

Specialized mass spectrometer for determining the isotopic composition of lithium by ERIAD (electrospray with in source atomization)

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A specialized isotope mass spectrometer for determining the isotopic ratio of lithium by ERIAD (electrospray with atomization in an ion source) is described. The device uses a Mattuha–Herzog–type mass analyzer with double focusing to use ion beams with a large spread in energy and simultaneous registration of signals of both lithium isotopes (⁶Li and ⁷Li), and a two–channel receiver based on a doublet of microchannel plates. The gas–dynamic interface is built according to the Kontorowitz–Gray scheme; from the gas–dynamic point of view, it is „long“, that is, the distance between the nozzle and the skimmer is 4 times the size of the „Mach barrel“ at the operating pressure (200 Pa). The device is desktop, its weight does not exceed 20 kg. The measurement time is 1000 s, sample replacement time is 100 s, measurement accuracy is ~ 0.1%.

Keywords: mass spectrometry, electrospray, ion source, isotopes of lithium.

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Employment of different lithium isotopes in atomic technologies [1] is greatly important both for solving defense tasks and improving operating stability of nuclear reactors [2]. In nature, lithium is represented by two isotopes, ⁶Li (~ 7.5%) and ⁷Li (~ 92.5%). The first one is an efficient neutron absorber, while the second one, vice versa, absorbs neutrons only slightly. The difference in properties defines also differences in applications and in requirements for the extent of isotopic enrichment, and, hence, for the accuracy of measuring the isotopic ratios.

ERIAD (electrospray with in–source atomization) is a state–of–the–art technique for measuring the isotopic composition based on electro spraying highly diluted solutions of the target material salts under the atmospheric conditions and introducing the generated ions into vacuum through the gas–dynamic interface with simultaneous collision–type atomization. The technique is suitable for the great majority of elements, is highly sensitive, ensures the analysis time of about 3–5 min, and does not require opening the device for replacing the sample. All these characteristics make the technique quite valuable, especially in using it in solving technological tasks or research tasks aimed at elaboration of an isotope separation technique needing performance of a large number of measurements within relatively short timeframes.

At present, no any specialized mass–spectrometers for the lithium isotopic analysis are available on the market; conventional devices like TRITON produced by Thermo Scientific (USA–Germany) are too cumbersome and expensive for such a task. Moreover, this device became

almost inaccessible for Russian users under sanctions. This study is devoted to developing a specialized compact mass–spectrometer for determining the content of ⁷Li isotope.

To solve the assigned task, there was proposed a device whose ion–optical and gas–dynamic schemes are presented in Fig. 1. The sample is supplied into the spraying capillary 4 via a syringe pump; the spraying voltage ranging from 2600 to 2800 V is applied to the capillary inlet. Charged droplets formed during electrospray evaporate due to friction in the atmospheric pressure region; released lithium–containing ions are being pulled into the interface through the nozzle 5, pass through its gas–dynamic system where they get atomized, and then enter the high–vacuum region 3 through the skimmer 6. After that, the ion beam is formed by the immersion lens 7 and sent to the mass analyzer 8 and 9; then it is detected by the two–channel detector with simultaneous registration of both the isotopes 10. The last one is very important since electrospray is not a stable process, and concurrent detection eliminates the major part of the isotope measurement errors caused by that instability.

Gas–dynamic calculations of the interface were performed using program code Fluent in the axially symmetric approximation. The interface was designed according to the so–called „long“ scheme with the „Mach barrel“ length (11 in Fig. 1) at least 4 times shorter than the distance between nozzle 5 and skimmer 6 over the entire operating pressure range. This scheme ensures stability of the interface operation with respect to pressure variations and enables its adjustment to the optimal mode of ion atomization

