

# Extraction of Yttrium from Carbonate Media Using Mixtures of Aromatic Dihydroxy Compounds and Methyltrioctylammonium Carbonate

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Received November 14, 2022; revised January 11, 2023; accepted February 10, 2023

**Abstract**—The solvent extraction of the  $^{90}\text{Y}/^{90}\text{Sr}$  pair from carbonate media with mixtures of aromatic dihydroxy compounds and a quaternary ammonium salt—methyltrioctylammonium carbonate (MTOAC)—in toluene and butyl acetate was studied. It was found that MTOAC increases the distribution coefficients of both the extractant itself and its solvate with yttrium due to the formation of a mixed complex of yttrium and a dihydroxyaromatic ligand with MTOAC. During extraction from alkaline carbonate media in the pH range of 12–13.5 with mixtures of 0.01 M 2,3-dihydroxynaphthalene and 0.015 M MTOAC in butyl acetate or toluene, the distribution coefficients of yttrium exceed 80; the separation factors of the  $^{90}\text{Y}/^{90}\text{Sr}$  pair under these conditions are more than  $10^5$ . Dilute solutions of hydrochloric, nitric, and sulfuric acids can be used for the complete stripping of yttrium. The studied mixtures are chemically stable and do not change the extraction properties upon multiple extraction/stripping cycles. Model experiments on the leaching of yttrium from natural samples showed that the percentage of stable yttrium extraction from sand is 70–80%, while the percentage of yttrium extraction from soil is 50–60%.

**Keywords:** extraction, yttrium, strontium-90, aromatic dihydroxy compounds, methyltrioctylammonium carbonate

**DOI:** 10.1134/S1066362223020091

## INTRODUCTION

The isotope  $^{90}\text{Sr}$ , formed during the fission of uranium and plutonium nuclei, together with  $^{137}\text{Cs}$  makes the main contribution to the global pollution of water and soil on Earth. Atmospheric nuclear testing in 1945–1980 released  $10^{18}$  Bq of  $^{90}\text{Sr}$  into the environment, the Chernobyl disaster in 1986 added  $10^{16}$  Bq, the explosions at the Fukushima nuclear power plant in 2011 added another  $10^{15}$  Bq. The high migratory mobility of  $^{90}\text{Sr}$  brings about its distribution in the biosphere and the inevitable entry into the organisms of living beings, where it concentrates in the bones and damages the surrounding tissues. The obvious need for constant monitoring of the  $^{90}\text{Sr}$  content in the

environment is complicated by its nuclear-physical properties. Unlike  $^{137}\text{Cs}$ , which is easily detected by the  $\gamma$ -radiation of the  $^{137}\text{Ba}$  daughter, both  $^{90}\text{Sr}$  and the  $^{90}\text{Y}$  daughter are pure  $\beta$ -emitters ( $^{90}\text{Sr}$  with  $E_{\text{max}} = 546$  keV and  $^{90}\text{Y}$  with  $E_{\text{max}} = 2280$  keV). Classical methods of analysis involve the chemical separation of  $^{90}\text{Sr}$  from the matrix material, exposure until equilibrium with  $^{90}\text{Y}$ , and its determination by hard  $\beta$ -radiation. Liquid–liquid extraction is widely used for the separation of radionuclides. Strontium-90 is efficiently and selectively extracted from nitric acid media by crown ethers [1]. Alkyl phosphoric acids can be used to extract  $^{90}\text{Y}$  from acidic media [2]. But in both cases, a preliminary acid digesting of the samples is necessary, which involves the use of toxic and aggressive reagents. We proposed

