
PROCESSES AND APPARATUSES
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On the Separation of Rare Earth Metals in the Cascade of Extraction Columns by Liquid–Liquid Chromatography Methods

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Abstract—The results of experimental study of the chromatographic behavior of La(III), Nd(III), Sm(III), and Eu(III) chlorides in a cascade of multistage extraction columns operating on the basis of elution chromatography are described. The possibility of extraction–chromatographic separation of rare earth metals in a cascade of multistage extraction columns is demonstrated.

Keywords: liquid extraction, liquid–liquid chromatography, extraction columns, separation of rare earth metals

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INTRODUCTION

Separation processes largely determine the technological level and environmental safety of production, as well as the quality of products, in many industries. To improve the methods used for the isolation and purification of organic and inorganic compounds from technological solutions and purification of industrial effluents in the production of chemical, pharmaceutical, hydrometallurgical, and other related industries, combined extraction technologies are being developed at the Institute of General and Inorganic Chemistry, Russian Academy of Sciences, with the use of both classical liquid-extraction processes and liquid–liquid chromatography methods together with liquid-membrane techniques [1–10]. The isolation and purification of substances from solutions by the above methods are based on the different solubility of the mixture components in two liquid phases. The current study is devoted to extraction separation methods based on the principles of chromatography. In contrast to the processes of liquid extraction, which are typically carried out in a continuous stationary mode and ensure the separation of only binary mixtures in a single technological operation, chromatographic separation processes are carried out in a non-stationary mode, thereby making it possible to separate multicomponent mixtures in one operation. In contrast to classical chromatography, one of the phases (conventionally called the stationary phase) in liquid–liquid chromatography is not fixed on a solid carrier, but is held in a chromatographic device by centrifugal forces [11–17] or on account of viscosity and surface-tension forces [1, 18]; both phases are in a free liquid state and the stationary phase maintains mobil-

ity within the apparatus. The simplicity of the technological scheme and the small quantities of chemical reagents used is an advantage of chromatographic separation methods, permitting the use of more selective, but expensive extractants. The extraction methods have an advantage of high productivity, since the productivity of extraction devices used in industry is several orders of magnitude higher than the productivity of chromatographic devices.

The drawbacks of the liquid–liquid chromatography technological processes developed abroad include the complexity of their hardware design, taking the form of a tube that is wound on the drum of a planetary centrifuge in one or more layers, or of a cascade of chambers cut or fixed on the surface of a cylinder or a package of disks mounted on the shaft of a conventional centrifuge. These devices cannot be used in large-capacity industrial production. Sectioned (multistage) columns and mixing–settling extractors are being developed at the Institute of General and Inorganic Chemistry, Russian Academy of Sciences, on the basis of classical extraction equipment widely used in industry as alternative options for the extraction–chromatographic separation processes without the use of centrifuges. In the first case, the extraction–chromatographic separation processes are carried out in a cascade of multistage columns, in which the flowing (mobile) phase is a dispersed phase and the continuous phase is a nonflowing (stationary) phase. In column extractors, the volume occupied by the dispersed phase in the apparatus is 10–20% in the operating modes (retention capacity). In the chromatographic mode of operation, the proportion of volume occupied by the immobile phase (0.8–0.9) will be many

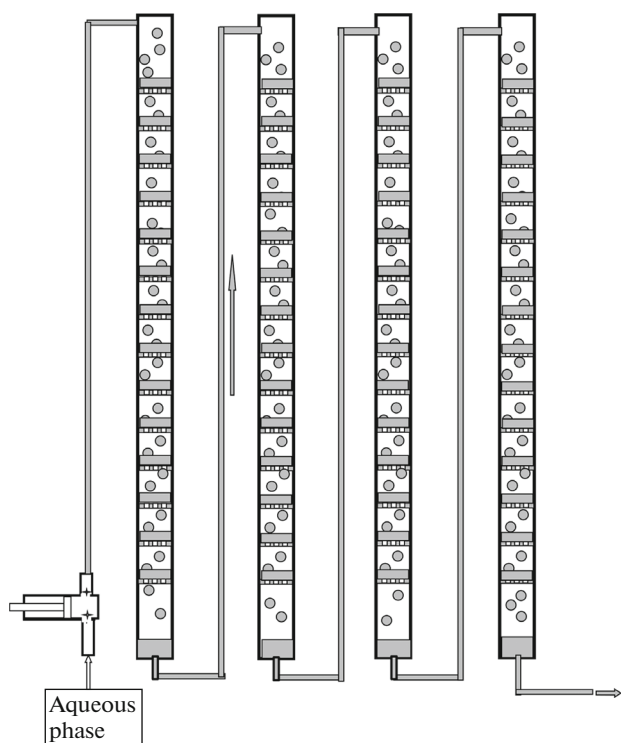


Fig. 1. Scheme of the laboratory unit.

