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Electrophoretic Separation of Ions, Including Isotopic Ones, with Similar Chemical Properties for Preparative and Analytical Purposes

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Abstract—The reasons for the failure of the first attempts at countercurrent electrophoretic separation of isotopic lithium ions are analyzed. It is concluded that the separation of these ions in the potentiostatic version of the countercurrent process scheme used by the authors is futile. As an alternative for the preparative separation of isotopic and other ions with similar chemical properties, a galvanostatic mode of countercurrent electrophoretic separation is proposed. Using examples of the separation of alkali metal ions and isotopic lithium and rubidium ions, it is shown that in this case the system enters a stationary self-regulating regime and significantly higher separation factors are achieved compared to the potentiostatic version of the process. It has been determined that a high separation efficiency is achieved with a minimum length of the separation space. For significant effects of the separation of isotopic lithium ions, a separating column 4 mm in height filled with quartz sand is sufficient. Additionally, to address the analytical challenges of electrophoretic separation of isotopic ions of light elements, such as lithium and boron, the required efficiency is also achieved under the potentiostatic conditions of the traditional scheme of capillary zone electrophoresis, as demonstrated in the examples of determining the isotopic composition of the aforementioned elements.

Keywords: electrophoresis, separation, potentiostatic and galvanostatic modes, isotopic ions

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Among the most complex challenges in the substance separation methodology is the problem of isotope separation, which has traditionally been addressed through mass separation, and in solving analytical problems, the corresponding mass spectrometry methods. However, the technical complexity and, accordingly, the high cost of these devices have led researchers to explore alternative approaches. Electrophoresis is one such alternative. The first attempts at the electrophoretic separation of isotopic ions were made in the middle of the 20th century focusing on the preparative separation of lithium isotopes [1, 2]. Despite the use of the countercurrent variant of the method, the authors of these works failed to achieve the required efficiency of the process. Given the expanded range of industrial applications of lithium, which often necessitate the preliminary separation of its isotopes, the search for a solution to the problem of separating lithium isotopes on the principles of electrophoresis has been revisited multiple times [3, 4]. Moreover, ongoing research aims to explore new principles for the separation of isotopic lithium ions. Proposed alternatives include a variant

involving the separation of lithium into liquid gallium [5] as a replacement for the environmentally hazardous amalgam method. An original sorbent with a crown ether functional group was proposed for the separation of lithium isotopes [6]. In addition, a method based on the principles of isotope exchange was developed [7]. The original scheme was developed using ionic liquids in the version of impregnated membranes [8]. A new solution for electro dialysis separation using ion-exchange membranes was found [9].

Of the aforementioned works, from the point of view of the simplicity of technical implementation, the solution proposed [3] is particularly attractive. This solution involves countercurrent electromigration in the galvanostatic mode, the possibilities of which have not been sufficiently studied. The purpose of the present work is to bridge this knowledge gap and investigate the possibilities offered by this method.

A prerequisite for choosing the conditions for countercurrent electrophoretic separation of ions is the ratio:

$$u_1 E > v > u_2 E, \quad (1)$$

where E is the potential difference at which separation is carried out, V; u_1 is the electrophoretic mobility of the more mobile of the separated ions, cm/(V s); u_2 is the electrophoretic mobility of the less mobile ion, cm/(V s); v is the linear countercurrent velocity, cm/s, equal to the hydrodynamic flow volumetric velocity, expressed in cm³/s, referred to the cross-sectional area of the separation column, expressed in cm².

When condition (1) is met in a countercurrent system, which involves an electrophoretic column located between the cathode and anode chambers, when a countercurrent is created in the column to the electromigration movement of cations by supplying a solution to the cathode chamber, the processes of enrichment of the solution in the cathode chamber with a more mobile ion and its depletion of ions will occur with a slower electromigration rate.