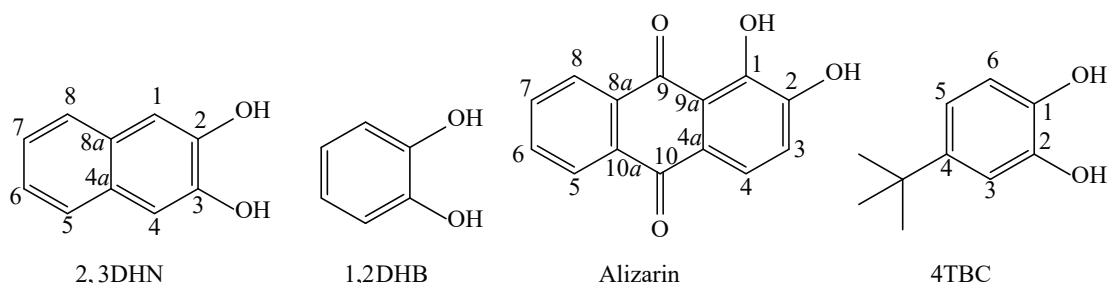
a variant of yttrium separation from carbonate media using aromatic dihydroxy compounds as extractants [3].

This work is aimed at studying extraction of yttrium and its separation from strontium by synergistic mixtures of dihydroxy compounds with methyltrioctylammonium carbonate in carbonate-alkaline media. Mixtures of alkylammonium salts with organic acids, binary extractants, efficiently extract metals [4]. Phenolic groups are known to dissociate in alkaline media, and a

similar effect can be expected for mixtures of dihydroxy compounds with alkylammonium salts.

## EXPERIMENTAL

The following aromatic dihydroxy compounds were studied in the work: 2,3-dihydroxynaphthalene (2,3DHN), pyrocatechol (1,2DHB), alizarin, and 4-*tert*-butylpyrocatechol (4TBC).



Methyltrioctylammonium carbonate (MTOAC) was used as the alkylammonium salt synthesized at the Mendelev University of Chemical Technologies of Russia according to the original method and provided by S.I. Stepanov. 2,3DHN was received from Schuhardt (Munich, Germany); 4TBC was purchased from Sigma-Aldrich (Germany); 1,2DHB and alizarin were manufactured by Lenreaktiv (Russia). Solvents, butyl acetate (BuAc), toluene (PhMe), inorganic salts and acids were produced by Ecos-1 (Russia). All reagents were of analytical grade and were used without further purification. Extractant solutions were prepared according to their exact weighted portion.

Extraction experiments were carried out as follows: 1 mL of the aqueous and organic phases were placed into a 5-mL polypropylene tube, stirred at  $21 \pm 1^\circ\text{C}$  for 10 min (sufficient to attain complete equilibrium according to the data of preliminary experiments), and the phases were separated by centrifugation (3000 rpm, 5 min). The concentration of stable strontium and yttrium was determined on a Varian 725-ES optical emission spectrometer with an error of no more than 5%. The activity of the  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  isotopes in the initial solution was found on a Quantulus 1220 liquid scintillation spectrometer (Perkin Elmer), measurement geometry

4 $\pi$ , with an error not exceeding 10%. The concentration of 2,3-dihydroxynaphthalene in the aqueous phase was determined on a Shimadzu UV-2600 UV spectrometer by absorbance at 237 nm. Aqueous media with different pH and constant ionic strength were prepared by mixing solutions of 1 M  $\text{NaHCO}_3$  and 1 M  $\text{NaOH}$ . The pH values of the solutions were determined using a Hanna Instruments HI-8314 pH meter with an I-1330B micro-electrode.

The distribution coefficients ( $D$ ), separation factors (SF), and the degree of extraction ( $E$ , %) were calculated using Eqs. (1)–(3)

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}}, \quad (1)$$

$$\text{SF} = \frac{D_1}{D_2}, \quad (2)$$

$$E = \frac{C_{\text{org}}}{C_i} \times 100, \quad (3)$$

where  $C_i$ ,  $C_{\text{org}}$ , and  $C_{\text{aq}}$  are the initial and equilibrium concentrations (activities) of metals or extractant in the organic and aqueous phases, respectively. All extraction experiments were carried out twice. The average values of the determined parameters were used.

