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FAST METHOD FOR STUDYING THE EXTRACTION OF THE MAIN HLW COMPONENTS WITH CROWN ETHERS IN NEW FLUORINE-CONTAINING DILUENTS

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Abstract. *The study of the interphase distribution of a large number of target and impurity components of highly radioactive wastes is a necessary and very laborious stage in the creation of new extraction systems. With the quantitative extraction of cesium-137 and strontium-90 from spent nuclear fuel for the purposes of further industrial and commercial use, difficulties arise associated with competing complexation and the concomitant extraction of impurities of stable elements. We have developed an express method for determining the distribution ratios of metals using inductively coupled plasma mass spectrometry (ICP-MS). A feature of the proposed method is the joint extraction of trace amounts of all studied metals, followed by direct ICP-MS analysis of equilibrium aqueous and organic phases.*

Key words: *Cesium; crown ethers; distribution ratios; extraction; fluorinated diluents; High Level Radioactive Waste (HLW); Inductively Coupled Plasma Mass Spectrometry (ICP-MS); separation of radionuclides; spent nuclear fuel (SNF); strontium*

1. INTRODUCTION

One of the main problems of modern civilization, in addition to the degradation of the natural environment, is the rapid depletion of natural resources, primarily energy. Today and shortly, the growing need of mankind for energy can be satisfied due to the rapid growth of atomic (more precisely, nuclear) energy. At the same time, its role in the production of electricity increases significantly.

It is also noted that nuclear power, unlike hydrocarbon, does not create large emissions of carbon dioxide and other "greenhouse" gases into the atmosphere, which are apparently responsible for the deterioration of the climate on our planet.

However, it should be recognized that the intensive growth of nuclear power has given rise to several serious problems, in particular, environmental problems. This is due both to the possible leakage of radionuclides into the natural environment in the form of radioactive waste (RW), and to unforeseen man-made accidents at nuclear power plants or other industries of the nuclear industry. For example, the accidents that occurred at Chernobyl in 1986 and Fukushima in 2011 had a serious negative impact on the local environment, and the surrounding areas are still classified as hazardous regions contaminated with long-lived radionuclides. At the top of the list is the isotope Cesium-137, with a half-life of about 30 years, and high values of the energy of β- and γ-radiation. Strontium-90 isotope, which has a similar set of nuclear-physical properties, is no less dangerous when released into the environment. Therefore, in order to ensure the safe and sustainable development of nuclear power, close attention, with the same degree of responsibility, should be paid both to the issues of ensuring the safe and sustainable operation of nuclear power plants and to solving the problem of efficient management of spent nuclear fuel (SNF) and high-level waste (HLW) (Fig. 1).

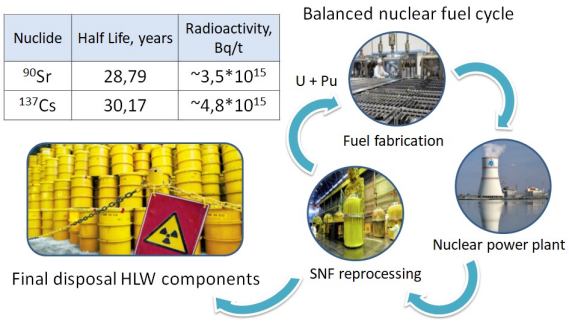

Figure 1. Most hazardous components of HLW (cesium-137 and strontium-90) & balanced nuclear fuel cycle

The development of a general technology for SNF extraction processing and HLW fractionation is an important and rapidly developing area of modern radiochemistry. Cesium-137 and strontium-90, which are part of the HLW, are hazardous, heat-generating, and potentially interesting isotopes for industrial use. An increased interest in the isolation of these isotopes in recent years has grown in Russia in connection with the emergence of the concept of a balanced nuclear

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technological cycle "Balanced NFC" and the growing commercial demand for radionuclides [1].

