Extraction of Cesium, Strontium, and Stable Simulated HLW Components with Substituted Crown Ethers in New Fluorinated Diluents

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ABSTRACT
The extraction of cesium, strontium, and a number of stable components of simulated high-level waste solutions from nitric acid media with solutions of crown ether derivatives in new fluorinated diluents was studied. Based on the data on the solubility of the extractants into the aqueous phase and the physicochemical properties of the diluents used, the most promising extraction systems were chosen: crown ethers 4,4'(5')-di-tert-butyl dibenzo-18-crown-6 (L1) and 4,4'(5')-di-tert-butyldicyclohexyl-18-crown-6 (L2) in bis (2,2,3,3-tetrafluoropropyl) carbonate (BK-1) and bis(2,2,3,3-tetrafluoropropoxy)methane (FN-1). For these systems, the extraction of a number of stable components and their subsequent stripping with water and solutions of chelating agents were studied. Lead was found to be co-extracted to the greatest extent. To a lesser extent, barium and calcium cations are co-extracted with strontium, and rubidium and potassium cations with cesium. Lead, barium, and silver are the most difficult to strip; however, the problem of lead stripping can be solved by using DTPA or citric acid solutions neutralized with ammonia to weakly alkaline (pH 8) media.

KEYWORDS
Extraction; crown ethers; fluorinated diluents; cesium; strontium; HLW components

Introduction
Interest in the separation of cesium and strontium radionuclides from spent nuclear fuel in Russia has grown significantly in recent years. This is due to the emergence of the “Balanced Nuclear Fuel Cycle” concept\textsuperscript{[1]} and the growing commercial demand for radionuclides, primarily for strontium-90. The concept of a balanced nuclear fuel cycle (NFC) provides for partitioning of high-level waste (HLW) with the separation of actinides and a fraction containing isotopes of cesium and strontium, free of long-lived actinides. The high-level fraction of cesium and strontium is solidified and delivered for controlled storage until the radionuclides pass into the category of intermediate-level waste (ILW), which allows for near-surface disposal. Actinides in a balanced
NFC are subjected not to disposal but to transmutation. This approach makes it possible to abandon the complex and expensive disposal of HLW in deep geological formations and the construction of radioactive waste disposal sites.

Numerous options for the extraction and sorption of cesium and strontium from HLW can be found in reviews.\textsuperscript{[2–6]} The most frequently used extractants are derivatives of 18-crown-6, 21-crown-7 or calix[4]arene-crown ethers for cesium recovery\textsuperscript{[2]} and substituted 18-crown-6 for strontium recovery\textsuperscript{[4,7]} or their mixtures for the joint extraction of cesium and strontium.\textsuperscript{[8]} Aliphatic alcohols and their mixtures with paraffins,\textsuperscript{[7–9]} fluorinated telomer alcohols and their mixtures,\textsuperscript{[10,11]} and ionic liquids\textsuperscript{[12,13]} are mainly used as diluents for crown ethers and calix-crown ethers. 2-Nonanone was used as a diluent for six dialkoxy derivatives of calix[4]arene-crown-6, which ensured high efficiency of the separation of cesium from nitric acid media.\textsuperscript{[14]} For the extraction of cesium from alkaline media, solutions of calix[4]arene-crown ethers in Isopar L paraffin with a fluorinated modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, were successfully used.\textsuperscript{[15–17]} It is now the only calix-crown ether extraction system used commercially in the United States. In Russia, full-scale dynamic trials of the technology of combined extraction of cesium and strontium radionuclides from simulated HLW were carried out.\textsuperscript{[11]} As extractants, a solution of two crown ethers – dicyclohexyl-18-crown-6 (DCH18C6) and dibenzo-21-crown-7 (DB21C7)—in a mixture of telomer alcohol n-3 (H(CF\textsubscript{3}CF\textsubscript{2})\textsubscript{3}CH\textsubscript{2}OH) and oxyethylated alcohol (Syntanol ALM-2) were used. The main advantage of telomer alcohol n-3 was its ability to significantly reduce the DCH18C6 washout into the aqueous phase.