Model experiments with natural samples were conducted as follows. A sample of building sand was homogenized, sifted through a sieve and dried in an oven. After that, a sample of sand weighing 1 g was taken. A solution of stable yttrium nitrate was added to the sample in such an amount that its concentration in the final sample was 30 mg/L, everything was thoroughly mixed and dried in an oven, after which 3 g of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  were added to the sample. The resulting mixture was calcined in a muffle for 1 h at  $500^\circ\text{C}$ . After cooling the mixture to room temperature, the sample was placed in a polypropylene test tube, 50 mL of the leaching agent solution was added to the sample (5 leaching agents were tested in total— $\text{H}_2\text{O}/\text{H}_2\text{O}_2$  (3 : 2),  $\text{NaHCO}_3/\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{HCO}_3/\text{H}_2\text{O}_2$ , and  $(\text{NH}_4)_2\text{CO}_3/\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{CO}_3$ ). For 2 h, a sample of sand was contacted at stirring with the aqueous phase to transfer yttrium carbonate into the aqueous phase. Then the aqueous phase was separated and sent for extraction with a mixture of 0.01 M 2,3DHN + 0.015 M MTOAC in toluene at a volume ratio of the organic and aqueous phases O : A = 1 : 1 and a contact time of 10 min. Afterwards, the phases were separated by centrifugation. Yttrium was stripped from the organic phase with a 0.05 M  $\text{HNO}_3$  solution at O : A = 5 : 1, after which the nitric acid aqueous solution was separated by centrifugation. The content of stable yttrium was measured therein by the spectrophotometric method.

A soil sample (500 g), taken in a forest belt on the territory of the Leningrad Region, was homogenized, sifted through a sieve and mixed with a radioactive label containing a  $^{90}\text{Y}/^{90}\text{Sr}$  pair being in radioactive equilibrium with a total activity of 530 Bq (the specific activity of the soil was about 1 Bq/g).

A soil sample labelled with  $^{90}\text{Y}/^{90}\text{Sr}$  was dried in an oven, after which a sample (2 g) was taken. Solutions of stable yttrium and strontium nitrates in the molar ratio Y : Sr = 10 : 1 were added to the sample, everything was thoroughly stirred and dried in an oven; then 10 g of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  were added to the sample. The resulting mixture was calcined in a muffle for 1 h at a temperature of  $300^\circ\text{C}$ , and then for another 4 h at a temperature of  $550^\circ\text{C}$ . After the mixture was cooled to room temperature, the sample was placed in a polypropylene test tube, and 50 mL of distilled water was added. The sample was contacted for 2 h at stirring with water to transfer yttrium carbonate into the aqueous phase. Then the aqueous phase was

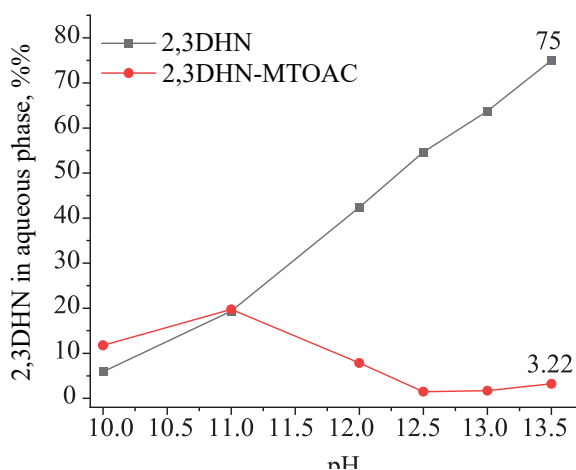
separated. Yttrium was extracted from it with a mixture of 0.01 M 2,3DHN + 0.015 M MTOAC in toluene according to the standard procedure at O : A = 1 : 1 and a contact time of 10 min. Afterwards, the phases were separated by centrifugation. Yttrium was stripped from the organic phase with a 0.05 M  $\text{HNO}_3$  solution at O : A = 4 : 1, then the nitric acid aqueous solution was separated by centrifugation. The content of stable yttrium was measured by the spectrophotometric method and the content of yttrium-90 by the radiometric method on a Teflon target using an A-85 radiometer with a plastic scintillator (the counting efficiency was 25%, the measurement error at the selected exposure time was no higher than 5%). The percentage of yttrium-90 extraction from the soil was calculated based on the measurement results.