The stationary regime of enrichment of the solution in the cathode chamber with a more mobile ion and depletion with a less mobile one can be achieved by maintaining the parameters of the electromigration process constant. Therefore, it is necessary to carry out the countercurrent electromigration separation of ions at constant values E and v . However, the attempts made by the authors [1, 2] to separate isotopic lithium ions under potentiostatic conditions did not yield successful results. By setting arbitrary constants E and v , the authors believed that the system, under constant temperature, would spontaneously reach a stationary regime due to the continuous change in ion mobilities in solution caused by changes in their concentration. However, considering the gradual nature of the concentration dependences of ion electromigration rates, compensation for even a slight discrepancy E and v conditions of a stationary process is possible only with significant changes in the concentration of electrolytes, which, in particular, was observed in the experiments described [1]. Furthermore, in order to maintain constant values of u_1 and u_2 , it is necessary to ensure a stable temperature. However, this becomes practically impossible due to the manifestation of the self-heating effect in the system as a result of the electric current passing through the solution. All this leads to instability of the potentiostatic mode of separation and, as a result, to irreproducible results.

As an alternative, we have proposed a galvanostatic version of the countercurrent electrophoretic process [3]. In this approach, fixed values of the current strength and countercurrent rate are maintained. This is based on the principle that, according to Faraday's laws, the amount of a substance carried by an electric current is directly proportional to its strength. In the stationary mode of countercurrent separation using this method, there will be a balance between the masses of substances carried by electric current and countercurrent per unit time.

Establishing this balance will lead to the fulfillment of condition (1) as a consequence of the system enter-

ing the stationary regime, and not the initial condition for setting up the experiment.

The above considerations made it possible to assume that in this case the mode of ion separation becomes self-regulating; any given value of v will correspond to the automatically set value of E .

When performing continuous electrophoretic separation of two cations with different mobilities, it is possible to obtain a final product enriched in a more mobile ion. The enrichment process should be carried out in the cathode chamber according to the following scheme. In the "cathode chamber—electrophoretic column—anode chamber" system, the solution to create a countercurrent to the electromigration movement of the separated ions must be supplied to the cathode chamber. In this case, if the linear velocity of the hydrodynamic flow v is maintained by a lower rate of electromigration of a more mobile ion ($v < u_1 E$) and a higher rate of electromigration of a less mobile ion ($v > u_2 E$), there is an enrichment of the solution in the cathode chamber with a more mobile ion and its depletion with a less mobile one, which is carried out by the hydrodynamic flow from the cathode chamber to the anode one.

An experimental verification of the validity of the statements made was carried out using the separation of ions of various alkali metals and isotopic ions of lithium and rubidium as an example.

EXPERIMENTAL

According to the theoretically considered scheme of the process of countercurrent separation, a self-regulating countercurrent electromigration process can be carried out in the variant of accumulation of a more mobile ion in the cathode chamber. The installation scheme for its implementation is shown in Fig. 1.

Separator column 3, the frit in which is Schott filter 8, and the filler was quartz sand or KU-2 cation exchanger, in both cases with a particle size of 50–100 μm, was used. Its upper part forms cathode chamber 5, and the column itself is immersed in a vessel filled with a saturated solution of ions to be separated, which serves as an anode chamber. To ensure the constancy of their concentration in the solution filling the anode chamber, weights of solid-phase hydroxides of the elements to be separated or a mixture of isotopes in a similar hydroxide form, equal in molar number of components, were placed on the bottom of the vessel forming the anode chamber. A constant level of the solution in the anode chamber is automatically maintained by allowing the excess solution to drain through drain pipe 6 located at a fixed height from the bottom of the vessel. The counterflow rate is controlled by the level of the solution in the Mariotte vessel, the diameter, and length of the capillary through which deionized water is supplied from it, which creates a countercurrent in the system.

The experimental technique was developed to verify the adequacy of the above theoretical considerations. The verification was conducted by separating pairs of ions $\text{Cs}^+ - \text{Na}^+$; $\text{Cs}^+ - \text{Rb}^+$ from their mixed alkaline solutions with the initial ratio of their concentrations, spontaneously established in the anode chamber when saturated solutions of hydroxides of the corresponding metals are mixed in an equilibrium three-component system: a mixture of solid-phase hydroxides—a saturated solution in equilibrium with them. The lithium and rubidium isotopes were separated in LiOH and RbOH solutions, respectively, when the anode chamber was filled with their saturated solutions. The volume of the cathode chamber was from 2 to 4 mL. The counterflow, as noted above, was carried out with deionized water, which, in addition to creating a countercurrent in the system, compensated for its losses during electrolysis in the cathode chamber. To determine the degree of separation and concentration of alkali metal ions, their radioactive tracers ^{137}Cs , ^{22}Na , and ^{86}Rb were used. Concentrations of ^6Li and ^7Li , as well as ^{85}Rb and ^{87}Rb were measured on an MI-1201 mass spectrometer equipped with a multi-sample ion source with surface ionization. The separation process was characterized by the enrichment factor of the mixture of ions being separated in the cathode chamber, the more mobile of them, which was calculated according to the following equation:

