

A Model for Calculating the Characteristics of Separation of Transplutonium and Rare Earth Elements by High-Performance Liquid Chromatography

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Abstract—A mathematical model was developed for calculating the characteristics of a process for chromatographic separation of metals as applied to the problem of preparing pure transplutonium elements for their subsequent return into the fuel cycle or long-term storage. The model includes interrelated blocks allowing solution of the following problems: calculation of the separation factors of the mixture components, calculation of the installation parameters, determination of the distribution profile of the components being separated in the eluted fractions, determination of the dynamic characteristics of the process and of the volume and composition of the target products and by-products, estimation of thermal effects due to the heat evolution from the mixture components, and estimation of the extent to which the complexone degrades in the course of storage of the fractions. The model is being continuously improved. It meets the requirements of the process developers and is being refined in accordance with the newly obtained experimental data.

Keywords: rare earth elements, transplutonium elements, separation, high-performance liquid chromatography, mathematical modeling

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Return of minor actinides into the fuel cycle for their subsequent afterburning attracts attention of researchers in the field of nuclear power engineering for a long time. Implementation of this approach requires isolation of pure fractions of transplutonium elements. Displacement complexing chromatography (DCC) was chosen as the priority method for TPE separation from each other and from REE. This method allows preparation of Am and Cm fractions of required purity with acceptable productive capacity and relatively simple implementation [1].

In accordance with the requirements to the research and development within the framework of Proryv (Breakthrough) project, the development of new technologies should be accompanied by the development of the corresponding computer models of the processes. These models should furnish information for balance calculation of material streams, optimization

of the process taking into account the monitoring and control systems, and evaluation of risks and simulation of emergency situations [2]. The VIZART program complex was developed for solving one of the problems. It includes several interrelated modules: a module for performing balance calculations with the corresponding database of models of process operations, a module for calculating the cyclogram of a process as a whole, and a library of autonomous models of processes [3, 4]. Autonomous models of processes include their own calculation algorithms and databases for each particular process and allow calculation of process and product parameters taking into account the composition and properties of working media, operation conditions, equipment characteristics, etc. [4].

Here we report on the development of a self-contained process model of chromatographic separation of TPE, allowing calculation of the installation

parameters, volume and composition of products and waste, consumption of chemicals, and dynamic characteristics of the process. It also allows consideration of additional effects associated with such specific properties of target components as radioactivity and heat evolution.

CHROMATOGRAPHIC SEPARATION OF TPE AND REE

Chromatographic separation of TPE and REE by DCC consists in sorption of the mixture in a column packed with a strongly acidic sulfonic cation-exchange resin, followed by elution of the mixture through a series of separating columns packed with the same cation exchanger in the form of a retaining ion (H^+ , Zn^{2+} , Ni^{2+} , etc.), i.e., of a component exhibiting the lowest affinity for the resin. The eluent contains a displacing agent, i.e., a component exhibiting the highest affinity for the resin, and complexing components (DTPA, NTA, etc., in the form of ammonium or sodium salts). Additional introduction of a separating component (intercalator) for separating the components with close properties is possible in the sorption step. This component should exhibit intermediate affinity for the resin and thus should form a band between the bands of the elements being separated, allowing mutually pure fractions of the components being separated to be obtained [5]. If the sorption is performed "to saturation," the target components are discharged and the sorbent is depleted. If the sorption is performed "to breakthrough," the ratio of the mixture components in the sorbent remains the same as in the initial solution [6].

It should be noted that the complexones themselves should have certain affinity for the resin and form their own band. Owing to higher affinity for the resin, the displacing agent introduced with the eluent displaces from the resin the component whose affinity for the resin is the highest. This component, in turn, acts as a displacing agent for the component whose band is farther. Correspondingly, the displacing agent also forms its own band [7].

By the end of the separation, the parallel transfer mode is attained in the column, with steady state of the leading and rear edges of the sorption bands for all the components being separated. The rate of movement of the steady-state front along the column is given by Wilson's formula

$$v = 60u\tilde{D}_p / (\varepsilon\tilde{D}_p + Q), \quad (1)$$

where v is the velocity of the front movement along the column, $cm\ h^{-1}$; u , eluent feeding rate, $mL\ min^{-1}\ cm^{-2}$; \tilde{D}_s , displacing agent concentration, $g\text{-equiv}\ L^{-1}$; Q , volume capacity of the cation-exchange resin, $g\text{-equiv}\ (L\ resin)^{-1}$; ε , fraction of the void volume of the resin in the column.

After the complete displacement of the retaining ion, the components being separated appear in the eluates at the column outlet. In complexing chromatography, in contrast to common ion-exchange chromatography, the differences in the affinities of the elements being separated are mainly due to differences in their complexation. The stronger are the complexes formed by the ion being displaced, the faster it is eluted from the column. The curve describing the distribution of the concentrations of the components being separated in the eluates has a plateau.

The process is performed on an installation with stainless steel columns of equal height and successively decreasing diameter. Each column is equipped with a heating jacket and with tubes for feeding and discharging the solutions and for loading and unloading of the sorbent. The number and geometric characteristics of the column are determined by the task of separation. Along with chromatographic columns, the installation has additional equipment: measuring vessels, dosing pump, circulation thermostat, and system of commutating valves and stopcocks.