Despite a fairly wide range of solvents for the cesium and strontium separation by extraction,\textsuperscript{[18]} they all have well-known drawbacks: the flammability of aliphatic alcohols and paraffins, poor hydrodynamic characteristics of telomer alcohols, the instability of the composition of mixed solvents due to different solubilities of components, and high cost and high viscosity of ionic liquids. An ideal diluent for crown ethers can be a moderately polar nonflammable single-component fluorinated solvent that does not form difficult-to-remove hydrolysis and radiolysis products. New fluorinated diluents were suggested recently for actinide extractants such as tributyl phosphate (TBP) and N,N,N′,N′-tetra-\textit{n}-octylamide of diglycolic acid (TODGA) and others.\textsuperscript{[19–21]} Our attention was attracted by derivatives of tetrafluoropropyl alcohols bis(2,2,3,3-tetrafluoropropyl) carbonate and bis(2,2,3,3-tetrafluoropropoxy)methane (see Table 1).

Their physicochemical properties made it possible to use them as diluents for crown ether extractants. The proposed diluents are one-component, which is useful for scaling, and it can be assumed that the composition of the extraction mixtures is practically unchanged during the technological process, in contrast, for
example, to compositions based on telomer alcohols. Fluorinated diluents are nonflammable, which is important for radiochemical production. They also have optimal viscosity and density and are quite nonvolatile.

This study deals with the extraction of radioactive isotopes of cesium and strontium, as well as stable components of simulated HLW from nitric acid media with solutions of crown ethers in promising fluorinated diluents, tetrafluoropropanol derivatives. During the research it was planned to demonstrate the applicability of the proposed diluents for applied purposes as components of new extraction systems. In the experiments, it was planned to analyze the possibility of efficient extraction and separation of a number of elements that are part of the simulated HLW, including cesium and strontium.

Table 1. Crown ethers and diluents used.

| Structure | Chemical name |
|-----------|---------------|
| Crown ethers | 4,4'(S')-di-tert-butyl dibenzo-18-crown-6 L1 |
| | 4,4'(S')-di-tert-butyl dicyclohexyl-18-crown-6 L2 |
| | dibenzo-21-crown-7 L3 |
| | dicyclohexyl-18-crown-6 L4 |
| Diluents | nitrobenzene |
| | 1,1,7-trihydroperfluoroheptanol telomer alcohol n-3 |
| | 3-nitrobenzotrifluoride F-3 |
| | bis(2,2,3,3-tetrafluoropropyl) carbonate BK-1 |
| | bis(2,2,3,3-tetrafluoropropoxy)methane FN-1 |
| | bis(2,2,3,3,4,4,5,5-octafluoropentoxy)methane FN-2 |
Experimental

Reagents

Crown ethers 4,4‘(5’)-di-tert-butyldibenzo-18-crown-6 (L1), 4,4‘(5’)-di-tert-butyldicyclohexyl-18-crown-6 (L2), dibenzo-21-crown-7 (L3), and dicyclohexyl-18-crown-6 (L4), as well as telomer alcohol n-3, were purchased from LLC Neohim (Volzhsky, Russia). The declared chemical purity of the compounds was ≥95%. The diluents bis(2,2,3,3-tetrafluoropropyl) carbonate (BK-1) and bis(2,2,3,3-tetrafluoropropoxy)methane (FN-1) were purchased from the Perm branch of the RRC Applied Chemistry (GIPH) (Perm, Russia), with a chemical purity ≥96%. Diluent 3-nitrobenzotrifluoride (F-3) was purchased from LLC Rehacor (Moscow, Russia), and nitrobenzene from Trading Company ANT (St. Petersburg, Russia). Before use, the diluents were washed sequentially with 1 M solutions of sodium carbonate and nitric acid and then with water. The other general-purpose chemicals used in the work were analytical grade.

Solutions of DTPA and citric acid for the stripping were prepared gravimetrically. The pH values were checked with a universal indicator. Methylamine and hydrazine carbonates for the stripping were prepared from a methylamine solution with an approximate concentration of 12–13 M and hydrazine hydrate, respectively. After saturation with CO₂ (pH < 7) by bubbling, the solutions were heated on a boiling water bath for 1 h, and the carbonate was titrated with nitric acid. Based on the concentration obtained, 3 M solutions of hydrazine and methylamine carbonates were prepared, and 0.02 M DTPA was added. An ammonium carbonate solution was prepared gravimetrically by dissolution while stirring and gently heating. The concentration of the resulting solution was determined by titration. Table S1 in the SI shows the structural formulae of the crown ethers and diluents used in the work and also some physical characteristics.