$$K = \frac{(c_1^c)_t (c_2^a)_0}{(c_1^a)_t (c_2^c)_0}, \quad (2)$$

where $(c_1^c)_t$ and $(c_1^a)_t$ are the concentrations of the more mobile ion in the cathode and anode chambers at a given time t , respectively; $(c_2^c)_0$ and $(c_2^a)_0$ are the initial concentrations of the less mobile ion in the cathode and anode chambers.

All experiments were carried out at constant current strength and countercurrent rate.

Patterns of changes in the concentration and composition of electrolytes in the cathode chamber during the separation of binary mixtures of $\text{Cs}^+ - \text{Na}^+$ and $\text{Cs}^+ - \text{Rb}^+$ are shown in Fig. 2.

Physically similar dependences were also obtained in the case of separation of isotopic Li and Rb ions (Figs. 3 and 4).

As shown in Figs. 2 and 3, linear dependencies $\ln K$ vs. time unequivocally testify to the stability of the process of enrichment of the final product with a more mobile ion, and maintaining a constant concentration of separated ions indicates the balance of the amounts of separated ions carried by electric current and hydrodynamic flow in the galvanostatic mode. Another consequence is the fact that with a minimum length of the separating electrophoretic column, large separation factors are achieved not only for ions of var-

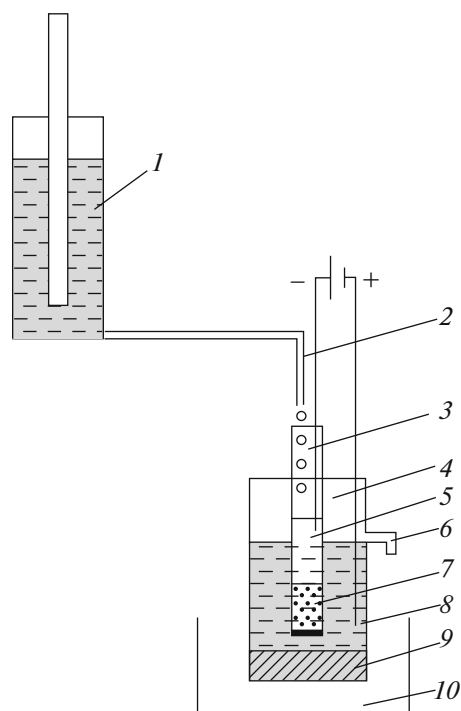


Fig. 1. Scheme of installation for countercurrent electro-migration separation of ions in galvanostatic mode: (1) Mariotte vessel for maintaining a constant level of deionized water, creating a countercurrent, (2) capillary, (3) separator column, (4) anode chamber, (5) cathode chamber, (6) drain pipe, (7) filler, (8) Schott filter, (9) solid-phase alkali mixture of ions to be separated, (10) vessel for collecting the solution flowing from the anode chamber.

ious alkali metals but also for isotopic ions. The large values of K obtained by separating ions with similar properties, including isotopic ones, at the minimum height of the separating column suggested that the effect of separating ions with similar mobilities under galvanostatic conditions can be achieved with an even smaller length of the separating space in which the countercurrent process is implemented. In particular, there is a possibility of replacing the electrophoretic column with microporous membranes, such as nuclear membranes or cellulose acetate membranes of the Millipor and Vladipor types. These membranes are attractive due to their uniform thickness and pore sizes, which allow for the creation of a uniform hydrodynamic flow over an arbitrarily large cross section of the separating layer. At the same time, with a thickness of such membranes at the level of tens of microns, minimum potential gradients across the membrane and, accordingly, minimum currents are required to separate ions. This characteristic helps prevent significant self-heating of the system and the corresponding changes in ion mobilities that could disrupt the stationary mode of the countercurrent electrophoretic separation process.