times larger than in classical chromatography processes, which should increase the productivity and selectivity of separation processes. In the second version of the equipment design, extraction–chromatographic separation processes are carried out in a cascade of mixing–settling extractors. In this case, the dispersed and continuous phases can be both flowing and nonflowing. However, it follows from what has been said above about the performance and selectivity that the dispersed phase must be flowing, as in the first case. It should be noted that this is also advisable to reduce the negative effect of the phase-entrainment phenomenon. The retention of the organic phase (extractant phase) in a mixing–settling extractor cascade is ensured by its complete recycling between the mixing and settling zones in each stage of the cascade.

The possibility of separating rare earth metals in a cascade of centrifugal mixing and settling extractors operating in the chromatographic mode has been demonstrated earlier [19, 20]. The current study is devoted to exploring the possibility of extraction chromatographic separation of rare earth metals in a cascade of multistage extraction columns.

Application of a Multistage Extraction Column Cascade in Liquid–Liquid Chromatography Processes

Multistage column extraction devices can be divided into the following two groups: (i) columns with external energy supply (intensified extractors), in

which kinetic energy supplied from the outside by means of stirrers or pulsations is used to disperse one of the phases (dispersed) in the volume of another phase (solid) (sectioned columns with stirrers of various types, plate pulsation extractors, columns with vibrating plates, etc.); (ii) spray columns with perforated plates, in which one of the phases is dispersed by the gravity forces when flowing through the holes of the plates.

The columns have two settling zones when operating in the counterflow extraction mode: at the top of the column used for the separation and withdrawal of the light phase flow, and at the bottom of the column used for the separation and withdrawal of the heavy phase flow. To operate in the mode of conventional elution chromatography, it is sufficient to equip the column with only one settling zone for the separation and withdrawal of the flow of the dispersed phase after its coalescence. Evidently, columns with two settling zones should be used to carry out counterflow chromatography processes (which may be a very promising option of the extraction chromatographic separation methods discussed here).

To conduct extraction–chromatographic separation processes, an industrial plant must have two containers for the flowing (aqueous) phase: one with the initial solution of the mixture of the components to be separated and another with a pure flowing phase with an aqueous solution at a certain pH value. Flow streams are supplied to the plant in an alternating sequence from both tanks. The process of separation in such an apparatus can be conducted in various schemes, depending on the tasks to be solved.

This paper describes the results of an experimental study of the chromatographic behavior of rare earth metals in a cascade of multistage extraction columns that operate using the principle of elution chromatography.

EXPERIMENTAL

The experimental apparatus consists of four columns connected in series along the aqueous phase flow. There are 25 fluoroplastic plates with a thickness of 3 mm with 13 holes with a diameter of 0.25 mm in each column (made of a FEP tube with a size of 6.4×9.6 mm), which are arranged at intervals of 35 mm. The total volume of the apparatus is 119 mL; the volume of each step in the columns is 1.13 mL; the number of steps in each column is 26; and the total number of steps in the apparatus is 104. A diagram of the laboratory setup is shown in Fig. 1. The aqueous phase is supplied to the unit by means of a dispenser configured for discrete liquid supply. The dispenser is equipped with instruments for controlling the frequency, speed, and length of the rod stroke.

The apparatus operates as follows: the columns are filled with an organic phase (extractant phase), and

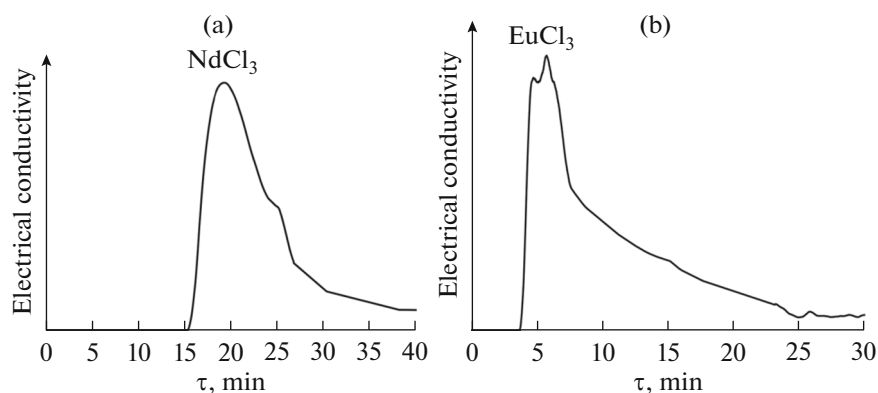


Fig. 2. Experimental chromatograms of (a) NdCl_3 and (b) EuCl_3 .

the aqueous phase is pumped through them in a pulsation cyclic mode by means of a dispenser. The aqueous phase is fed into the upper stage of the first (along the movement of the aqueous phase) of the columns and is withdrawn from the lower stage of the last column.