The cycle of separation of a TPE-REE mixture includes the following main operations: preparation of the initial solution for sorption, loading of the sorbent into columns, sorbent pretreatment in the sorption column, sorption of the mixture being separated, sorbent pretreatment in separating columns, preparation of an eluent of required composition, elution of fractions of the components being separated, REE desorption, and sorbent unloading.

STRUCTURE OF THE MODEL

Mathematical description of the process was performed by specialists from the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, and from the Bochvar High-Tech Institute of Inorganic Materials. Team from the Zababakhin All-Russia Research Institute of Technical Physics participated in implementation of the mathematical model in a program incorporated in the VIZART program complex.

Simulation of the process was performed in three steps. The characteristics calculated in each step were included in the list of the initial data and parameters for the next step of the calculation. In the first step at a preset composition of the eluents we calculated the equilibrium distribution of the components over the height of the separating bed, the velocity at which bands of the components being separated moved along the columns, and the separation factors between the mixture components. Also, we determined the configuration and size of the chromatographic installation. The second step of the simulation dealt with separation on the chromatographic installation and included determination of the time of the process and its separate steps and of the volume and composition of fractions and secondary liquid radioactive waste (LRW). The third step consisted in refinement of the model and in consideration of the heat evolution and radioactivity effects.

In accordance with the development steps, the model includes the following modules: (a) calculation of the equilibrium concentrations of the individual components in the solid and liquid phases, (b) calculation of the separation factors of the mixture components, (c) calculation of the installation parameters, (d) calculation of the distribution profile of the components along the separating bed height, (e) calculation of the process time and of the volume and composition of target products and secondary LRW, (f) calculation of thermal characteristics of the process taking into account the heat evolution, and (g) calculation of the DTPA degradation in TPE fractions under the action of ionizing radiation. The purpose, structure, and functions of each module are considered in more detail below.

(a) Calculation of the equilibrium concentrations of the individual components in the solid and liquid phases. The concentrations of the working mixture components in the solid (sorbed form) and liquid (eluate solution) phases for each band are determined individually using a system of nonlinear equations including the equations of the material balance, electroneutrality, functional relationships of complexation and ion exchange, and recurrent relationships characterizing the parallel transfer [8, 9]:

$$\begin{aligned} \bar{M}/M_s &= (\bar{D} - \bar{D}_0)/(D_s - \tilde{D}_s) = (\bar{H} - \bar{H}_0)/(H_s - \tilde{H}_s) \\ &= (\bar{A} - \bar{A}_0)/(A_s - \tilde{A}_s) = \bar{D}_0/\tilde{D}_s, \end{aligned} \quad (2)$$

where \tilde{D}_s , \tilde{H}_s , \tilde{A}_s , \bar{D}_0 , \bar{H}_0 , and \bar{A}_0 are the initial concentrations of the displacing agent, hydrogen ions, and

complexone in the eluent band (tilde refers to the liquid phase, and overscore, to the solid phase); \bar{M} , \bar{D} , \bar{H} , and \bar{A} are the calculated concentrations of the metal ions, displacing agent, hydrogen ions, and complexone in the solid phase; M_s , D_s , H_s , and A_s are the total concentrations of the metal ions, displacing agent, hydrogen ions, and complexone in the liquid phase of the band of each element being eluted.

In the overwhelming majority of cases, an eluent with $\text{pH} > 5$ is used, i.e., when \bar{H}_0 , $\bar{A}_0 \rightarrow 0$, $\bar{D}_0 \rightarrow Q$, where Q is the sorbent capacity, g-equiv L^{-1} , and the complexation of the displacing agent in the band of the elements being separated is negligible; i.e., $D_s = D$. In this case, the following relationship is observed:

$$\bar{M}/M_s = \bar{D}/D_s = \bar{H}/(H - \tilde{H}_s) = \bar{A}/(A_s - \tilde{A}_s) = Q/\tilde{D}_s, \quad (3)$$

The main equation relating the complexation and ion exchange, i.e., the dependence of the degree of the metal complexation (P_M) on the constants of the ion exchange with the displacing agent, K_{M-D} , and on the concentration of the displacing agent in the eluent, is as follows:

$$P_M = M_s/[M] = K_{M-D}Q^{n_M-1}(1/\tilde{D}_s)^{n_M-1}, \quad (4)$$

where n_M is the charge of the metal ion; $[M]$, concentration of the free metal ion; Q , capacity of the ion-exchange resin, g-equiv L^{-1} ; K_{M-D} , concentration constant of the ion exchange, i.e., concentration coefficient of the equilibrium.

P_M is the function of the complexation of component M:

$$\begin{aligned} P_M &= (1 + [A]K_{MA} + 2[A]\beta_{M_2A}[M] + [A]\beta_{MHA}[M] \\ &\quad + [A]^2\beta_{MA_2} + \dots), \end{aligned} \quad (5)$$

where $[A]$ and $[M]$ are the concentrations of the complexone and metal in the solution; K_{MA} , stability constant; and β_{M_2A} , β_{MHA} , and β_{MA_2} , total stability constants of the corresponding complex species (reference data).