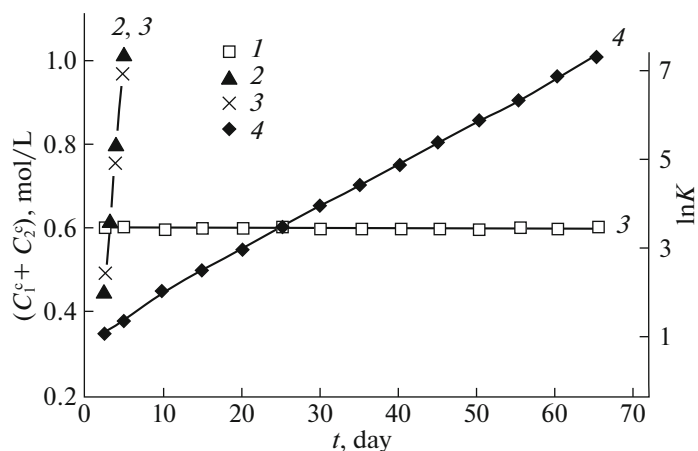


Fig. 2. Total concentration of separated ions in the cathode chamber (I) and the logarithm of the cesium enrichment coefficient of the mixture of ions $\text{Cs}^+ - \text{Na}^+$ (2) and $\text{Cs}^+ - \text{Rb}^+$ (4) vs. time ($I = 20$ mA, $v = 0.27$ mL/h, cathode chamber volume 2.5 mL, separation layer height 4 cm); ($2, 3$) separation of $\text{Cs} - \text{Na}$ ions on a column with quartz sand and KU-cation exchanger, respectively; (4) separation of ions $\text{Cs}^+ - \text{Rb}^+$.

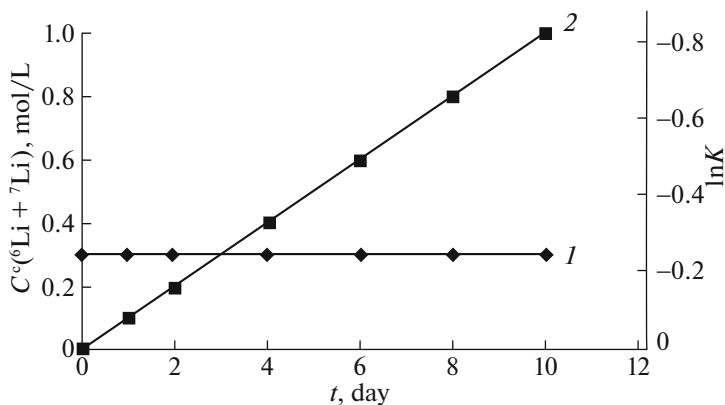


Fig. 3. Total concentration of lithium isotopes in the cathode chamber (I) and the logarithm of the enrichment factor of the isotope mixture $^6\text{Li} + ^7\text{Li}$ by isotope ^7Li (2) vs. time ($I = 20$ mA, $v = 0.26$ mL/h, column filled with quartz sand, separation layer height 4 cm, cathode chamber volume 3 mL).

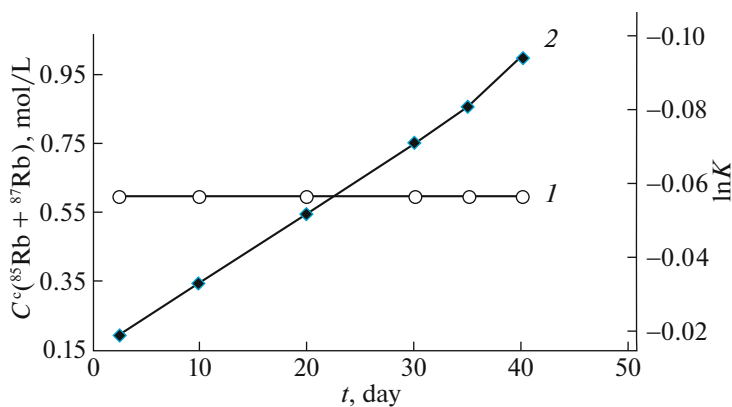


Fig. 4. Total concentration of Rb isotopic ions in the cathode chamber (I) and the logarithm of the enrichment factor of the isotope mixture $^{85}\text{Rb} + ^{87}\text{Rb}$ by isotope ^{87}Rb vs. time (2) ($I = 20$ mA, $v = 0.26$ mL/h, separation layer height 4 cm, cathode chamber volume 3 mL).