## RESULTS AND DISCUSSIONS

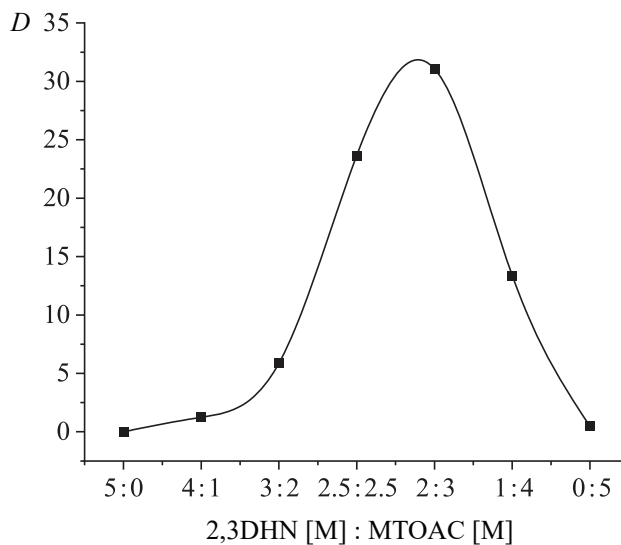
Preliminary experiments showed that all the studied aromatic dihydroxy compounds weakly extract yttrium from alkaline media. The low extraction efficiency may be due to the washing out of the extractant into the aqueous phase because of the formation of hydrophilic sodium phenolates. According to the literature data [5], 2,3-dihydroxynaphthalene has  $\text{p}K_{\text{a}1} = 8.8$ ,  $\text{p}K_{\text{a}2} = 12.6$ , which indicates its complete transition to the monosodium salt in highly alkaline media. The MTOAC cation generates hydrophobic salts with the phenolate anion and helps to reduce the loss of the extractant with the aqueous phase. Figure 1 shows data on the distribution of 2,3-dihydroxynaphthalene and its salt with MTOAC between the organic and aqueous phases.

From the data in Fig. 1, it can be seen that at pH below 11, the addition of MTOAC does not significantly affect the distribution of 2,3DHN between the aqueous and organic phases. At pH 13.5, the transition of 2,3DHN from butyl acetate into the aqueous phase decreases from 75 to 3.2% in the presence of MTOAC. Obviously, during the yttrium extraction in a strongly alkaline medium, the anionic complex of 2,3DHN with the metal interacts with the MTOAC cation and passes into the organic phase. It should be noted that the yttrium extraction with dihydroxy compounds sharply increases at pH of aqueous solutions above 11 (see below).

The optimal ratio of MTOAC/dihydroxy compound, which provides the maximum synergistic effect in the



**Fig. 1.** Effect of MTOAC on distribution of 2,3DHN between aqueous and organic phases. Aqueous phase: 0.5 M  $K_2CO_3$ , organic phase: 0.01 M 2,3DHN or mixture of 0.01 M 2,3DHN + 0.015 M MTOAC in butyl acetate.



**Fig. 2.**  $D_Y$  vs. ratio of 2,3DHN and MTOAC. Organic phase: 0.005 M isomolar mixtures of 2,3DHN + MTOAC in toluene, aqueous phase: 0.001 M  $Y_2(CO_3)_3$ , 1 M ( $Na_2CO_3$  + NaOH, pH 12.6).

yttrium extraction, was determined by the method of isomolar series (Fig. 2). It can be seen that a 1.5-fold excess of MTOAC with respect to 2,3DHN is optimal, which suggests the formation of a solvate of the composition  $[Y(2,3DHN)_2(MTOAC)_3]$  [6]. The existence of a complex of this composition is confirmed by the MS-ESI(–) data: in addition to the 2,3DHN monoanion ( $m/z = 159.0448$ ), there is a signal with  $m/z = 404.8723$  of the  $[Y(2,3DHN)_2]^-$  monoanion. The MS-ESI(–) spectra contain signals from anionic complexes, which, in addition to yttrium and 2,3DHN, include carbonate and hydroxyl groups and water molecules.