Using the reduced ion exchange constant,

$$K_{M-D}^* = K_{M-D}Q^{n_M-1}, \quad (6)$$

we can express the content of components in the solid phase in fractions (or %) of the capacity:

$$\bar{x}_M = n_M\bar{M}/Q. \quad (7)$$

The stability, protonation, and ion exchange constants were converted to the working temperature us-

ing the equation

$$\log K_T = \log K_{st} - (\Delta H^0/2.303R)(T^{-1} - T_{st}^{-1}), \quad (8)$$

where K_T and K_{st} are the stability or protonation constants at the working and standard temperatures, respectively; ΔH , standard enthalpy of formation of the complex or protonated compound, J mol⁻¹; R , universal gas constant, J mol⁻¹ K⁻¹; T and T_{st} , working and standard temperatures, K.

(b) Calculation of the separation factor. One of basic tasks of the model is determination of the order in which the components of the mixture being separated (separating elements, complexones, buffer additives, displacing and retaining ions, inert components) are eluted from the column. However, it is impossible to consider the behavior and evaluate the mutual influence of all the system components because of the lack of experimental data for constructing multidimensional isotherms. Therefore, the approach that we used for solving this problem consists in subdivision of the multicomponent working system into a set of binary systems, for each of which the separation factor and the corresponding elution order are determined. The separation factor is determined by calculation. After determining the separation factors for all the possible component pairs, it is possible to conclude in what order the components will be eluted from the column. In so doing, not only the initial components of the mixture being separated, but also the eluent components are included in the consideration.

The separation effect in chromatography is due to differences in the rates at which the components being separated pass from the liquid phase to the solid phase and vice versa. The transition of the components into the solid phase is determined by the ion exchange with the cation-exchange resin, and the transition to the liquid phase, by the formation of a complex with the complexone used. Multiple repetitions of the phase transfer events allow the single separation effect to be multiplied and the mutual separation of the components to be reached. Interaction of the components being separated with the resin is characterized by ion-exchange constants, and the transition to the liquid phase, by the complexation constants. Correspondingly, the separation factor for each pair of the components in the working system is determined by these constants.

The separation factor characterizes the individual

selectivity of two components irrespective of the total number of exchanging ions and in the general case is determined by the following relationship:

$$\alpha_{M(b)-M(a)} = K_{pM(b)}/K_{pM(a)} = [P_{M(a)}/P_{M(b)}][K_{M(b)-D}/K_{M(a)-D}] \times [Q^{n_{M(b)}}/Q^{n_{M(a)}}](1/\tilde{D}_s)^{n_{M(b)}-n_{M(a)}}, \quad (9)$$

where $K_{dM(b)}$ and $K_{dM(a)}$ are the distribution coefficients of the components being separated; $P_{M(a)}$ and $P_{M(b)}$, complexation functions of the metal ion, determined as the sum of the products of the concentrations of various complex species and the corresponding stability constants; $K_{M(a)-D}$ and $K_{M(b)-D}$, constants of the ion exchange of the metal with the displacing agent (alkali metal or ammonium ion), determined experimentally or from reference data; \tilde{D}_s , displacing agent concentration (M); Q , volume capacity of the cation-exchange resin (g-equiv L⁻¹), indicated in its certificate; $n_{M(a)}$ and $n_{M(b)}$, valences of the corresponding metal ions.

If $\alpha_{M(b)-M(a)} < 1$, which corresponds to a concave isotherm, component M(b) is eluted first; on the contrary, if $\alpha_{M(b)-M(a)} > 1$ (convex isotherm), component M(a) is eluted first.

For elements with different valences, expression (9) takes the form

$$\alpha_{M(b)-M(a)} = [K_{M(b)-D}/K_{M(a)-D}][P_{M(a)}/P_{M(b)}]. \quad (10)$$

For further calculations, we use the mean values of the separation factors in the limiting points of the ion exchange isotherm, $\alpha_{M(b)-M(a)}(0)$ and $\alpha_{M(b)-M(a)}(\max)$. The quantity $\alpha_{M(b)-M(a)}(0)$ corresponds to the lower point of the M(a)-M(b) ion exchange isotherm, when $(\bar{x}_M)_a, M(a)_p \rightarrow 0$ and $(\bar{x}_M)_b, M(b)_p$ tends to values determined from system (2) for the band of the pure component M(b):

$$\alpha_{M(b)-M(a)}(0) = [K_{M(b)-D}/K_{M(a)-D}]\{P_{M(a)}[M(b)]/P_{M(b)}[M(b)]\} = P_{M(a)}[M(b)]/K_{M(a)-D}^*. \quad (11)$$

Similarly, we can obtain equations for $\alpha(\max)$:

$$\alpha_{M(b)-M(a)}(\max) = [K_{M(b)-D}/K_{M(a)-D}]\{P_{M(a)}[M(a)]/P_{M(b)}[M(a)]\} = K_{M(b)-D}^*/P_{M(b)}[M(a)]. \quad (12)$$

The value of $\alpha_{M(b)-M(a)}(\max)$ corresponds to the upper point in the M(a)-M(b) ion exchange isotherm, i.e., when $(\bar{x}_M)_b, M(b)_p \rightarrow 0$ and $(\bar{x}_M)_a, M(a)_p$ tends to the maximal value determined from system (2) for the band of pure component M(a).