Preparation of stock solutions

To study the extraction of cesium, we used aqueous solutions containing nitric acid, 50 mg/L (3.8 × 10⁻⁴ M) of stable cesium, and tracer amounts of ¹³⁷Cs. To study the extraction of strontium, we used solutions containing nitric acid and 50 mg/L (3.8 × 10⁻⁴ M) of stable strontium. To study the extraction of stable HLW components, we used a simulated multicomponent solution containing the following elements: Na, K, Rb, Cs, Ag, Mg, Ca, Sr, Ba, Cu, Pb, Pd, Rh, Al, Cr, Fe, Ni, Co, Mn, Ce, Y, Nd, Zr, Mo, Sb, Bi, and Re; see Table 2.

For each metal, a one-component solution (10 mg/mL) was prepared from 0.1 M nitric acid with the corresponding salts or oxides. 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, three solutions with specified metal concentrations were obtained as presented in Table 2. Solutions of nitric acid 0.1, 0.5, 1, 2, 3, 4, 5 M, prepared from nitric acid (high
purity) and distilled water, 50 mL each. The following solutions from Table 2 were mixed in a 15 mL polypropylene test tube: 0.3 mL of Solution No.1, 0.3 mL of Solution No.2, 0.3 mL of Solution No.3, and then brought to a mark of 15 mL with the necessary nitric acid solution. Thus, seven different aqueous solutions were prepared for extraction. The total amount of elements in the simulated solutions of HLW was selected in such a way that no more than ten percent of the crown ether capacity was filled during extraction. Control measurements of the metals concentration were made by an inductively coupled plasma atomic emission spectrometer.

**Table 2.** Compositions of initial solutions containing stable components of simulated HLW.

| Metal | Chemical form | Sample weight, g | Concentration measured, mg/L | Molar concentration, mol/L |
|-------|---------------|------------------|-----------------------------|---------------------------|
| Solution 1 |               |                  |                             |                           |
| Na    | NaNO₃        | 0.740            | 911                         | 4.0 × 10⁻²                 |
| K     | KNO₃         | 0.518            | 902                         | 2.3 × 10⁻²                 |
| Rb    | RbNO₃       | 0.35             | 970                         | 1.1 × 10⁻²                 |
| Cs    | CsNO₃       | 0.295            | 932                         | 7.0 × 10⁻³                 |
| Ag    | AgNO₃       | 0.315            | 1062                        | 9.8 × 10⁻³                 |
| Mg    | Mg(NO₃)₂·6H₂O| 2.13             | 966                         | 4.0 × 10⁻²                 |
| Ca    | Ca(NO₃)₂·4H₂O| 1.12             | 977                         | 2.4 × 10⁻²                 |
| Sr    | Sr(NO₃)₂     | 0.48             | 952                         | 1.1 × 10⁻²                 |
| Ba    | Ba(NO₃)₂     | 0.385            | 1060                        | 7.7 × 10⁻³                 |
| Solution 2 |               |                  |                             |                           |
| Cu    | Cu(NO₃)₂·6H₂O| 0.925            | 1045.2                      | 1.6 × 10⁻²                 |
| Pb    | Pb(NO₃)₂     | 0.32             | 834.6                       | 4.0 × 10⁻³                 |
| Pd    | Pd(NO₃)₂     | 0.1              | 66.9                        | 6.3 × 10⁻⁴                 |
| Rh    | Rh₂O₃       | 0.25             | 8.1                         | 7.9 × 10⁻⁵                 |
| Al    | Al(NO₃)₃·9H₂O| 2.78             | 1008.4                      | 3.7 × 10⁻²                 |
| Cr    | Cr(NO₃)₃     | 0.385            | 949.8                       | 1.8 × 10⁻²                 |
| Fe    | Fe(NO₃)₃·9H₂O| 1.445            | 950.6                       | 1.7 × 10⁻²                 |
| Ni    | Ni(NO₃)₂·6H₂O| 1.26             | 1104.0                      | 1.9 × 10⁻²                 |
| Co    | Co(NO₃)₂·6H₂O| 0.99             | 802.1                       | 1.4 × 10⁻²                 |
| Mn    | Mn(NO₃)₂·6H₂O| 1.044            | 536.8                       | 9.8 × 10⁻³                 |
| Solution 3 |               |                  |                             |                           |
| Ce    | Ce(NO₃)₃·6H₂O| 0.53             | 94.7                        | 6.8 × 10⁻⁴                 |
| Y     | Y(NO₃)₃     | 0.065            | 6.8                         | 7.6 × 10⁻⁵                 |
| Nd    | Nd(NO₃)₃·6H₂O| 0.065            | 12.7                        | 8.8 × 10⁻⁵                 |
| Zr    | Zr           | 0.2              | 97.9                        | 1.1 × 10⁻³                 |
| Mo    | (NH₄)₂Mo₇O₂₄ | 0.25             | 0.5                         | 4.7 × 10⁻⁶                 |
| Sb(V) | Sb₂O₅       | 0.27             | 3.2                         | 2.6 × 10⁻⁵                 |
| Bi(III)| Bi(NO₃)₃  | 0.038            | 103.7                       | 5.0 × 10⁻⁴                 |
| Re    | NH₄ReO₄      | 0.29             | 73.2                        | 3.9 × 10⁻⁴                 |