Starting solutions of lanthanum(III) and neodymium(III) chlorides were prepared by dissolving salts $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (reagent grade) in distilled water. The initial solutions of Sm(III) and Eu(III) chlorides were prepared by dissolving the oxide of these metals (reagent grade) in concentrated HCl with subsequent repeated evaporation of the solutions together with water in a water bath to remove excess acid.

The parent lanthanide chloride solutions were used to prepare aqueous solutions of metal chlorides by adding sodium chloride (0.1 M NaCl) and hydrochloric acid (0.01 M HCl). Cyanex 572 (a mixture of mono-2-ethylhexylphosphonic acid, mono-2-ethylhexylphosphonic ester, and bis-2,4,4-trimethylpentylphosphonic acid) from Cytec was used as an extractant. Hexane of reagent grade was used as a solvent.

To experimentally verify the possibility of extraction–chromatographic separation of rare earth metals in the cascade of extraction columns, the chromatographic behavior of La(III), Nd(III), Sm(III), and Eu(III) chlorides in a two-phase liquid system of 0.1 M Cyanex 572 in a hexane–isopropyl alcohol–aqueous solution of Ln(III) (0.01 M HCl and 0.1 M NaCl) with a volume ratio of all components of 2 : 1 : 1.5 was investigated.

After a stable hydrodynamic regime was established, in which only the aqueous phase leaves the apparatus, an aqueous solution of metal salts was injected into the upper stage of the first column with a syringe, and the concentration of the corresponding metal was measured by the conductometric method at the exit from the lower stage of the last column.

RESULTS AND DISCUSSION

As found from the experiments devoted to studying the retention of the nonflowable organic phase, the retention value depending on the mode of pumping of the aqueous phase in the selected two-phase system through the columns ranged within 80–90%.

Figure 2 shows the experimental chromatographic peaks of NdCl_3 and EuCl_3 . In Fig. 3, the individual chromatographic peaks of lanthanum and samarium chlorides are compared, and a chromatogram of a mixture of salts of these metals is given. The experimental chromatograms given in Figs. 2 and 3 indicate the possibility of separating metals in a cascade of extraction columns operating in the mode of elution chromatography.

Metal extraction is usually associated with a chemical reaction on the contact surface between the aqueous and organic phases. Therefore, intensified column extractors can be used to increase the efficiency of the processes of extraction–chromatographic separation of metals in a cascade of extraction columns. The efficiency of metal separation in such apparatuses can also be greatly increased by conducting the extraction–chromatographic separation process in a closed circulation loop. The separated components are repeatedly pumped through the apparatus when separation processes are arranged in a circulation loop, so substantially fewer extraction stages will be required to separate metals by the recycling scheme in comparison to the scheme without recycling. For example, an experimental chromatogram of samarium obtained in the above apparatus after two sample passes through the cascade of columns is given in Fig. 4. The productivity of the recycle process can also be substantially increased. In addition, if certain conditions are fulfilled for the introduction of a solution of the separated components into the apparatus in such a process, then concentrated fractions of the target components can be isolated from mixtures with a complex composition [21]. To simulate and calculate the considered procedure of