Thus, the calculation algorithm included the calculation of the eluent composition with determination of the displacing agent concentration, calculation of the equilibrium compositions of the solid and liquid phases in the displacing agent band, calculation of the separation factors in the binary systems, and determination of the order in which the components are eluted.

It should be noted that the above-described approach has a number of drawbacks: limited volume of the available reference data on the constants and insufficient trueness and accuracy of the calculated separation factors. Therefore, preference should be given, if possible, to the use of experimental separation factors [9].

(c) Calculation of installation characteristics.

In the next step, we determined the installation characteristics, namely, the ion-exchange resin volume required for the separation and the number and size of the column. The installation characteristics are determined taking into account the separation task, i.e., the composition of the mixture being separated, the separation factors of the target components, and the volume loaded in one cycle. The composition of the mixture being separated and the separation factors of the target components characterize the presence of components with close physicochemical properties and their quantitative ratio. The volume loaded in one cycle is set taking into account the requirements of the nuclear and radiation safety of the process.

To determine the required volume of the separating bed, the number of bands is calculated. This quantity is the ratio of the resin volume in the separating columns to the volume in the sorption column. It depends on the separation factor of the limiting pair of the target components (with the lowest separation factor);

$$v = [(\alpha - 1)\bar{X}_{M(a)} + 1]/(\alpha - 1), \quad (13)$$

where $\bar{X}_{M(a)}$ is the mole fraction of the first component in the starting mixture.

Because the degree of utilization of the resin capacity can be different in sorption and elution, the required effective number of bands v^* should be determined:

$$v^* = v\bar{x}_{M(sor)}/\bar{x}_M, \quad (14)$$

where $\bar{x}_{M(sor)} = q/q_\Sigma$ is the fraction of a mixture of components $M(a)$ and $M(b)$ in the mixture of TPE and REE; $q = n_a m_a / M_{M(a)} + n_b m_b / M_{M(b)}$, number of equivalent

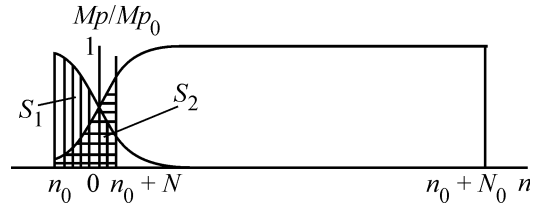


Fig. 1. Concentration distribution curves in the course of elution. (n) Plate number counting from the middle of the mixing band.

lents of the binary mixture being separated; $q_\Sigma = \sum_i n_i m_i M_{M(i)}$, number of equivalents of the whole REE + TPE mixture; n, m, M_M , valence, mass, and molecular mass of each component of the mixture being separated, respectively; \bar{x}_M , content of the target component in the solid phase in fractions of capacity in elution.

Then, it is necessary to calculate the number of separation steps, i.e., the number of theoretical plates N_0 required for separating the target components to obtain the required degree of purity at the outlet of the last column.

Within the framework of the plate theory as applied to chromatographic separation, the required degree of separation of the limiting pair of the target components is reached on a certain number of plates N_0 , which can be set, to a first approximation, in accordance with the requirements to the purity of the components being separated. N_0 is the number of plates corresponding to the length of the band of the mixture being separated in the last column in elution:

$$N_0 = V_q / (S_{pk} h). \quad (15)$$

At a preset number of plates N_0 , the area of the figure (Fig. 1) corresponding to the distribution of the concentrations of component $M(a)$ is described by Tremillon's integral (16)

$$X_{M(a)} N_0 = \int_{n_0}^{n_0 + N_0} dn / [1 + \alpha_{M(b)-M(a)}^n], \quad (16)$$

where n is the number of theoretical plate, counting from the middle of the mixing band (the plate in the middle of the mixing band, i.e., the plate on which the concentrations of components a and b are equal, is taken as zero plate); N_0 is the total number of plates.

By solving Tremillon's integral, it is possible to calculate n_0 and $n_0 + N_0$, i.e., the numbers of plates corresponding to the head and tail fractions.

The quantity n_0 is determined from the equation

$$\alpha^{n_0} = [\alpha^{-X_{M(a)}N_0} - \alpha^{N_0}] / [1 - \alpha^{-X_{M(a)}N_0}], \quad (17)$$

at $N_0 \gg 1$, $n_0 = -X_{M(a)}N_0$.

The yield of component M(a) in the fractions, corresponding to plate no. $n_0 + N$, is determined by the following relationships:

$$P_a = 100\% \times S_1 / X_{M(a)}N_0, \quad (18)$$

$$S_1 = \int_{n_0}^{n_0+N} dn / (1 + \alpha^n), \quad (19)$$

where P_a is the yield of component M(a) in the fractions, corresponding to plate no. $n_0 + N$, %; $X_{M(a)}$, fraction of component M(a) in the mixture with component M(b); and N , number of plates corresponding to plate no. n .

The purity of component M(a) with respect to component M(b) (p_a , %) is calculated from the equation

$$p_a = P_a X_{M(a)} N_0 / N = 100\% \times S_2 / (S_1 + S_2). \quad (20)$$

The calculation shows what fraction of the component can be recovered in the pure fraction in one cycle at the given content of impurity components.