**Extraction**

Extraction experiments were carried out in 1.5 mL and 15 mL polypropylene tubes. Equal volumes of organic and aqueous phases were placed in a test tube. The organic phase was a 0.05 M solution of crown ether in an appropriate organic diluent. The aqueous phase contained nitric acid of the required concentration (0.1–5 M) and the elements studied; when checking the extraction of radionuclides, the aqueous phase was spiked with the appropriate radionuclide. The organic phase was pre-equilibrated with a nitric acid solution of the
appropriate concentration. The phases were vigorously stirred for 5 min at room temperature (22 ± 1 °C), after which they were separated by centrifugation for 15 min at 1000–4000 rpm. Preliminary experiments have shown that the equilibrium in the extraction systems studied is attained in 3 min.

**Back-extraction**

Into a 1.5 mL polypropylene test tube, 0.4 mL of a loaded organic phase and 0.8 mL of a stripping solution were added. A series of tubes with loaded extractants (organic phase) and a double portion of the stripping solution (aqueous phase) were placed in a special container and vigorously stirred for 10 min at room temperature. Then they were allowed to settle for 5 min. These manipulations are sufficient to attain the chemical equilibrium. The tubes were then centrifuged for 10 min at 4000 rpm. Next, after the first stripping, a 0.7 mL aliquot of the aqueous phase (upper layer) was taken for ICP-MS analysis. The organic phase (lower layer) was transferred into a separate tube, a fresh portion of stripping agent was added in a double volume, and the steps of stirring and centrifugation were repeated. After phase separation, a 0.6 mL aliquot was taken from the upper layer (equilibrium aqueous phase after the second stripping). A separate 0.1 mL aliquot was taken from the organic phase and diluted tenfold with 0.9 mL of distilled isopropyl alcohol acidified with 3 M HNO₃. For each of the loaded organic solutions, two consecutive contacts were performed with fresh portions of the stripping agents at a phase ratio O:A = 1:2.

**Determination of the concentration of stable elements in solutions**

Samples containing strontium were analyzed with a Varian 725-ES optical emission spectrometer (Australia) at the V.G. Khlopin Radium Institute. Multicomponent solutions were analyzed at the Institute for Problems of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences (IPTM RAS) with a Thermo Scientific iCAP TQ ICP-MS device and at the central laboratory of the A.P. Karpinsky Russian Geological Research Institute (VSEGEI) with an Agilent 7900 ICP-MS device.

**Analysis of samples containing ¹³⁷Cs**

The activities of samples containing ¹³⁷Cs were determined at the V.G. Khlopin Radium Institute using a DeskTopInspektor 1270 scintillation γ-ray spectrometer (Canberra) based on a 51 × 51 mm NaI detector with a well.
Quantitative characteristics of extraction/stripping

To assess the efficiency of metal extraction, the distribution ratios ($D$) were calculated:

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}}$$

where $[M]_{\text{org}}$ is the metal concentration in the equilibrium organic phase, and $[M]_{\text{aq}}$ is that in the equilibrium aqueous phase.

In addition, the stripping percentage (total) was calculated for each operation, as well as the material balance (the sum of the metal in all stripped phases and the organic phase, referred to as the initial content in the extract). It was ensured that mass-balance calculations have a maximum error of ±5% for radiometry and less than ±3% for ICP-AES and ICP-MS analyses.