Compared to pure 2,3DHN and MTOAC, their synergistic mixture extracts yttrium with distribution coefficients approximately 2 orders of magnitude higher: for 0.005 M MTOAC in PhMe,  $D_Y = 0.47$ , for 0.005 M 2,3DHN  $D_Y = 2.5 \times 10^{-5}$ , and for their mixture  $D_Y = 32$  (Fig. 2).

As already noted, the maximum extraction of yttrium by mixtures of dihydroxy compounds with MTOAC is detected at pH above 11. We found that the specific form of distribution coefficient curve for yttrium vs. pH of the aqueous phase is determined by the type of dihydroxy compound and the type of organic solvent (Fig. 3).

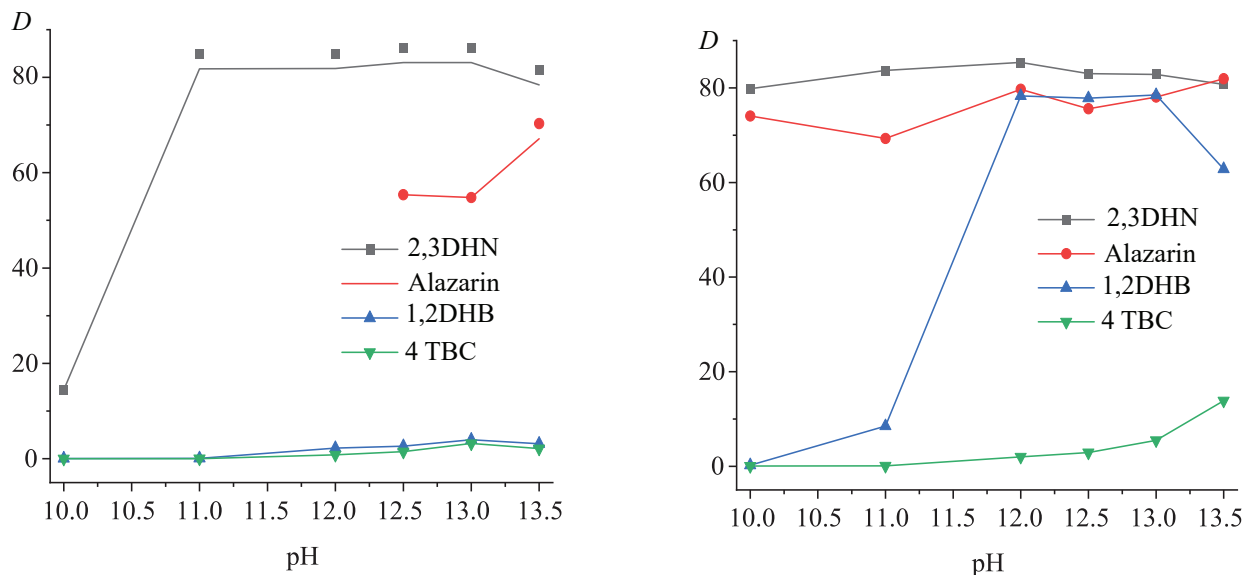
The most effective extractant in both solvents is 2,3-dihydroxynaphthalene. The lowest distribution coefficients of yttrium, regardless of the type of solvent,

are demonstrated by 4-*tert*-butylpyrocatechol. Its unsubstituted analog, pyrocatechol, extracts yttrium well only into toluene solutions. This may be due to steric factors, since the properties of phenolic groups in these extractants are very similar. High distribution coefficients of yttrium were found in a water-soluble chelating agent, alizarin, giving a hydrophobic complex with MTOAC, which is concentrated in the organic phase.