Removing these isotopes makes HLW management much easier. To solve the above problem, it is necessary to carry out a targeted search for promising extraction systems, with the use of which it is possible to individually isolate valuable radionuclides.

Both isotopes are widely used in various areas of the national economy, for example, in industry, scientific research, and medicine. In general, as noted in [2], the task of extracting individual radionuclides for their wide practical use is closely linked with the task of fractionation of HLW, improvement of existing, and development of new technologies for their complex processing. At the same time, an increase in the level of safety in waste management will be ensured, as well as the release of valuable radionuclides for practical use. HLW fractionation technology is being actively developed in countries adhering to a closed nuclear fuel cycle strategy.

Thereby the problem of on-line determination of metals is undoubtedly relevant for the field of nuclear technology. The ability to carry out operational technological control of the production process, which allows real-time determination of deviations from standard operating conditions, is of paramount importance for the nuclear industry in general and the sphere of SNF reprocessing in particular.

2. Experimental

It is known that derivatives of 21-crown-7 and calix[4]arene-crown-6-ethers often used to isolate cesium, dicyclohexyl-18-crown-6 to isolate strontium or their mixtures for joint extraction of cesium and strontium [3], [4].

For our experiments, we have chosen modified crown ethers: di-tert-butyldicyclohexyl-18-crown-6 and di-tert-butyldibenzo-18-crown-6.

Despite a wide choice of diluents for the extraction processes of cesium and strontium separation, they all have well-known disadvantages: the flammability of aliphatic alcohols and paraffins; poor hydrodynamic characteristics of telomeric alcohols (polyfluorinated alcohols with the general formula $H(CF_2CF_2)_nCH_2OH$); high cost and high viscosity of ionic liquids [5], [6], [7].

Ideal for crown ethers can be a one-component non-flammable moderately polar fluorinated diluent that does not form hard-to-remove hydrolysis and radiolysis products. Our attention was attracted by two derivatives of tetrafluoropropyl alcohol - carbonate and formal (Tab. 1). Their main advantages are good hydrodynamic properties, chemical stability, moderate polarity, and the ability to dissolve well both the used extractants and the resulting metal complexes. Earlier, these diluents were proposed for the isolation of actinides from HLW [8], [9], [10].

Table 1. Physical properties of the diluents used

Name	Structural formula	BP °C	d_{20}°C (g/cm³)	η_{20} (mPa·s)
FN-1	$[H(CF_2)_2CH_2O]_2CH_2$	200-210	1.49	4.22
BK-1	$[H(CF_2)_2CH_2O]_2C=O$	183	1.578	7.00

2.1. Materials and reagents

Crown ethers 4,4'(5')-di-tert-butyl-dibenzo-18-crown-6 (DTBDB18C6) and 4,4'(5')-di-tert-butyl-dicyclohexyl-18-crown-6 (DTBDCH18C6) were acquired from OOO "Neohim" (Volzhsky, Russia). The declared chemical purity of the compounds was ≥ 95%. The diluents bis-tetrafluoropropyl carbonate (BK-1 = bis(2,2,3,3-tetrafluoropropyl) carbonate) and bis-tetrafluoropropyl formal (FN-1 = bis-(2,2,3,3-tetrafluoro-propoxy)-methane) were purchased from the Perm branch of the RSC Applied Chemistry (GIPH) JSC (Perm, Russia), with a chemical purity of ≥ 96% (Fig. 2).

Before use, the diluents were washed sequentially with solutions of 1 mol/L sodium carbonate, nitric acid, and water. The rest of the general-purpose chemical reagents used in this work were no lower than analytical grade.