By setting the column length and the amount of the mixture ($m_{M(a)} + m_{M(b)}$) loaded in one cycle, it is possible to calculate successively the parameters of the last and first columns and then of the installation as a whole.

To calculate the resin volume in separating columns V_{sep} using the formula

$$V_{sep} = V_{sor} V^*, \quad (21)$$

it is necessary to calculate the required volume of the sorption column V_{sor} ,

$$V_{sor} = q / [Q \bar{x}_{M(sor)}]. \quad (22)$$

At the preset column height L (provided that all the columns are of the same height), it is possible to calculate the cross section of the sorption column using the relationship

$$S_{sor} = V_{sor} / L. \quad (23)$$

To ensure the balance between the required numbers of bands and of equivalent theoretical plates, it is necessary to decrease the diameter of the columns arranged after the sorption column. In this case, the recommended volume of the last separation column will be

$$V_{pk} = V_q L / (N_0 h), \quad (24)$$

where h is the height equivalent to a theoretical plate. and V_q is the resin volume occupied by the binary mixture, taking into account the band smearing in the course of elution:

$$V_q = q / (Q \bar{x}_M). \quad (25)$$

In so doing, the requirement that the mutually connected separating columns should differ in the cross section by a factor of no more than 4 should be taken into account, and the intermediate number of columns should be determined in accordance with this requirement. Thus, the cross section of each next column is calculated as the cross section of the previous column, divided by a parameter ranging from 1 to 4. The number of columns and their geometric characteristics are thus determined.

Also, it is possible to calculate the corrected total column volume V_{Σ}^* , equal to the sum of the volumes of all the columns, and the corrected total number of theoretical separation steps N_0^* . The corrected values of the initial parameters should be no less than the initially obtained values.

The total volume of the resin is

$$V_{\Sigma} = V_{sor} + V_{sep}. \quad (26)$$

Thus, in this step of the calculation the initial data include the following groups of parameters:

(1) separation factor for the limiting pair of the target components α , mole fraction of the first component in the initial mixture $X_{M(a)}$, fraction of the mixture of components M(a) in M(b) in the mixture of TPE and REE $\bar{x}_{M(sor)}$, the content of the target component in the solid phase in fractions of the capacity in elution \bar{x}_M , and the concentration of the displacing agent in the eluent \tilde{D}_s (the values of all these parameters should be obtained in the previous step of the calculation);

(2) data on the amount of the mixture loaded for sorption in one cycle and the calculated total amount of equivalents of cations, q , in the mixture loaded in one cycle;

(3) Q , sorption capacity of the resin;

(4) column height L , required number of theoretical plates for mixture separation N_0 (or data for its calculation), and HETP values h .

From the implementation viewpoint, if the installa-

tion operation will involve separation of mixtures of different compositions with different productive capacities (it is assumed that the respective parameters for these cases vary within an order of magnitude), the installation parameters should be chosen conservatively for the “worst case.”

(d) Calculation of the profile of the component distribution between the eluted fractions. To determine ultimately the volumes and compositions of the fractions of the components being separated, it is important to know the component distribution along the height of the distribution bed, which can be expressed as the dependence of the concentration of the component of interest in the eluate on the ordinal number of the separation step.

The calculation should be performed for each binary system in accordance with the order of the component elution, determined in the previous steps of the calculation. The calculation result is the set of the distribution curves (Fig. 2).

The concentrations in fractions *I*, *II*, and *III*, and also the separation factor and the order of elution are determined with the aid of the theory of equilibrium chromatography individually for bands of each of the components being separated [module (a), calculation of the equilibrium concentrations of the individual components in the solid and liquid phases]. Mixing bands *II* and *IV* are calculated with the aid of the plate theory taking into account the installation parameters.

(e) Calculation of the dynamic characteristics of the process. The dynamic characteristics of the process, such as the time of each operation and of the whole process, the time of the onset and end of elution of each fraction, consumption of the reagents, and volumes and compositions of the target products and secondary liquid radioactive waste are calculated in the next step. The values obtained in this calculation are required for determining the actual productive capacity of the installation and optimum conditions of its functioning and for ensuring the rated time characteristics when connecting the installations to automatic process control systems.

The initial data for the calculation include the following groups of the parameters: sorbent characteristics (grade, grain size, capacity); chromatographic installation parameters (number and size of the columns, molar volume of the portion loaded in one separation cycle); composition of the mixture being separated

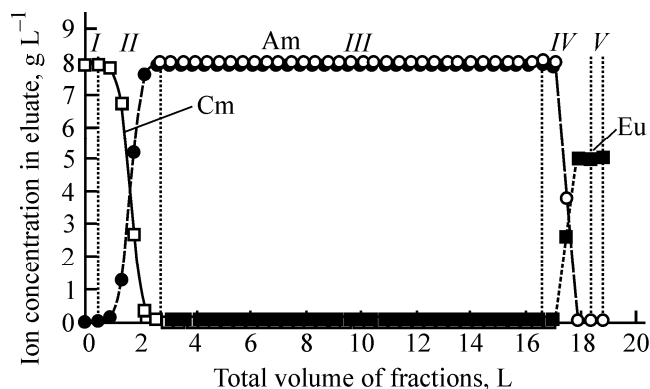


Fig. 2. Calculated breakthrough curves of Cm, Am, and Eu. (*I*) Pure Cm fractions (Cm purity with respect to Am no less than 99.99%), (*II*) mixed Cm + Am fractions, (*III*) pure Am fractions (Am purity with respect to Cm and Eu no less than 99.99%), (*IV*) mixed Am + Eu fractions, and (*V*) pure Eu fractions (Eu purity with respect to Am no less than 99.99%).