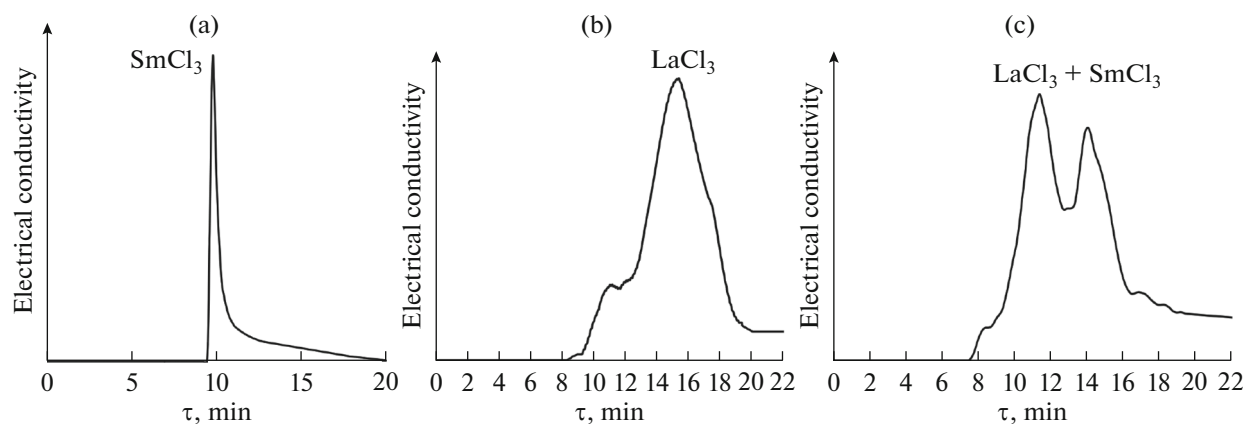


Fig. 3. Experimental chromatograms of (a) SmCl_3 , (b) LaCl_3 , and (c) $\text{SmCl}_3 + \text{LaCl}_3$ mixtures.

separation of rare earth metals, the analytical dependences published in [5, 6, 21] can be used.

For practical implementation, the following technology of extraction–chromatographic separation of rare earth metals is proposed: a continuous or periodic separation process is conducted in a closed circulation loop consisting of a cascade of extraction columns and an aqueous-phase-flow recycling system that includes a pump, an automatic analyzer (or sampler), and connecting pipelines. The loop is opened at certain time intervals, and a solution of a mixture of rare earth metals is fed into the first stage of the first column with a volumetric flow velocity equal to the rate of circulation of the aqueous phase in the loop. After the completion of the stage of loading of the initial solution, the loop is closed and metals are separated during a certain number of recirculation cycles. After that, the loop is opened and an appropriate aqueous solution

(with a certain pH value) is fed into the first column of the apparatus (at a volumetric rate equal to the rate of circulation of the aqueous phase in the loop), and then metal fractions are removed from the last column. The supply of the initial solution to the apparatus and the removal of the separated metal fractions can be accomplished at different time periods.

CONCLUSIONS

In this study, an extraction–chromatographic technology has been proposed for the separation of rare earth metals in a cascade of multistage extraction columns. The experimental results confirm the possibility of operating the cascade of extraction columns in the mode of chromatography. For practical implementation, a scheme of the process of extraction–chromatographic separation of rare earth metals in a closed circulation loop composed of a cascade of extraction columns and a system for recycling the aqueous phase flow has been proposed. For the further development of the considered technology of separation of rare earth metals, it is necessary to conduct experiments on cascades containing column extractors of various designs.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

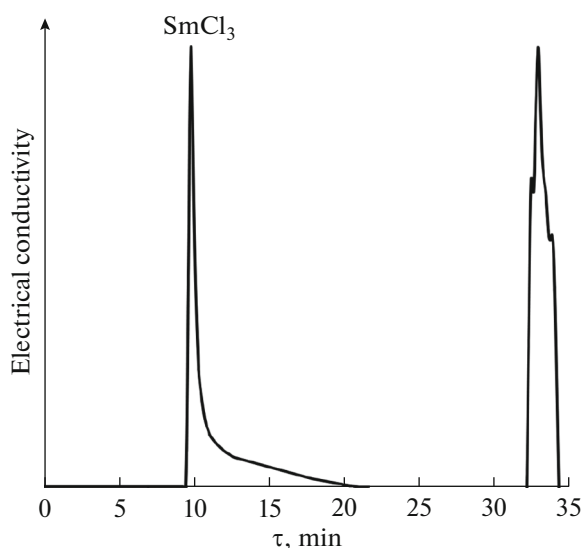


Fig. 4. Experimental chromatogram of SmCl_3 after two passes of the sample through a cascade of columns.