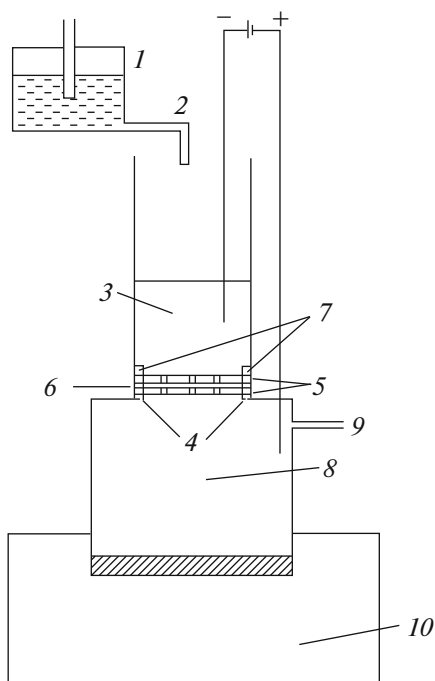


Fig. 5. Scheme of installation for countercurrent electromigration separation of ions on porous membranes: (1) vessel of Mariotte, (2) capillary at the outlet of the Mariotte vessel, (3) cathode chamber with annular protrusions 4 for fixing discs with symmetrically arranged holes 5, between which membrane 6 is installed, (7) clamping ring for fixing discs with a membrane sandwiched between them, (8) anode chamber with a drain pipe 9, (10) vessel for collecting drains from the anode chamber.

To test this idea, a special setup was developed for countercurrent electrophoretic separation of ions on porous membranes (Fig. 5). It almost completely repeats the design of the installation for electrophoretic separation on columns with the only difference in the scheme of fixing membranes instead of columns. Accordingly, the scheme of its operation is completely identical to the scheme of separation on an electrophoretic column, shown in Fig. 1.

An experimental verification of the possibility of electromigration separation of ions on microporous membranes was carried out on alkaline solutions of a mixture of ions Na^+ and Cs^+ , as in the column version. The data on the influence of the countercurrent velocity on the value of K at different pore diameters in the Vladipor membranes are shown in Fig. 6.

The data shown in Fig. 6 indicate that membranes with regular pores were found to be an almost ideal medium for countercurrent electromigration separation of ions. In this case, despite a small extent of the separation space ($100\ \mu\text{m}$), the influence of the pore diameter is significant: as it decreases, the separation efficiency increases. During the study of countercurrent separation of ions on porous membranes, it was found that separation efficiency practically is not

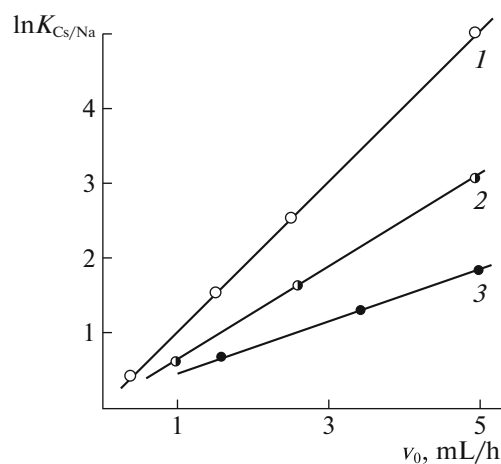


Fig. 6. Dependencies $\ln K_{\text{Cs/Na}}$ on the countercurrent velocity in the countercurrent electrophoretic separation of Na^+ and Cs^+ ions on Vladipor membranes with different pore diameters: (1) 0.45, (2) 0.8, (3) 1.2 μm , $I = 300\ \text{mA}$.

affected by the current density which increases proportionally to the size of membrane pores. This means that the productivity of the process can be controlled by varying parallel the countercurrent velocity and current strength.

In all cases of countercurrent electrophoretic separation considered above, both in the column and in the membrane version, its frontal scheme is realized. This scheme is particularly useful for addressing preparative challenges.