(gravimetric and molar content of cations, nitric acid, and water) and of the eluent (weights of water, DTPA, ammonia, etc.); rates of loading/unloading the columns and elution and washing rates.

The calculation is performed with the following assumptions: All the processes are performed in succession, the delay between the operations is not taken into account, and the time of conjugate processes that can be performed in parallel with the main process (e.g., decomposition of complexones in the starting mixture or in fractions) is not taken into account either.

The time of the operations (when the column is treated in succession) for the transfer into the hydrogen and nickel forms, for the sorption, and for aqueous washings was calculated using the formula

$$\tau_{dur,k} = \sum_{i=1}^I (V_{sol}/US_{col}) \times 1000/60, \quad (27)$$

where V_{sol} is the volume of the solution fed into the column, L; U , solution feeding rate, 1 unit = 1 mL cm⁻² min⁻¹; S_{col} , cross section of the column for which the calculation is performed, cm²; 1000/60, conversion factor from liters to milliliters and from minutes to hours; i , column number; and I , number of columns, determined when calculating the configuration of the separation installation.

The solution volume for different operations is determined taking into account the operation task. For the sorbent pretreatment, namely, for its conversion to the hydrogen or nickel form and for aqueous washing, it is

assumed that

$$V_{\text{sol}} = nV_{\text{col}}, \quad (28)$$

where n is the multiplier with which the solution volume is calculated; for the sorbent conversion to the hydrogen or nickel form, $n = 4$, and for aqueous washing, $n = 2$; V_{col} is the volume of the column for which the calculation is performed (in this case, the volume of the first column), L.

For the sorption of the mixture being separated, the loaded solution volume is calculated from the volume of the sorption column V_{col} and degree of its filling η , taking into account the concentrations of the ions being separated in the starting solution c_j :

$$V_{\text{sol}} = \eta Q V_{\text{col}} / (\sum c_j z_j), \quad (29)$$

where Q is the volume capacity of the cation-exchange resin, specific for each resin, mol L⁻¹ resin; η , degree of filling of the sorption column (fractions of unity, set in the calculation, default value 1); c_j , concentration of j th cation in the starting solution of the elements being separated, taken from the initial data on the composition of the mixture being separated, M; and z_j , charge of j th cation.

The solution feeding (elution) rate U is taken equal to 20 units for the transfer to the hydrogen or nickel form and for the sorption of the TPE + REE solution. For the aqueous washing, $U = 50$ units is taken.

The volume of the fractions was determined using the formula

$$V_M = NhS(\varepsilon \tilde{D}_p + Q) / \tilde{D}_p, \quad (30)$$

where V_M is the volume of fraction of the given component of the mixture being separated, mL; N , number of theoretical plates occupied by the fraction; h , column height, cm; and S , column cross section, cm².

The content of separate elements $m_{M(i)}$ in each fraction is calculated on the basis of data on the yield of these components in the given step $P_{M(i)}$ and on the total amount of the component loaded in one separation cycle $g_{M(i)}$:

$$m_{M(i)} = P_{M(i)} g_{M(i)}. \quad (31)$$

Correspondingly, the concentrations of elements in each fraction are calculated as follows:

$$C_{M(i)} = m_{M(i)} / V_M. \quad (32)$$

The duration of elution of each fraction, $\tau_{\text{dur},M(i)}$, is

determined by formula (3), where $V_{\text{sol}} = V_M$, S_{col} (by default) is the cross section of the last column, and U is the band movement velocity (default value 20 units, or 50 units if specially indicated).

The elution duration is the sum of the elution durations for separate i th fractions:

$$\tau_{\text{dur}} = \sum_{i=1}^I \tau_{\text{dur},M(i)}. \quad (33)$$

Thus, the calculation results include the following characteristics: time for loading the sorbent into the columns and water volume used; sorbent regeneration time, acid and water volumes, volume of retaining ion solutions (if required), volume and composition of secondary LRW; duration of the sorption and elution steps, taking into account the distribution of the components and changes in the elution rate with the transfer of the target component from a column with a certain cross section to a column with the other cross section; duration of the elution of each fraction (pure fractions with the preset level of purity and mixed fractions located between the bands of the pure fractions); volume and composition of all the fractions; duration of the REE desorption, volume and composition of secondary LRW, time for resin unloading.

It is possible to calculate the time that can be saved by performing separate operations in the mode of simultaneous treatment of all the columns, which, however, will require additional equipment and is not always economically justified.