Results and discussion

Properties of fluorinated solvents

Preliminary data on the washout of crown ethers from organic solvents into aqueous phases of different acidities allowed us to estimate the operation range of the potential extraction systems. As seen from Table S2 (SI), extraction systems of crown ethers L1–L3 in n-3 telomer alcohol, as well as L1 and L2 in F-3 or BK-1, show promise. Crown ether L4, already studied as an extractant of radionuclides, an analog of L2 proposed in the work, is significantly (up to 3%) washed out into the aqueous phase from all studied solvents in a single contact. The lower solubility of L1 and L2 in the aqueous phase compared to L3 and L4 is due to the introduction of lipophilic tert-butyl substituents into the benzene and cyclohexyl rings of crown ethers. L3 is poorly soluble in BK-1. It can also be noted that with an increase in the acidity of the medium for all crown ethers, the solubility in the aqueous phase increases. This is due to the partial formation of complexes with hydronium ions, which makes the extractant molecules more hydrophilic and simplifies the transition to the aqueous phase.

Extraction of cesium and strontium

Cesium was extracted with solutions of crown ethers L1 and L3 in various organic diluents, and strontium was extracted with a solution of crown ether L2. The following diluents were used:

1. nitrobenzene, as it is one of the most frequently used diluents in studies of the extraction behavior of crown ethers;
(2) telomer alcohol n-3, since it is used in the Russian technology for extracting cesium and strontium from HLW\textsuperscript{[21]};
(3) 3-nitrobenzotrifluoride F-3, nitroaromatic fluorinated diluent;
(4) bis(2,2,3,3-tetrafluoropropyl) carbonate BK-1;
(5) bis(2,2,3,3-tetrafluoropropoxy)methane FN-1;
(6) bis(2,2,3,3,4,4,5,5-octafluoropentoxy)methane FN-2.

Diluents 4–6 have not previously been used for crown ethers. Figures 1 and 2 shows how the distribution ratio $D$ of cesium and strontium in extraction with crown ethers solutions depends on the nitric acid concentration.

The experimental data allow us to draw the following conclusions regarding the diluent effect on the radionuclide extraction efficiency:

- For L3, the highest distribution ratios are achieved when using nitroaromatic diluents with high dielectric constant: nitrobenzene and F-3, as well as telomer alcohol n-3.
- In the case of L1, on the contrary, the use of nitroaromatic solvents leads to the lowest cesium recovery efficiency;
- For the extraction of strontium with crown ether L2, the highest extraction is observed with fluorinated ether/ester diluents: BK-1, FN-1, and FN-2. The low strontium distribution ratios when using telomer alcohol are

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Cesium distribution ratio as a function of HNO\textsubscript{3} concentration. Organic phase: 0.05 M crown ether in the diluent (L3 is poorly soluble in BK-1).}
\end{figure}
probably associated with strong interaction of the crown ether and fluorinated alcohol molecules, due to which the crown ether is firmly retained in the organic phase and is not washed out into the aqueous phase.

It can be noted that the strontium distribution ratios tend to increase with a decrease in the dielectric constant of the solvent. For detailed studies, we chose two diluents, BK-1 and FN-1, because they have more acceptable physical characteristics compared to more viscous FN-2.

**Extraction of stable components simulated of HLW**

In the targeted extraction of cesium-137 and strontium-90 from HLW from SNF reprocessing, difficulties arise due to the competing complexation and co-extraction of a number of elements present in HLW. To study their effect and evaluate the separation efficiency, a series of experiments were carried out using four extraction mixtures based on crown ethers L1 and L2 in new fluorinated diluents FN-1 and BK-1.

**Extraction systems based on BK-1 diluent**

Comparison of the results of studying the ability of systems based on crown ethers L1 and L2 (0.05 M) in BK-1 to extract stable elements shows that both extractants do not noticeably extract Na, Cr, Ni, Co, Fe, Mn, Eu, Y, Zr, Mo,
and Pd ($D << 0.01$). Aluminum is extracted only slightly ($D < 0.01$ in most cases, in some cases $D$ is up to 0.1). For a system based on L1 in BK-1, abnormally high co-extraction of lead is not observed: the maximum values of its distribution ratio are 0.3, Figure 3. In this case, cesium is extracted most efficiently, Figure 4.