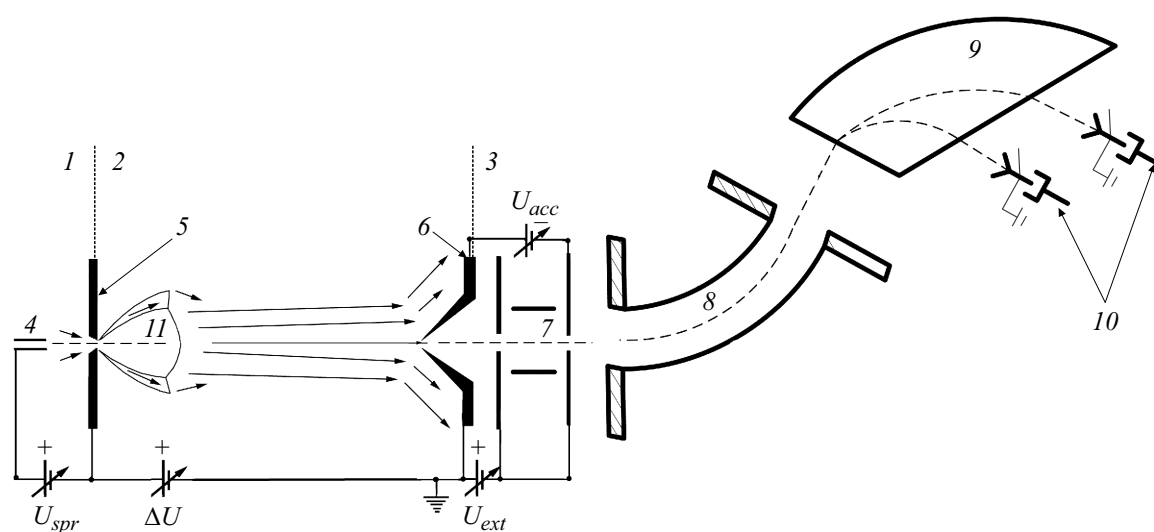


Figure 1. Schematic diagram of the mass-spectrometer ion-optical and gas-dynamic systems. 1 — atmospheric pressure region, 2 — medium vacuum region, 3 — high vacuum region, 4 — spraying capillary, 5 — nozzle, 6 — skimmer, 7 — ion source immersion lens, 8 — electrostatic energy analyzer, 9 — dispersing magnet, 10 — two-channel receiver, 11 — „Mach barrel“.

and collection by varying in the user-operation mode the evacuation rate and, hence, the structure of the self-similar gas jet that transports the ions. The positive-polarity atomizing voltage is applied to the interface inlet nozzle, while the outlet skimmer is earthed [3].

To draw out and focus the ions leaving the skimmer to high vacuum, a cylindrical immersion lens is used. The skimmer opening or, more exactly, the surface where the last ion-gas collision takes place (the region of transition to the high-vacuum mode) is assumed to be the ion place of origin in terms of the mass analysis. The source outlet slot $500\mu\text{m}$ wide was under the accelerating voltage. The calculation shows that it cuts off a significant portion of ions with initial energies above 20–25 eV and passes almost 100% of ions with lower initial energies.

The mass analyzer was constructed according to the double-focusing Mattuha-Herzog-type scheme with a non-zero outlet arm. The double focusing makes it possible to work with ion beams characterized by a wide spread in energy. The mass analyzer was designed and optimized in the aberration approximation. The main ion-optical scheme characteristics are listed in the Table.

The dispersing magnet was $60 \times 80 \times 160$ mm in size and was able to create magnetic field of about 0.03 T in the gap 10 mm high. As the energy analyzer, a cylindrical capacitor was used. When the ion source slot was 0.5 mm, the resolution was ~ 20 , which was more than sufficient for solving the assigned problem.

The device design (see below) allowed employing a mass analyzer with a „suspended“ magnet: the accelerating voltage is being applied to the mass analyzer dispersing components, and ions arise at the earth's potential. Such a design allows avoiding the main factor complicating the use

of static electrospray-based mass analyzers, that is, charge ignition in the high-vacuum region near the skimmer.

As the ion receiver, an assembly of two microchannel plates (secondary electron multiplier VEU-7) was used, behind which two collectors were placed; this made it possible to receive two ion beams simultaneously. VEU-7 was operated in the ion counting mode. On the side of inlet it was covered with a mask having two slots 3 mm wide; the distance between the slots matched with the distance between the lines of lithium isotopes.

For designing the mass-spectrometer, an up-to-date technique known as „MS-platform“ was chosen. This is that all the critical ion-optical components (the mass analyzer as a whole, ion source high-vacuum part, and ion receiver) are mounted on a common plate located in high vacuum. The dispersing magnet was constructed by using Nd-Fe-B magnetomotive components; its weight was ~ 1900 g. The magnetic field was ~ 0.03 T. The mass analyzer was under high voltage; the ion-optical path as a whole was enclosed in electrostatic screens. The entire high-vacuum system of the mass-spectrometer was located in one and the same vacuum chamber $250 \times 320 \times 100$ mm in size, which was evacuated by using a turbomolecular pump with the pumping rate of 300 l/s. The device was produced by „MS-Bio“ Ltd. The mass-spectrometer was controlled from a personal computer using a special-purpose software under WINDOWS OS.