Taking into account that in recent years capillary electrophoresis (CE) has been implemented as a variant of a hybrid method that combines the electrophoretic separation of ions with their detection directly in a separating capillary [10], and specialized devices have been created for determining the ionic forms of analytes. In conclusion, the possibility of analyzing isotopic mixtures of light elements (lithium and boron) was considered in the traditional version of zone electrophoresis in a potentiostatic mode [11, 12]. The obtained electrophoregrams are shown in Figs. 7 and 8.

RESULTS AND DISCUSSION

In all the above cases of countercurrent electrophoretic separation, linear dependences $\ln K$ vs. time are observed. Therefore, the total concentration of electrolytes in the cathode chamber on the considered time scale remains unchanged, which indicates the stability of the parameters of the ion separation process in the galvanostatic mode. The change in the potential difference occurs only in the initial period of time, while the system enters the stationary mode. In the case under consideration, this period lasted

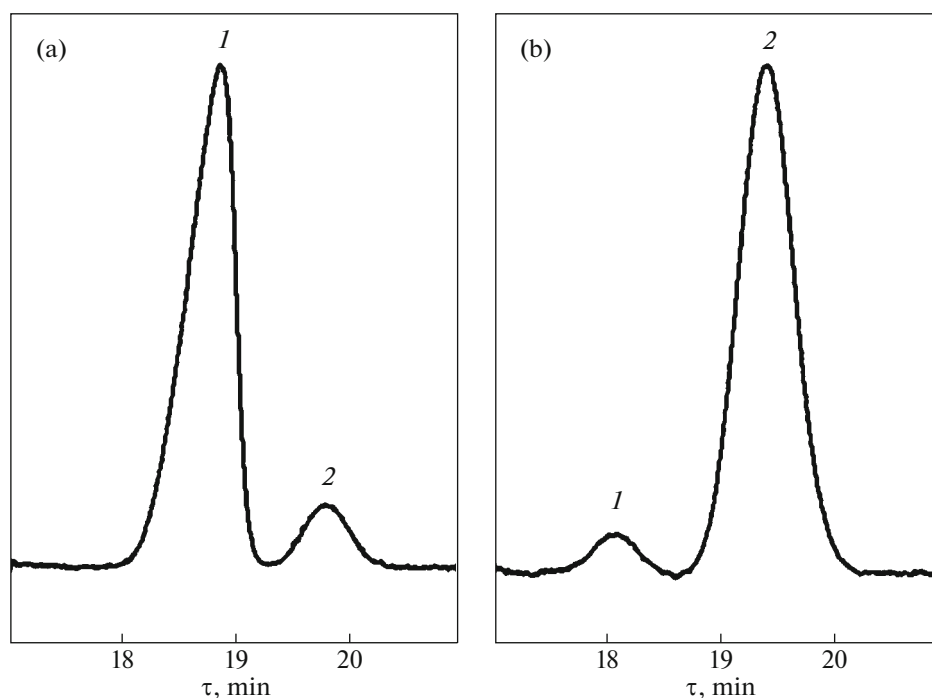


Fig. 7. Electrophoregrams of lithium isotope separation in the zone capillary electrophoresis mode at different isotope content in the sample: molar fraction of ${}^6\text{Li}$ is (a) 90.38 and (b) 3.44%. Background electrolyte: 5 mM 4-aminopyridine, 0.9 mM oxalic acid, 0.25 mM CTAB, 0.025% Tween 20. Voltage, +25 kV; temperature, 30°C; detection wavelength, 261 nm; (1) ${}^6\text{Li}^+$, (2) ${}^7\text{Li}^+$.

~20 min. In the same period of time, there was some change in the total concentration of electrolytes in the cathode chamber, which does not appear on the curve in the time scale used in Figs. 2–4. However, these deviations are not commensurate with those previously observed in the potentiostatic mode [1], when the initial lithium concentration equal to 0.7 mol/L decreased to 0.04 mol/L by the end of the experiment. The significant aspect lies in the stabilization of the electrolyte concentration in the cathode chamber and the consistent increase in enrichment factors over time. This demonstrates the self-regulation of the process of electrophoretic separation in the galvanostatic mode.