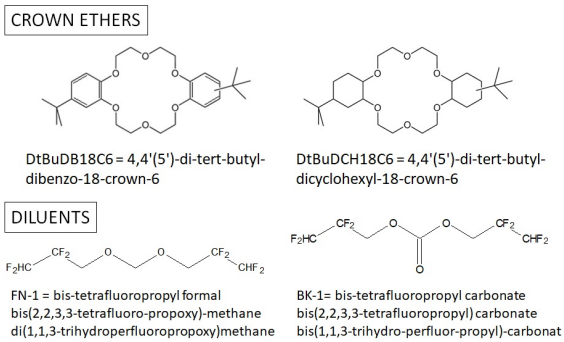

Figure 2. Structural formulas and complete and short names of used crown esters and diluents

2.2. Preparation of model solutions

For the preparation of model aqueous solution, nitric acid of high purity "Vekton" was used with bidistilled water, with a concentration of 0.1 M. Before the preparation of multicomponent solutions, one-component solutions of individual metals were prepared. For this, a weighed portion of the corresponding metal nitrate was taken from the calculation of the preparation of 20 ml of a solution with a metal concentration of 10 mg / ml. The weighed portion was dissolved in 20 ml of 0.1 M nitric acid. To prepare a multicomponent solution from vials with one-component solutions, a 10 ml aliquot was taken into a 100 ml volumetric flask and adjusted to the mark with 0.1 M nitric acid solution. As a result, a solution was obtained with specified concentrations of metals: Cs, Sr, Rb, Ba, Pb, Ag, Re, Tl, Na, Cr, Ni, Co, Fe, Mn, Eu, Y, Zr, Mo, Pd - 1000 mg/L. A 1 ml aliquot was taken from the obtained solutions using a dispenser, diluted 10 times with 0.1 M nitric acid, and control measurements of the concentration of metals were made on an atomic emission spectrometer with inductively coupled plasma PlasmaQuant PQ9000 (Analytik Jena).

To carry out the extraction, we prepared seven different aqueous solutions with a nitric acid content of 0.1; 0.5; 1; 2; 3; 4; 5 mol/L, Nitric acid solutions were prepared from nitric acid (high purity grade) and distilled water - 50 ml each.

0.3 ml of a model solution of each metal was added to a 15 ml polypropylene test tube, then 15 ml of the required nitric acid solution was brought to the mark.

Also, four extraction systems were prepared: 4,4'(5')-di-tert-butyl-dicyclohexyl-18-crown-6 in tetrafluoropropyl alcohol carbonate (BK-1), 4,4'(5')-di-tert-butyl-dibenzo-18-crown-6 in tetrafluoropropyl alcohol carbonate (BK-1), 4,4'(5')-di-tert-butyl-dicyclohexyl-18-crown-6 in the bis-tetrafluoropropyl formal (FN-1), 4,4'(5')-di-tert-butyl-dibenzo-18-crown-6 in the bis-tetrafluoropropyl formal (FN-1) form with crown ether concentrations of 0.05 mol/L.

2.2. Extraction procedure

In a centrifuge polypropylene tube with a volume of 1.5 ml (Eppendorf type) was placed 0.6 ml of the aqueous phase, then 0.6 ml of the extractant was added. Thus, in all experiments, the ratio Org:Aq = 1:1. The room temperature during the experiment was 24±1 °C. The tubes mustn't be in direct contact with the surface of the hands to avoid changes in the temperature of the experiment. A batch for one aqueous phase and different organic phases was placed in a special container and stirred slowly (in a pendulum manner) for 15 minutes to ensure that the extraction equilibrium was fully achieved. In preliminary experiments, it was found that five minutes of stirring is sufficient to achieve complete equilibrium. Then they were allowed to settle for 5 minutes. 1.5 ml polypropylene centrifuge tubes were removed from the container and placed in a centrifuge. Centrifugation for 15 minutes at 4000 rpm. The phase separation boundary is clear. First, the aqueous phase, which is located on the top, was taken in a volume equal to 0.5 ml into a separate centrifuge polypropylene tube with a volume of 1.5 ml (Eppendorf type). Then, 0.1 ml of the organic phase (bottom layer) was also taken into a separate centrifuge polypropylene tube with a volume of 1.5 ml (Eppendorf type) and diluted ten times with 0.9 ml of distilled isopropyl alcohol acidified with 3M HNO_3. The obtained samples of the equilibrium aqueous phase, the saturated organic phase, and the initial aqueous phase were sent for elemental analysis by inductively coupled plasma mass spectrometry - ICP-MS analysis. The samples were analyzed in two independent places: at the Institute for Problems of Microelectronics Technology and High Purity Materials of the Russian Academy of Sciences (IPTM RAS) on a Thermo Scientific iCAP TQ ICP-MS instrument and at the central laboratory of the A.P. Karpinsky (FGBU VSEGEI) on Agilent 7900.