(f) Calculation of thermal characteristics of the process. A specific feature of elements to be chromatographically separated using the technology under consideration is the heat evolution. The elements being separated can be concentrated in separate bands, which can lead to local heating of the working system. Sorbent granules and working solution components containing organic compounds can be sensitive to overheating and can degrade, and the separation efficiency can decrease. Therefore, it seems important to include in the model the functions that allow description of the thermal processes and estimation of thermal characteristics of the object.

The chromatographic column can be described by the plug-flow model. However, because it is necessary to take into account the liquid retention in the column, we proceeded from an intermediate model between the plug-flow and ideal mixing models.

The following assumptions were made when developing the model: The column is divided in several ideal mixing segments; the model describes only the thermal processes occurring in the column but does not take into account the sorption and ion exchange; the thermal equilibrium in the column cross section is attained instantaneously (the temperatures of the column wall, sorbent, and solution are equal to each other in each cross section); no radial and axial mixing takes place; the liquid flow rate through any cross section along the apparatus axis is equal to the flow rate of the feed; the sorbent is uniformly distributed in the apparatus; the apparatus wall has the same profile along the apparatus length; the specific heat capacity of the solution remains constant.

The following quantities are used as input parameters for the model: apparatus wall weight m_w , total sorbent weight m_{sor} , total liquid retention in the apparatus m_{sol} , feed flow rate M_f , ambient temperature T_{amb} , feed temperature T_f , starting temperature of the apparatus T_{start} , specific heat capacity of the apparatus wall material C_w , specific heat capacity of the sorbent material C_{sor} , specific heat capacity of the solution in the apparatus C_{sol} , specific heat evolution from the feed HE_f , specific heat evolution from the solution in the apparatus by the moment of calculation start HE_{start} , area of the surface in contact with the environment S , and coefficient of the heat exchange with the environment K . All the parameters in the model have the dimensions in SI units. The calculation is based on the equation of thermal balance in unit volume:

$$\partial H_i / \partial t = H_{\text{sol}}^{i-1} - H_{\text{sol}}^i + HE_i - Q_{\text{loss}}^i. \quad (34)$$

The energy accumulated in unit volume is distributed for heating of the wall material, sorbent, and solution:

$$\partial H_i / \partial t = Q_w^i + Q_{\text{sor}}^i + Q_{\text{sol}}^i. \quad (35)$$

Let us consider the calculation of each term. The amount of heat transferred with the solution is determined by the solution temperature:

$$H_{\text{sol}}^i = M_f C_{\text{sol}} T_i. \quad (36)$$

The heat evolution in unit volume is calculated from the amount of the liquid in the cross section:

$$HE_i = m_{\text{sol}}^i HE_{\text{sol}}^i. \quad (37)$$

If the sorbent also evolves heat (owing to the

sorbed heat-evolving nuclides), an additional term characterizing the sorbent will appear in the equation:

$$HE_i = m_{\text{sol}}^i HE_{\text{sol}}^i + m_{\text{sor}}^i HE_{\text{sor}}^i. \quad (38)$$

Because the model is based on the principle of column division into ideal mixing segments, variation of the heat evolution from the solution in the cross section is calculated as follows:

$$\partial HE_{\text{sol}}^i / \partial t = M_f (HE_{\text{sol}}^{i-1} - HE_{\text{sol}}^i) / m_{\text{sol}}^i. \quad (39)$$

The heat loss through the wall is calculated using the main equation of heat transfer:

$$Q_{\text{loss}} = KS_i (T_w - T_{\text{amb}}). \quad (40)$$

The heat consumption for heating of the wall, sorbent, and solution is calculated by equations similar to each other:

$$\partial T_w^i / \partial t = Q_w^i / (m_w^i C_w), \quad (41)$$

$$\partial T_{\text{sor}}^i / \partial t = Q_{\text{sor}}^i / (m_{\text{sor}}^i C_{\text{sor}}), \quad (42)$$

$$\partial T_{\text{sol}}^i / \partial t = Q_{\text{sol}}^i / (m_{\text{sol}}^i C_{\text{sol}}). \quad (43)$$

Thus, the following parameters are calculated: sorbent temperature T_{sor} , wall temperature T_w , specific heat evolution from the solution in the apparatus HE_{sol} , specific heat evolution from the sorbent in the apparatus HE_{sor} , heat loss through the apparatus wall Q_{loss} , amount of thermal energy H , amount of heat transferred with the solution H_{sol} , total heat evolution HE , thermal flux for wall heating Q_w , thermal flux for sorbent heating Q_{sor} , and thermal flux for solution heating Q_{sol} . The temperature profile of the apparatus and its variation in time in relation to the input parameters are evaluated on the basis of the calculation results (Fig. 3).

The profiles obtained allow determination of the maximal temperature reached in the installation during the process, which can be taken into account for estimating the probability that the admissible temperature in any point of the process will be exceeded.