REFERENCES

1. Kostanyan, A.E., Voshkin, A.A., Khol'kin, A.I., and Belova, V.V., Patent RF 2403949, Pulsed cyclic method of extraction separation of a mixture of components and a device for its implementation, 2010.
2. Kostanyan, A.E., Khol'kin, A.I., Erastov, A.A., and Belova V.V. Patent RF 2014144416, Countercurrent cyclic method of multistage extraction separation of a mixture of components, 2015.
3. Kostanyan, A.E., Erastov, A.A., Belova, V.V., and Khol'kin, A.I., New extraction-chromatographic processes for separation of organic and inorganic substances, *Khim. Tekhnol.*, 2015, vol. 16, no. 4, pp. 239–245.
4. Belova, V.V., Analysis of separation processes of binary liquid mixture components by recirculating liquid–liquid chromatography, *Khim. Tekhnol.*, 2017, vol. 18, no. 10, pp. 469–474.
5. Kostanyan, A.E., Extraction Chromatographic Separation of Rare-Earth Metals in a Cascade of Centrifugal Extractors, *Russ. J. Inorg. Chem.*, 2018, vol. 63, no. 2, pp. 287–292.
6. Kostanyan, A.E. and Erastov, A., Theoretical study of closed loop recycling liquid–liquid chromatography and experimental verification of the theory, *J. Chromatogr. A*, 2016, vol. 1462, pp. 55–62.
7. Kostanyan, A.E., Belova, V.V., and Voshkin, A.A., Phenol-removing wastewater treatment with butyl acetate in a three-phase extractor, *Khim. Tekhnol.*, 2005, vol. 6, no. 9, pp. 41–43.
8. Kostanyan, A.E., Safiulina, A.M., and Tananaev, I.G., Analysis of linear models of processes of three-phase extraction, *Khim. Tekhnol.*, 2006, vol. 7, no. 8, pp. 35–40.
9. Belova, V.V., Kostanyan, A.E., Zakhodyaeva, Y.A., Kholkin, A.I., and Logutenko, O.A., On the application of bulk-supported liquid membrane techniques in hydrometallurgy, *Hydrometallurgy*, 2014, vol. 150, pp. 144–152.
10. Kostanyan, A.E., On the application of the principle of liquid membranes in a system of mixer–settler extractors, *Khim. Tekhnol.*, 2012, vol. 13, no. 6, pp. 376–379.
11. Ignatova, S. and Sutherland, I., The 8th International Conference on Countercurrent Chromatography held at Brunel University, London, UK, July 23–25, 2014, *J. Chromatogr. A*, 2015, vol. 1425.
12. Friesen, J.B., McAlpine, J.B., Chen, S.-N., and Pauli, G.F., The 9th International Countercurrent Chromatography Conference held at Dominican University, Chicago, USA, August 1–3, 2016, *J. Chromatogr. A*, 2017, vol. 1520, pp. 1–8.
13. Chami, M.C., Bouju, E., Lequemener, C., de Vaumas, R., Hadji-Minaglou, F., Fernandez, X., and Michel, T., Purification of two valepotriates from *Centranthus ruber* by centrifugal partition chromatography: From analytical to preparative scale, *J. Chromatogr. A*, 2018, vol. 1580, pp. 126–133.
14. Friesen, J.B., McAlpine, J.B., Chen, S.-N., and Pauli, G.F., Countercurrent separation of natural products: An update, *J. Nat. Prod.*, 2015, vol. 78, pp. 1765–1796.
15. Sutherland, I.A., Hewitson, P., Siebers, R., Heuvel, R., et al., Scale-up of protein purifications using aqueous two-phase systems: Comparing multilayer toroidal coil chromatography with centrifugal partition chromatography, *J. Chromatogr. A*, 2011, vol. 1218, pp. 5527–5530.
16. Huang, X.-Y., Pei, D., Liu, J.-F., and Di, D.-L., A review on chiral separation by counter-current chromatography: Development, applications and future outlook, *J. Chromatogr. A*, 2018, vol. 1531, pp. 1–12.
17. Müller, M., Wasmer, K., and Vetter, W., Multiple injection mode with or without repeated sample injections: Strategies to enhance productivity in countercurrent chromatography, *J. Chromatogr. A*, 2018, vol. 1556, pp. 88–96.
18. Kostanyan, A.E., Voshkin, A.A., and Kodin, N.V., Controlled-cycle pulsed liquid–liquid chromatography: A modified version of Craig's counter-current distribution, *J. Chromatogr. A*, 2011, vol. 1218, pp. 6412–6415.
19. Kostanyan, A.E., Erastov, A.A., and Tsareva, Yu.V., On the operation of centrifugal extractors in liquid–liquid chromatography mode, *Khim. Tekhnol.*, 2020, vol. 21, no. 2, pp. 91–96.
20. Galieva, Zh.N., Semenov, A.A., Kostanyan, A.E., and Aldushkin, A.V., Pilot plant for studying REE separation by extraction chromatography based on a cascade of centrifugal extractors, *Khim. Tekhnol.*, 2020, vol. 21, no. 12, pp. 565–573.
21. Kostanyan, A., Martynova, M., Erastov, A., and Belova, V., Simultaneous concentration and separation of target compounds from multicomponent mixtures by closed-loop recycling countercurrent chromatography, *J. Chromatogr. A*, 2018, vol. 1560, pp. 26–34.

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