Thus, seven extraction series of experiments were carried out with different acidity of the aqueous phase from 0.1 M to 5 M HNO_3 with solutions of the corresponding extractants No. 1-4. Additionally, four extraction series were carried out for the aqueous phase with a concentration of HNO_3 3M and solutions of extractants No. 1-4 with a crown concentration of 0.025M; 0.013M; 0.006M; and 0.003M, respectively.

During the extraction, the initial solutions during the addition of the components and stirring of the aqueous phase were colorless, the solutions of the extractants had a color from yellow to the orange of varying intensity depending on the type of extractant. Then, after centrifugation, solutions of the aqueous phase with an acid concentration of 2M, 3M, 4M, 5M acquired a terracotta color, and the higher the concentration of the solution, the more intense the color of the aqueous phase.

3. Results and dicussion

In the classic version, the extraction experiment is carried out separately for each element [5], [7], [11]. After extraction, it is necessary to re-extract the metal from the organic phase. This technique results in a large number of samples for analysis. To calculate the distribution ratios of metals in this case, it is necessary to know the concentrations in all aqueous phases. This significantly complicates the experiment and increases its time and the number of errors.

To carry out experiments on extraction were prepared to a model solution of metals with a known concentration and different content of nitric acid. In addition, four different extraction systems were prepared with crown ethers (concentration of 0.05 mol/L). In all experiments, the ratio of the aqueous and organic phases was one to one. After extraction, the obtained samples of the equilibrium aqueous & organic phase, and the initial aqueous phase were sent for elemental ICP-MS analysis. Thus, we completely excluded the stage of re-extraction, reduced the number of analyzed samples, and, accordingly, the time of the experiment.

3.1. Extraction of Cs & Sr

After measuring the mass spectra, we obtained an array of data on concentrations in equilibrium aqueous and organic phases for all elements of the model solution. Metal distribution ratios were calculated in two ways. In the first case, it was calculated as the ratio of the measured concentrations of metals in the equilibrium organic and aqueous phases.

$$D_M1 = \frac{[M]_{org}}{[M]_{aq}} \quad (1)$$

In the second case, the concentration of metals in the organic phase was calculated as the difference between the initial and equilibrium aqueous phase, as in the method of classical extraction.

$$[M]_{org} = [M]_{init} - [M]_{aq} \quad (2)$$

$$D_M2 = \frac{[M]_{init} - [M]_{aq}}{[M]_{aq}} \quad (3)$$

In the targeted extraction of cesium-137 and strontium-90 from SNF products, difficulties arise due to the competing complexation and co-extraction of the present stable elements. To study their effect and evaluate the separation efficiency, a series of experiments were carried out using four extraction systems based on modified crown ethers in new fluorinated diluents: bis-tetrafluoropropyl formal (FN-1) and bis-tetrafluoropropyl carbonate (BK-1). The obtained data set was used to construct the

dependences of the distribution ratios of cesium and strontium on the acidity of the medium. These results provide irrefutable evidence of the fact that cesium is significantly extracted only by systems based on DTBDB18C6 (Fig. 3), although in most cases with small distribution ratios.