Along with cesium, the following elements are extracted: rubidium with a maximum in the range of 2–4 M ($D = 0.64–0.68$), thallium, and, to a small extent, silver (in a narrow acidity range, 2–4 M, with $D_{Ag} < 0.5$). In contrast to the cyclohexyl analog, in L1, the extraction maximum is shifted to higher acidity: 2–4 M HNO$_3$. Both extractants slightly extract potassium with differences in $D$ values and acidity regions: L1 extracts potassium from more acidic solutions (3.0–4.0 M HNO$_3$) with a maximum $D = 0.33–0.39$, whereas the maximum of potassium extraction with L2 lies in the less acidic region (see

![Figure 3](image1.png)

**Figure 3.** Distribution ratios in extraction of a number of elements with L1 in BK-1 as function of the aqueous phase acidity.

![Figure 4](image2.png)

**Figure 4.** Distribution ratios of metals in extraction with a 0.05 M solution of L1 in BK-1 as function of the HNO$_3$ concentration.
Figure 5), 0.5–1.0 M, and the D values are higher than for L1 and are at a maximum of 0.8. Nevertheless, these data should be treated with caution: First, potassium is found in noticeable amounts in crown ethers (it is used in the synthesis), and second, the weak dependence of the potassium distribution ratio on the crown ether concentration for L1 in BK-1 suggest a possible error in the determination of potassium by ICP-MS (overlap with the ArH peak).

Calcium is extracted with the system based on L2 in the entire acidity range: the $D_{Ca}$ values are 2–5 times higher than those for the systems based on L1 and reach 1.14–1.28 at a maximum. Surprisingly, an abnormally high affinity of L2 for lead ($D_{Pb} > 1300$) was found.

As shown in Figure 6, in addition to lead, the extraction system (L2 in BK-1) under consideration extracts strontium and barium to a significant extent, and in the entire acidity range, the maximum extraction lies in the range of 0.5–2 M HNO$_3$ ($D_{Sr} = 15–21$). These different results can be explained by the similar ionic radius of Sr$^{2+}$ (1.18 Å) and Pb$^{2+}$ (1.19 Å), well matching the radius of the 18-crown-6 cavity (1.3–1.6 Å). Also, high distribution ratios were noted for thallium and silver. Rubidium and cesium are not noticeably extracted.

Analysis of the obtained data shows that the extraction system based on L1 in BK-1 is more efficient in recovering alkali metals than the system based on L2, which is more suitable for the extraction of alkaline earth and post-transition metals (Figure 7).

The slope analysis of the log – log plots of the distribution ratio vs crown ether concentration (initial conditions, Table S3 (SI)) furnishes information about the number of ligands involved in the complex formation. Both crown ethers form predominantly monosolvates, which is probably accompanied by the formation of a certain amount of disolvates, that is, sandwich complexes (aqueous phase: 3 M HNO$_3$; Table 3, Figure 8).
Extraction systems based on FN-1 diluent

As in BK-1 diluent, in FN-1 diluent both crown ethers do not extract Na, Cr, Ni, Co, Fe, Mn, Eu, Y, Zr, Mo, and Pd. DTBDB18C6 (L1) in FN-1 does not extract also K, Ag, and Ru. Barium and lead are well extracted with L2 at any acid concentration, while the system with its benzo-substituted analog does not noticeably extract these elements. For L2 in FN-1, abnormally high lead

| Crown-ether | M   | Slope, k (R²) | Solvate           |
|-------------|-----|--------------|--------------------|
| L1          | Pb  | 0.92 (0.98)  | ML                 |
|             | Rb  | 1.30 (0.99)  | ML + ML₂           |
|             | Tl  | 1.28 (0.99)  | ML + ML₂           |
|             | Re  | 0.88 (0.97)  | Predominantly ML   |
| L2          | Pb  | 0.85 (0.99)  | Predominantly ML   |
|             | Ba  | 1.30 (0.99)  | ML + ML₂           |
|             | Rb  | 1.15 (0.99)  | Predominantly ML   |
|             | Tl  | 1.32 (0.99)  | ML + ML₂           |
|             | Re  | 1.25 (0.99)  | ML + ML₂           |
|             | Ag  | 1.19 (0.99)  | Predominantly ML   |

Figure 6. Distribution ratios of metals in extraction with a 0.05 M solution of L2 in BK-1 as function of the HNO₃ concentration.

Figure 7. Distribution ratios of Cs, Rb, and Tl in extraction with 0.05 M solutions of crown ethers L1 and L2 in BK-1 as function of the aqueous-phase acidity.