The mass-spectrometer was tested by using the laboratory reference material: 99% pure LiCl salt produced by „Isotope“ (USSR), with the natural content of isotopes. Weighed portions of the salt were dissolved in bidistilled water; the obtained solutions were diluted with the same water to the concentration of $5 \cdot 10^{-4}$ M and then with chemically pure methanol or acetonitrile to the ratio of 1:5.

Design characteristics of the mass analyzer ion–optical circuit

Characteristic	Value
Magnet turning radius, mm	60
Turning angle in the magnet, °	63.96
Focal line slope, °	53
Turning angle in the electrostatic energy analyzer, °	37.87
Central trajectory radius in the electrostatic energy analyzer, mm	63
Magnet gap, mm	6
Electrostatic energy analyzer gap, mm	10
First arm, mm	35.28
Second arm, mm	29.45
Distance between the electrostatic energy analyzer and magnet, mm	30
Source slot width, mm	0.5

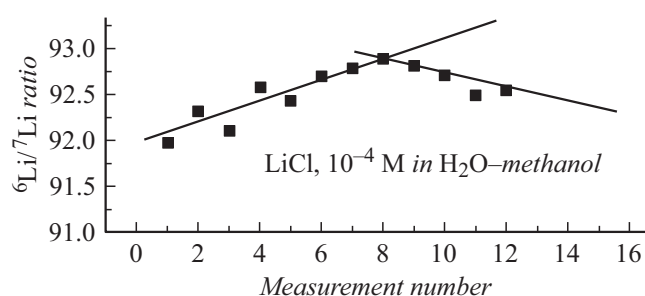


Figure 2. Temporal drift of the measured isotope ratio of the reference LiCl (10^{-4} M) sample in the 1:5 water–methanol mixture. The inter-measurement time was 1100 s, spraying voltage was 2800 V, solution flow rate was $5 \mu\text{l}/\text{min}$, atomizing voltage was 400 V. The basic line was interpolated by a piecewise–broken line using the ORIGIN software.

The sample was drawn up into a 1 ml disposable syringe and installed on the syringe pump for spraying. Spraying was performed at the potential of 2800–3200 V, the spraying current was 50–60 nA, the spraying rate was $5 \cdot 10^{-6}$ l/s. The interface pressure was ~ 200 Pa, the main–chamber pressure was 10^{-4} Pa. The accelerating voltage was 2300 V. At the interface, the lithium salt was properly fragmented with producing atomic ions whose current slightly depended on the fragmentation voltage ΔU ranging from 200 to 800 V. The ^6Li signal was detected in the first collector, that of the ^7Li was detected in the second collector. The counting rate was about 10 000 cps for ^7Li and 800 cps for ^6Li .

During measuring, the signal at each point was accumulated for 1000 s with recording once a second. Data differing from the mean values by more than 20% in magnitude were automatically rejected as corresponding to the moments of unstable spraying. Fig. 2 presents a typical dependence of the measured isotopic ratio in the reference sample and its temporal drift. Time of one measurement was 1000 s, time of the sample and reference material replacement was 100 s, which is approximately 30 times faster than in the case of using the surface ionization. Standard deviation in determining the isotope ^7Li fraction

based on 11 measurements appeared to be $\sim 0.03\%$ which is sufficient for most of process measurements.

Thus, an efficient isotope mass–spectrometer with an ion source ERIAD has been developed for the first time; being combined with a Mattuha–Herzog–type mass analyzer operating in the mode of simultaneous detection of signals of the isotopes under measurement, it appears to be a quite successful solution of the isotope–analysis problem, which provides high accuracy and fast sample replacement. The device is desktop, its weight does not exceed 20 kg. It is especially efficient for in–process control tests needing fast sample replacement. The created device may be used both in certifying finished products and in in–process measurements during isotopic enrichment. The ERIAD technique may be expected to be of the same efficiency also in measuring isotopic compositions of other elements, especially radioactive ones.

Conflict of interests

The authors declare that they have no conflict of interests.

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