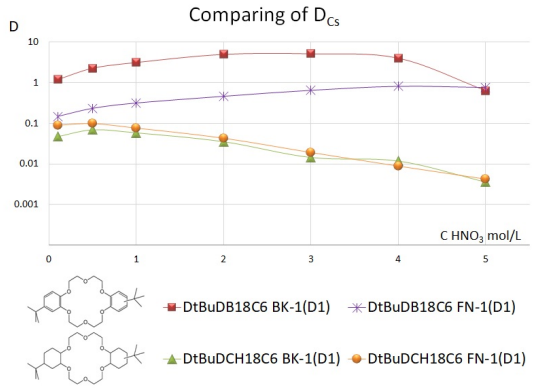

Figure 3. Dependences of the distribution ratios of cesium on the acidity of the medium for various extraction system: DTBDB18C6 & DTBDCH18C6 in BK-1 & FN-1

At the same time, strontium is well extracted only by systems based on the DTBDCH18C6 crown ether (Fig. 4).

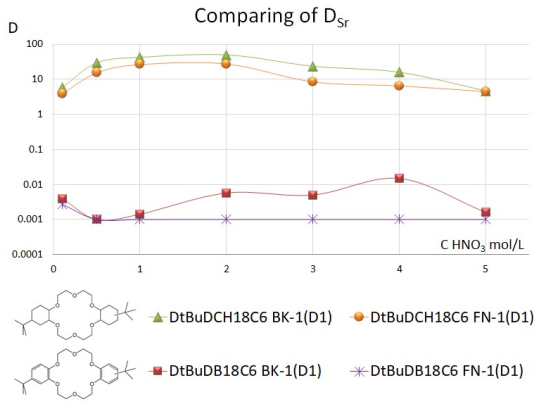

Figure 4. Dependences of the distribution ratios of strontium on the acidity of the medium for various extraction system: DTBDB18C6 & DTBDCH18C6 in BK-1 & FN-1

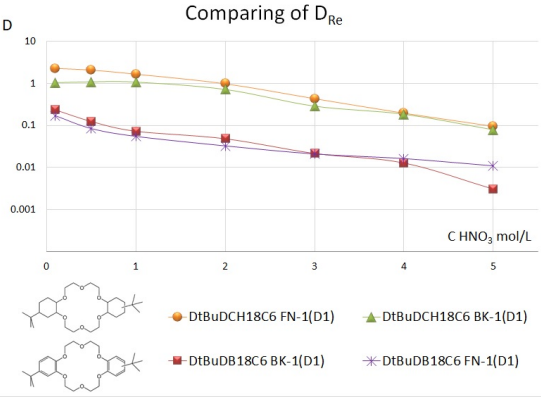

Figure 5. Dependences of the distribution ratios of rhenium on the acidity of the medium for various extraction system: DTBDB18C6 & DTBDCH18C6 in BK-1 & FN-1

The extraction of rhenium is of particular interest in these systems (Fig. 5). Because it is analogous to technetium and its behavior in similar media can be predicted by observing the extraction ability of its precursor. It should be noted that during complexation, unlike other elements of the model solution, rhenium is an anion and does not enter the macrocycle cavity. Rhenium is best extracted at low acidity by a system based on crown ether DTBDCH18C6 in FN-1.

3.2. Co-extraction of stable HLW components

To confirm the possibility of using new extraction systems in radiochemical processes, in addition to the extraction of radionuclides, it is necessary to study the co-extraction of stable HLW components.

A close look at the data (Figs. 6, 7) reveals that strontium and barium are perfectly extracted by this system. Thallium and rhenium also have noticeably high distribution ratios. Rubidium and cesium are practically not extracted.