Table 3. Analysis of the log – log plots of the element distribution ratio vs. The crown ether concentration (calculation of the apparent solvation numbers in BK-1).
distribution ratios are also observed ($D_{\text{Pb}} > 800$ at pH 0). Rhenium is well extracted with dicyclohexyl crown ether (L2) and only at low acidity (up to 2 M), and L1 does not noticeably extract it. Without lead, the extraction of strontium has a maximum in the $\text{HNO}_3$ concentration range of 1–2 M, Figure 9.

Thallium and, to a lesser extent, silver are also well extracted. Silver is extracted only with L2 in FN-1 at acid concentration from 0.1 to 3 M. Rubidium and cesium are not noticeably extracted under these conditions. With a solution of L1 in FN-1, only cesium, rubidium, and thallium are extracted. The distribution ratios for the other elements are $<< 0.05$, Figure 10.

Analysis of the log – log plots for the extraction of elements from 3 M $\text{HNO}_3$, allows estimation of the composition of the solvates formed in the organic phase. Table 4 shows that, as in the extraction in BK-1, both crown...
ethers form predominantly monosolvates with different metal cations. At the same time, the formation of a disolvate is noted in the extraction of silver with crown ether L2 in FN-1 (Figure 11).

Comparison of the extraction capacity of the proposed systems based on crown ethers L1 and L2 in new fluorinated diluents demonstrates higher performance of L2. This effect is well explained by the influence of substituents in heterocyclic crown ethers on the stability of complexes with cations. With the appearance of one and then two benzene rings in the 18-crown-6 heterocycle, the stability of metal complexes is noticeably and consistently reduced. This is caused by an increase in the rigidity of the entire ligand molecule and disturbance of the symmetry in the arrangement of oxygen atoms in the cycle.

Figure 9. Distribution ratios of metals in extraction with a 0.05 M L2 solution in FN-1 as function of the HNO₃ concentration.

Figure 10. Distribution ratios of metals in extraction with a 0.05 M L1 solution in FN-1 as function of the HNO₃ concentration.
On the contrary, the two cyclohexyl substituents in 18-crown-6 enhance the strength of the complexes owing to conformational flexibility and the ability to create a pre-organized structure. In addition, it can be noted that the stability
Figure 12. Extraction of lead and barium with 0.05 M solutions of crown ethers in various diluents.

of the complexes increases with an increase in the basicity of the crown ether. The basicity of the oxygen atom bonded to the aliphatic carbon atom is higher than the basicity of the oxygen atom bonded to the aromatic nucleus.

As for the diluents, there are no grounds to prefer FN-1 or BK-1 unambiguously, because, for a number of elements, the highest distribution ratios are achieved for systems containing BK-1 as a diluent, for example, for lead and barium (Figure 12).

At the same time, for thallium and rubidium, the extraction proceeds more completely in FN-1 for both crown ethers, Figure 13. This fact suggests the occurrence of more complex interactions in such multicomponent systems and requires further study.

Back-extraction of stable HLW components

In the extraction and stripping of the main HLW macrocomponents, an important point, along with concentrating the recovered substances, is the possibility of regenerating the extractant for its reuse. In the case of neutral extractants, including crown ethers, pure water can be used as a stripping agent. The stripping phase thus obtained contains minimal amounts of acid and is very convenient for further processing. The disadvantage of water as

Figure 13. Extraction of rubidium and thallium with 0.05 M solutions of crown ethers in various diluents.
a stripping agent is the low rate of phase separation and the possibility of precipitation of radionuclides with a minimal change in pH. In addition, organic acids, which can be formed during radiolysis or hydrolysis of the extractant and diluents, give synergistic extraction mixtures with crown ethers, which efficiently extract cations from weakly acidic media.

Taking into account the literature data, we chose and tested six solutions as stripping reagents:

(1) ultrapure water (Milli-Q purified bidistillate, Millipore),
(2) 0.02 M DTPA neutralized to pH 8 with ammonia,
(3) 0.02 M citric acid neutralized to pH 8 with ammonia,
(4) 3 M methylamine carbonate (MAC) with the addition of 0.02 M DTPA or citric acid (pH > 10),
(5) 3 M hydrazine carbonate with the addition of 0.02 M DTPA or citric acid (pH > 10),
(6) 3 M ammonium carbonate with the addition of 0.02 M DTPA or citric acid (pH > 10).

