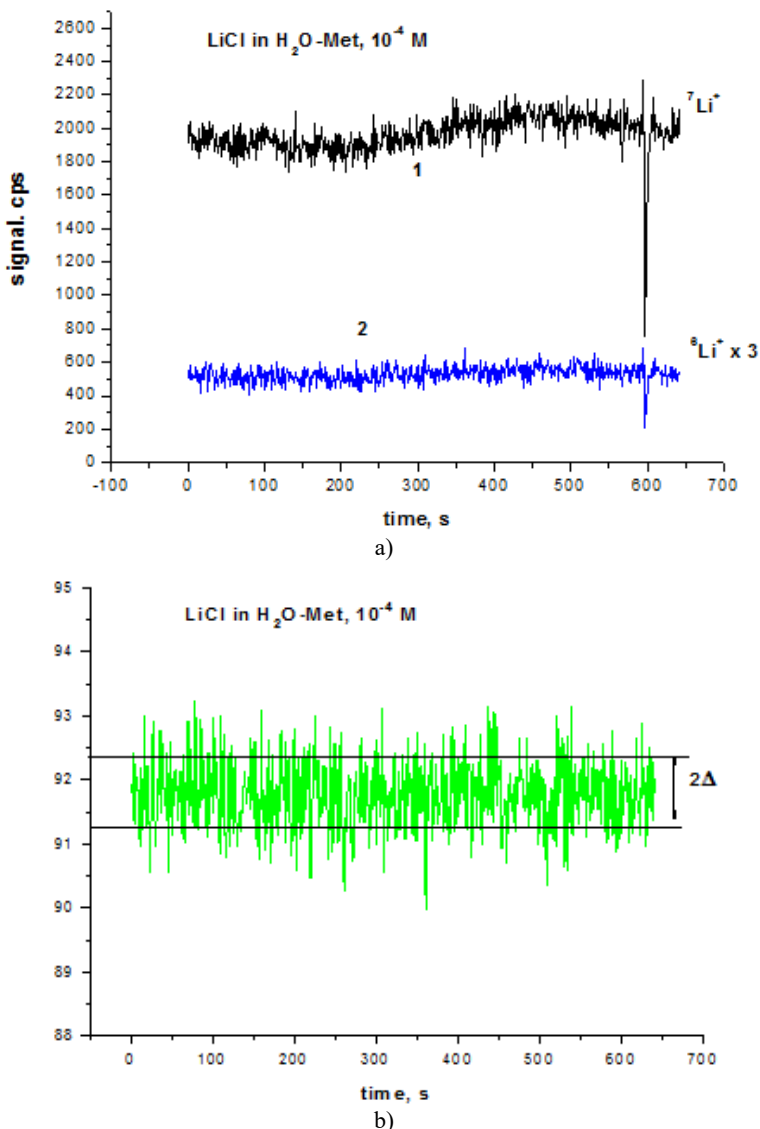
Samples of LiCl with natural isotope content (laboratory standard) and samples of crown ethers capable of isotope-selective sorption of lithium were used as objects of study. The salt samples were weighed on electronic scales and dissolved in bidistilled water; the resulting solutions were diluted with the same water to concentrations of  $5 \cdot 10^{-4} \text{M}$ . The solution was then diluted with methanol at a ratio of 1:4, placed in a disposable 1 ml syringe and mounted on a syringe pump for atomization. Electrospraying was carried out at a potential of 2800-3200V, the atomization current was 50-60 nA, and the atomization rate was  $5 \mu\text{L/s}$ . Solutions of crown ethers in chloroform were dissolved in isopropyl alcohol and then in a water-methanol solution to concentrations of  $5 \cdot 10^{-4} \text{M}$ . The electrospray remained stable for hundreds of seconds, but brief instabilities occurred periodically. The sample or standard exchange time was 100s and remained constant during the experiments.

Both lithium salts and crown ethers were well fragmented at the interface, producing atomic lithium ions at the output. Figure 1 shows the dependence of the  $^7\text{Li}$  ion current on the fragmentation voltage  $\Delta U$  for LiCl and for crown ether; it can be seen that at  $\Delta U > 300 \text{V}$  the dependence reaches a plateau, which is consistent with the expected data [2].



**Fig. 1.** Dependence of  $^7\text{Li}$  isotopes signal intensity from a standard - LiCl salt solution in water-methanol (1:4) solvent (1) and from an equimolar Li containing crown ether solution in a similar solvent (2) on the fragmentation voltage between the nozzle and skimmer  $\Delta U$ .

In the measurements, signal accumulation was performed for each point for 600 or 1000 sec with recording once per second; these data are shown in Figure 2A. All data were stored, including those that corresponded to moments of unstable atomization (e.g., the emission at 600 s of measurement in Figure 2A). Figure 2 shows a typical plot of the accumulated primary data. It is interesting to note that at moments of sputtering instability, only the magnitudes of the lithium isotope currents themselves change, but not their ratio (i.e., the measured isotope signals), which, with few exceptions, remains within a spread equal to the variance. Figure 2A clearly shows the drift of the instrument.