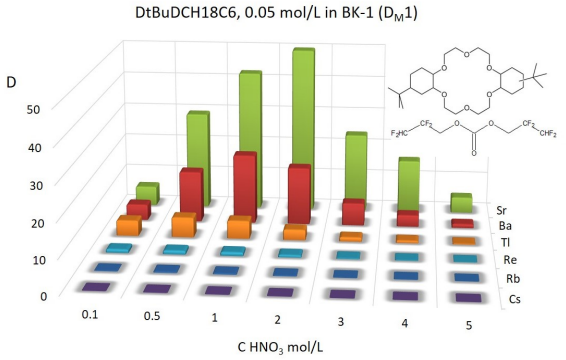

Figure 6. Dependences of the distribution ratios of metals (Sr; Ba; Tl; Re; Rb; Cs) on the acidity of the medium for extraction system DTBDCH18C6 in BK-1

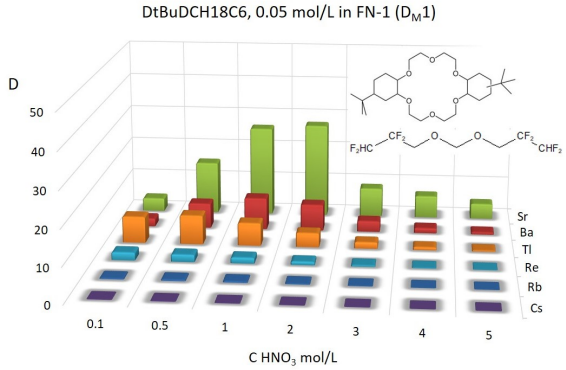

Figure 7. Dependences of the distribution ratios of metals (Sr; Ba; Tl; Re; Rb; Cs) on the acidity of the medium for extraction system DTBDCH18C6 in FN-1

The next figures (Figs. 8, 9) demonstrate a comparison of metal distribution ratios for similar extraction systems based on crown ethers in BK-1 and FN-1 diluents. It is clearly seen that under these conditions cesium and rubidium are preferentially extracted.

In general, it can be noted that the studied DTBDCH18C6 based extraction systems extract alkaline earth metals better, while DTBDB18C6 based systems extract alkaline metals better.

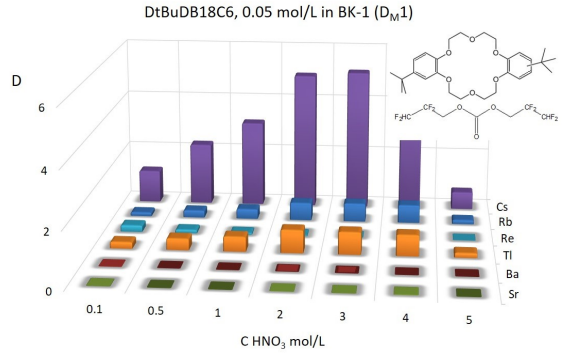

Figure 8. Dependences of the distribution ratios of metals (Sr; Ba; Tl; Re; Rb; Cs) on the acidity of the medium for extraction system DTBDB18C6 in BK-1

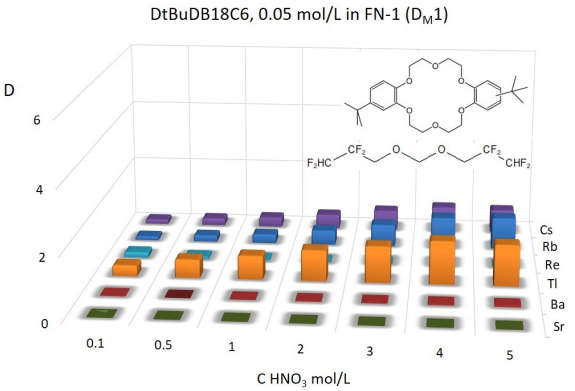

Figure 9. Dependences of the distribution ratios of metals (Sr; Ba; Tl; Re; Rb; Cs) on the acidity of the medium for extraction system DTBDB18C6 in FN-1

3.3. Comparison of extraction methods. Estimation of distribution ratios.

As stated earlier, the distribution ratios were calculated in two different ways. According to the classical version of extraction, where the concentration of elements in the equilibrium organic phase is found by subtracting the concentration of the equilibrium aqueous phase from the initial concentration of the working solution (D_M2). And by our proposed method, by direct measurement of the concentrations of equilibrium aqueous and organic phases using an ICP-MS spectrometer, their ratio (D_M1) will give the desired extraction ratios.