The main results obtained are given in Tables S4 and S5. As expected, water as a stripping agent in systems with crown ethers shows low performance. In the case of L1, after two successive stripping operations with an excess of stripping agent (O:A = 1:2), almost all of the lead (90%) and a noticeable amount (13%) of rubidium remain in the organic phase. The stripping efficiency increases sharply when DTPA or citric acid is added to the water with neutralization with ammonia to pH 8. The stripping solution of this composition completely removes all the stable metals studied from the organic phase. The use of ammonia instead of potassium hydroxide significantly reduces the salinity of the systems after stripping. A significant advantage of citric acid over DTPA is the lower price and simpler oxidative degradation after stripping.

Unexpectedly low efficiency of barium stripping was observed with solutions of amine carbonates with the addition of DTPA: about 10% of barium remains in the organic phase. The other metals are stripped with these solutions efficiency, but there were no advantages over DTPA or citric acid solutions neutralized with ammonia to pH 8. In the case of L2, pure water strips lead and silver inefficiently (the residual amount is 46%). For their stripping, one can use solutions of DTPA or citric acid, neutralized with ammonia to pH 8. Stripping of barium, efficiently extracted with L2, involves no problems in this case.

From the array of data obtained on the stripping of stable metals from systems with L1 to FN-1, it is possible to single out an effective group of stripping agents based on amine carbonates with the addition of DTPA. They ensure the most complete stripping of rubidium (0.2% residue) and
lead (0.6–0.8% residue). Water as a stripping agent under these conditions is less efficient, and after two successive operations of stripping with an excess of stripping agent (O:A = 1:2), noticeable amounts of potassium, rubidium, and probably lead remain in the organic phase (12%, 11%, and 20%, respectively). The results for lead require additional verification, because its extraction with L1 is several orders of magnitude lower than with L2, and the lead concentration in the organic phase after two contacts with the stripping agent is below the detection limit for the analysis method used. Therefore, the estimation of lead concentration has high uncertainties. Rubidium and potassium, on the other hand, are better extracted with L1 and are firmly fixed in the crown ether cavity. When a complexing agent, DTPA or citric acid neutralized with ammonia to pH 8, is added to water, the rubidium stripping efficiency increases significantly (the residue in the organic phase after two contacts with the stripping agent is about 3%).

Pure water does not ensure lead stripping (35% residue). For these purposes, one can use solutions of DTPA or citric acid, neutralized with ammonia to pH 8. The use of such a complexing agent allows the maximum removal of all stable metals studied from the organic phase. Stripping of barium, the closest analog of strontium, is also quite complete.

As in the case of L1, the most complete stripping of rubidium and all other metals is provided by stripping agents based on amine carbonates with the addition of DTPA. Ammonium carbonate and methylamine carbonate can be recommended for practical use. Hydrazine carbonate has strong reducing properties, and precipitation of silver and palladium in the form of black metallic interfacial formations was sometimes observed during the stripping.

**Conclusion**

New fluorinated diluents BK-1, FN-1, and FN-2 are promising for the extraction of cesium and strontium with crown ethers L1 and L2 respectively. They are nonflammable and low-toxic and can be used without modifiers. Experiments on the extraction of a number of stable HLW components with solutions of crown ethers in new fluorinated diluents and on their subsequent stripping have shown that lead is co-extracted with radionuclides most strongly. To a lesser extent, barium and calcium cations will be co-extracted with strontium, and rubidium and potassium with cesium.

The extraction selectivity is due not only to “size selectivity”, but also to coordination interactions or interactions in an ion pair of the counterion with the metal ion in the macrocycle, as well as to the properties of the diluent, in
particular its ability to solvate the cation and anion of the extracted ion pair. The L1 solution in BK-1 is more efficient in recovering alkali metals, whereas the L2-based system better extracts alkaline earth and post-transition metals.

The maximum co-extraction (minimum selectivity) of stable elements is observed for dicyclohexyl crown ether L2. Dibenzosubstituted crown ether L1 strongly extracts rubidium at acid concentration of 3 M and higher. Lead, rubidium, barium, and silver are the most difficult-to-strip HLW components. They are poorly stripped with water but are completely removed from the organic phase with solutions of DTPA or citric acid neutralized with ammonia to pH 8. In case of difficulties with the stripping of rubidium, solutions of ammonium carbonate or methylamine carbonate with the addition of DTPA can be recommended. All these stripping agents are non salt-forming and will not increase the amount of vitrified HLW. These stripping-solution formulations are, in our opinion, of the greatest interest and can be recommended for further use.

Disclosure statement

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