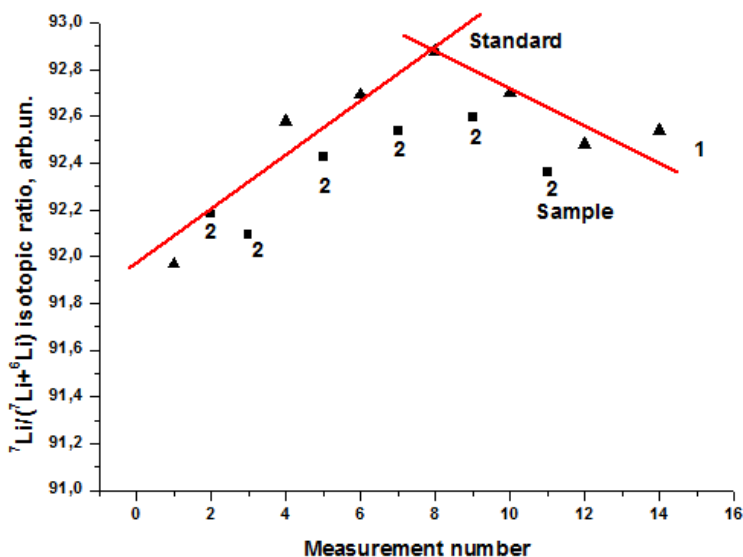


**Fig. 2.** Results of Li isotope ratio measurement by the ERIAD method. **A** - primary data: 1 - <sup>7</sup>Li<sup>+</sup> isotope signal, 2 - <sup>6</sup>Li<sup>+</sup> isotope signal (multiplied by 3). **B** - calculation of the isotopic ratio <sup>7</sup>Li/(<sup>6</sup>Li+<sup>6</sup>Li) obtained from the data of Figure 2A. Horizontal lines indicate the level of data scatter equal to twice the calculated variance.

Figure 2B shows the result of calculation of isotopic ratios, which are obtained by direct arithmetic calculation from the data of Figure 2A. It can be seen that there is almost no drift here and most of the data lie inside the confidence interval equal to two values of variance, however, about 30% of the data lie outside this interval. In calculating the final mean, points that fell outside the interval described by the double variance of the original data were removed from the data. Among these data are a number of points associated with moments of atomization instability when the measured data differ significantly from the mean. The physical cause of such effects is currently unclear, but they have a negative impact on the analytical performance of the instrument. Eliminating these data by the criterion described above increases the results convergence considerably.

In practice, measurements are always carried out using a standard, and long-term drifts of the instrument have to be taken into account to achieve high accuracy. In order to reduce the influence of these effects, the measurement technique involved measuring the isotopic ratios of the standard sample after each measurement in the sample, and the measurements of the sample and standard sample were performed rhythmically, every 12 or 20 min, depending on the chosen averaging time (600s or 1000s).

Figure 3 shows a typical dependence of the measured isotope ratios in the sample and standard obtained by the method described above. The long-term drift of the instrument, which affects the value of measured isotopic ratios in both the standard and the sample, reducing the accuracy of measurements, is clearly visible. According to the currently accepted methods of mass spectrometric data processing, the drift was approximated and subtracted, i.e... taken as a new baseline. To check the stability of this procedure, several types of approximation were compared: a piecewise broken line or polynomials of the 3rd, 4th, and 5th orders. The approximation procedure of the program "ORIGIN 7" was used.



**Fig. 3.** Lithium isotopic composition measurements from the LiCl standard (1, triangles) and the lithium sample in crown ether (2, squares). The approximation of the variation of the standard line (baseline) was made by a piecewise broken line in the «ORIGINE7» program.

Note that the mean values of isotope ratios and standard deviations calculated for all four types of approximation differ very slightly: the measured mean values differ from each other by less than 0.05%, and the deviations - by less than 0.01%. For practical purposes, the approximation by a polynomial of degree 5 was used. The relative accuracy of isotopic ratio determination for the standard, taking into account instrument drift, was ~0.03% over 11 measurements.

The following data were obtained for the sample of crown ether capable of isotopically selective sorption of lithium, indicated by number 2 in Figure 3:

$$\delta = (R_{st} - R_{7Li})/R_{st} * 1000 = 0.304 \pm 0.02\%$$

where  $\delta$  is the deviation of the isotopic ratio  ${}^7\text{Li}/({}^7\text{Li}+{}^6\text{Li})$ . It can be seen that there is a statistically reliable depletion of the sample by  ${}^7\text{Li}$  isotope at the level of ~ 0.3% as a result of sorption by crown ether.

## 4 Conclusion

Thus, it is shown that ERIAD mass spectrometry is a successful solution for lithium isotopic analysis, providing high accuracy and fast sample change provided that a specialized instrument with a short ion-optical path is used. It can be expected that the ERIAD method will be equally effective for measuring the isotopic compositions of other elements.

## References

1. T. Ault, *Lithium Isotope Enrichment: Feasible Domestic Enrichment Alternatives, Report UCBTH-12-005* (UK, University of California, Berkeley, 2012).
2. E. Mattar, N. Jawerth, Exploring Research Reactors and Their Use. IAEA Bulletin on Research Reactors **60(4)**, 1 (2019).
3. S.M. Bernasconi, B. Hu, U. Wacker, J. Fiebig, S.F.M. Breitenbach, T. Rutz, Rapid Commun. Mass Spectrom. **27**, 603-612 (2013).
4. N.S. Samsonova, N.M. Blashenkov, A.A. D'yachenko, A.A. Semenov, A.V. Lizunov, N.R. Gall', Instrum. Exp. Tech. **62(5)**, 653-658 (2019).
5. Herzog, R. Ionen- und elektronenoptische Zylinderlinsen und Prismen. I. *Z. Physik* **89**, 447-473 (1934).
6. E. Mossali, N. Picone, L. Gentilini, O. Rodriguez, J.M. Pérez, M. Colledani, Journal of Environmental Management, **264**, 110500 (2020).