(g) Calculation of DTPA decomposition. The eluates of the components being separated contain complexes of the corresponding metals with DTPA, which, like DTPA itself, tend to degrade under the action of ionizing radiation. On the one hand, this can negatively affect the separation process, because the complexing power of the eluent will decrease in this case. Further-

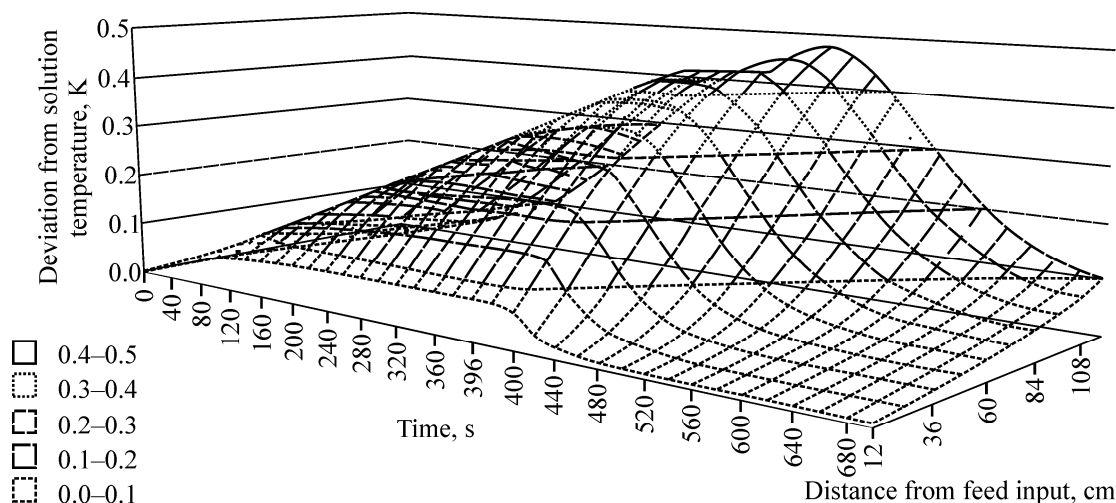


Fig. 3. Results of thermal calculation of the sorption–separation column.

more, the DTPA decomposition can be accompanied by the formation of poorly soluble organic precipitates plugging the void volume in the sorbent bed. On the other hand, DTPA is an interfering component in the subsequent steps of processing of the isolated fractions. Its radiolytic decomposition may be preferable compared to the use of additional methods and equipment.

Therefore, we included in the tasks of the model estimation of the variation of the DTPA concentration in the course of storage of pure and mixed eluate fractions. The calculation method was based on the published equation describing the experimentally observed decrease in the DTPA concentration in a ^{244}Cm solution [10]:

$$[\text{DTPA}]_t = [\text{DTPA}]_0 \exp(-0.0162 C_{\text{Cm}} t / [\text{DTPA}]_0), \quad (44)$$

where $[\text{DTPA}]$ is the DTPA concentration, M; C_{Cm} , ^{244}Cm concentration, g L^{-1} ; t , irradiation time, h.

Because the solution will contain not only ^{244}Cm but also other radionuclides, it is appropriate to introduce a coefficient taking into account the effect of other radioactive isotopes. To this end, we used an empirical dependence also given in [10]: 1.1 DTPA molecules decompose per 100 eV of the absorbed α -radiation energy and 5.2 DTPA molecules, per 100 eV of the absorbed γ -radiation energy. These data are valid for 4 M HNO_3 solution and were obtained for the initial DTPA concentration of 0.1 M.

^{244}Cm has the specific activity of 80.9 Ci g^{-1} (3 TBq g^{-1}) and mean decay energy of 5.9 MeV. Then, the above formula can be written as follows:

$$[\text{DTPA}]_t = [\text{DTPA}]_0 K \exp\{-0.0162 A Q_{\alpha} t / (1.77 \times 10^{19} [\text{DTPA}]_0)\} \quad (45)$$

where A is the radionuclide activity, Bq; K , coefficient equal to 4.73 for γ -radiation and 1 for α -radiation; Q_{α} , mean decay energy, eV.

For the mixed solution containing different radiation sources, the following expression can be written:

$$[\text{DTPA}]_t = [\text{DTPA}]_0 \sum_n (\omega_i K_i D_{ni} \exp\{-0.0162 A Q_{\alpha} t / (1.77 \times 10^{19} [\text{DTPA}]_0)\}) \quad (46)$$

where D_{ni} is the fraction of the given kind of decay of i th nuclide, and ω_i is the mole fraction of i th nuclide relative to all the radionuclides present in the solution.

The initial parameters for the calculations are as follows: absolute activity A in the solution, mean decay energy Q_{α} and kind of decay for each radionuclide, initial DTPA concentration $[\text{DTPA}]_0$, and eluate storage time t . The calculation results include the values of final DTPA concentrations in the fractions after the storage.

The use of the suggested mathematical model allows revealing the main physicochemical relationships in systems for displacement complexing chromatography; performing numerical experiments with variation of the initial parameters, including numerical experiments in ionization radiation fields; optimizing processes for chromatographic separation of multicomponent mixtures by DCC; and calculating the parameters of chromatographic installations and separation process parameters.

Today the model has been realized in the VIZART

program complex and can be used both independently for optimizing the process conditions or substantiating the equipment components and as a part of a complex for through calculation of complex flowsheets.

The model is being refined as new experimental data on the process are obtained. The calculated distribution profiles for components of the TPE–REE mixture being separated reasonably agree with the results of quantitative separation of Am and Cm by displacement complexing chromatography on an experimental installation of the Mayak Production Association [11].

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