Comparison of the results obtained both for all elements using one extraction system as an example and for a single metal (for example, cesium) of the subject under the conditions of all tested extraction systems shows good convergence (Figs. 10, 11).

The values of the ratios of the distribution ratios (D_M1 & D_M2) of the studied elements are close to unity with an average standard deviation of no more than six percent. This fact undoubtedly confirms the possibility of using a direct method for measuring equilibrium extraction phases bypassing the stage of back-extraction and additional sample preparation entailing unnecessary errors.

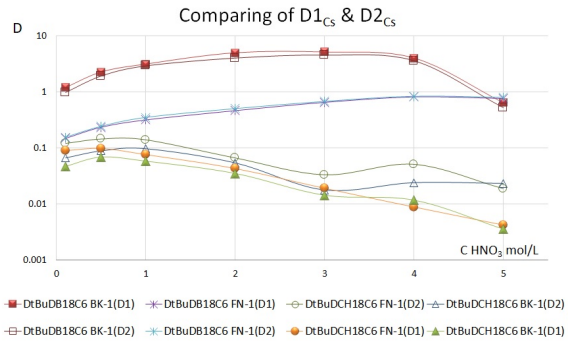

Figure 10. Dependences of the distribution ratios of cesium on the acidity of the medium, calculated by two different methods (D1 and D2) for four various extraction systems: DTBDB18C6 and DTBDCH18C6 in BK-1 and FN-1.

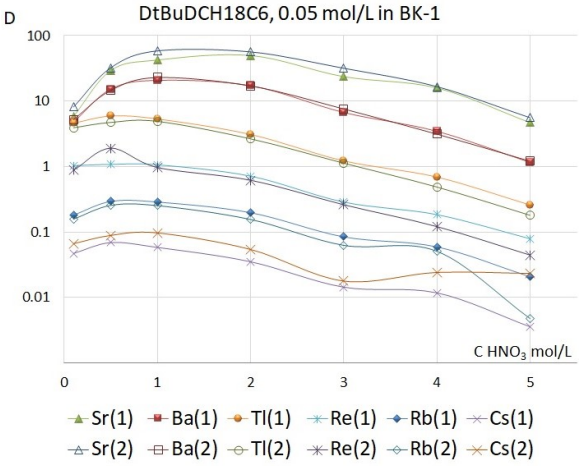

Figure 11. Dependences of the distribution ratios of metals (Sr; Ba; Tl; Re; Rb; Cs) on the acidity of the medium, calculated by two different methods (D1 and D2) for extraction system DTBDCH18C6 in BK-1

4. Conclusion

We used the developed express method when studying new extraction systems on model solutions designed for the processes of cesium-137 and strontium-90 separation from high-level waste (HLW) after spent nuclear fuel processing. In this case, extraction of cesium, strontium, and stable HLW components with substituted crown ethers in new fluorinated diluents has been studied.

Cesium is significantly extracted only by systems based on DTBDB18C6 crown ether. At the same time, strontium is well extracted only by systems based on DTBDCH18C6 crown ether. Extraction systems based on the crown ether DTBDCH18C6 showed an abnormally high extraction capacity for lead.

It is shown that the ICP-MS method can be used for the direct determination of the concentration of metals in the organic and aqueous phases in the extraction study. In this case, the need for re-extraction is

eliminated, and the experiment time is greatly reduced. The studies performed have confirmed the possibility of simultaneous determination of distribution ratios of a large number of metals using ICP-MS according to our express method. In the course of work, fundamentally new extraction systems were tested. They can be recommended for practical application.

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