The output of the system in a stationary regime provides a greater efficiency of separation of ions with similar properties. Comparison of the results of lithium isotope separation achieved in this work with those obtained earlier [1] indicates that the proposed self-regulating mode of electromigration separation is much more efficient. Thus, in our case, the enrichment of a mixture of lithium isotopes with lithium-7 was more than twice achieved on a separating column 4 cm high, whereas earlier [1] with a much longer column, it was possible to obtain the limiting degree of separation of lithium isotopes of 1.8. The advantages of the galvanostatic mode are also evident in the separation of rubidium isotopes. Information on achieving

such results could not be found in the available literature. All of the mentioned advantages and achievements are specifically related to the preparative purposes of separation.

In the potentiostatic version, the method is of interest for the isotope analysis of light elements, for example, for the determination of lithium isotopes in the interests of analytical control in the nuclear power industry [11]. In turn, physicians and biologists are interested in the isotope analysis of boron [12].

Thus, these studies made it possible to confirm the high efficiency of the electrophoretic separation of ions of various alkali metals with similar chemical properties, and in particular their isotopic ions, in a countercurrent galvanostatic mode. Along with the traditional column version of electrophoretic separation in the galvanostatic mode, a scheme of countercurrent electrophoretic separation of ions on porous membranes with regular pores of the Vladipor type was proposed and experimentally tested. This indicates the possibility of increasing the scale of the process and the transition to its use for preparative and industrial purposes.

Another notable aspect of the study is the development of methods for capillary electrophoretic isotopic analysis of lithium and boron. This highlights the potential for expanding the scope of capillary electro-

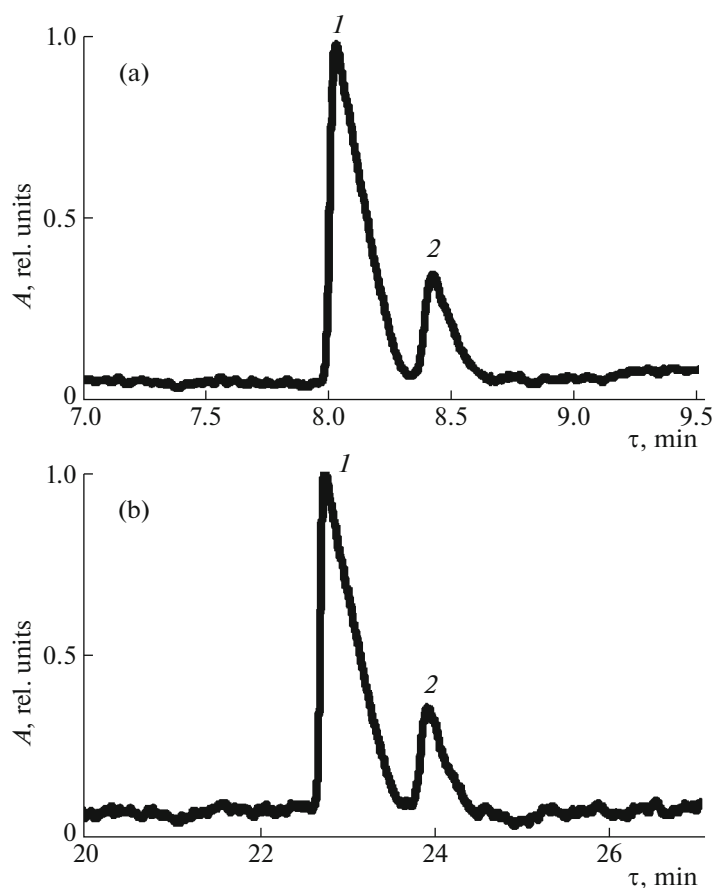


Fig. 8. Electrophoregrams of boric acid samples with natural isotope ratios ^{10}B and ^{11}B . Total capillary length: (a) 31, (b) 50 cm. Background electrolyte: 25 mM phenylalanine, 5 mM putrescine (pH 8.95). Voltage, +25 kV; temperature, 20°C; detection wavelength, 210 nm; (1) $\text{H}_3^{11}\text{BO}_3$, (2) $\text{H}_3^{10}\text{BO}_3$.

phoresis in the traditional zone version to address isotopic analysis challenges.

ADDITIONAL INFORMATION

The review is dedicated to the 300th anniversary of St. Petersburg State University.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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