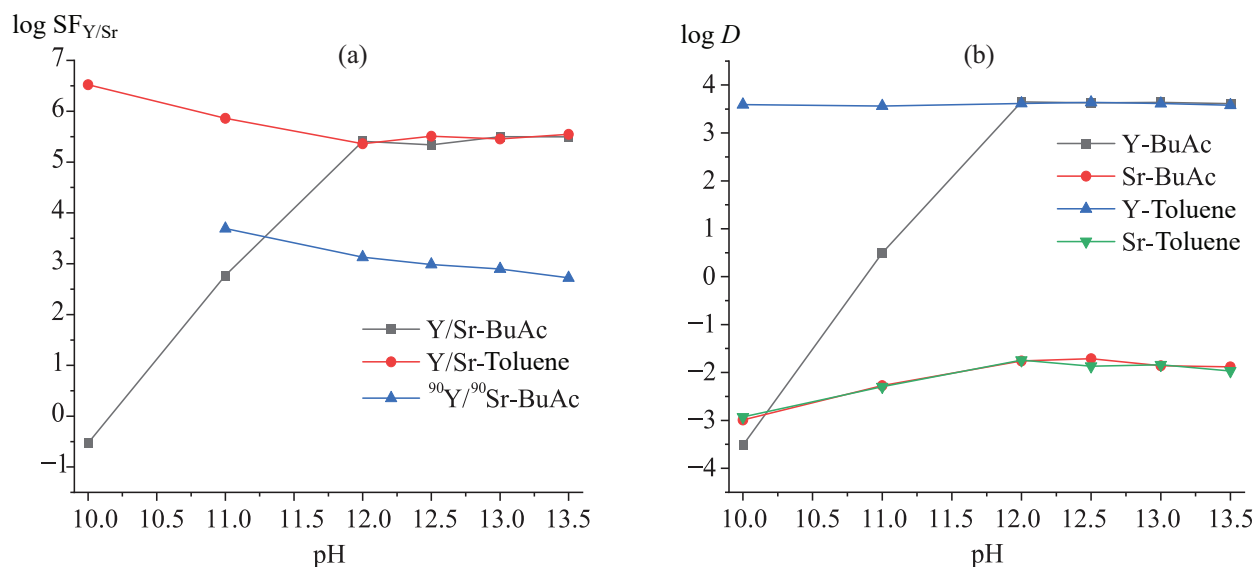
A solution of alizarin in butyl acetate upon contact with an aqueous phase with a pH below 12.5 forms a third phase.

The possibility of efficient separation of yttrium and strontium was demonstrated by the example of 2,3DHN, the most efficient of the studied extractants (Fig. 4). The data in Fig. 4 show that at pH > 12, Y/Sr pair separation factors exceed  $10^5$  in both toluene and butyl acetate. Such a high selectivity is unattainable in the extraction of strontium with crown ethers [1] or yttrium with alkyl phosphoric acids [2] from nitric acid solutions. Small differences in the behavior of stable and radioactive isotopes are most likely associated with a high error in determining the low activities of  $^{90}Sr$  and  $^{90}Y$  in saline solutions.

An additional advantage of the studied extraction systems is the simplicity of yttrium stripping with dilute acid solutions. For the quantitative stripping of yttrium, one contact of the extract with 0.05 M solutions



**Fig. 3.**  $D_Y$  vs. pH during extraction from carbonate solutions containing 0.001 M  $Y_2(CO_3)_3$  and 1 M  $(Na_2CO_3 + NaOH)$  with mixtures containing 0.01 M 2,3DHN, 1,2DHB or 4TBC with 0.015 M MTOAC, 0.005 M alazarin with 0.01 M MTOAC in (a) butyl acetate and (b) toluene.



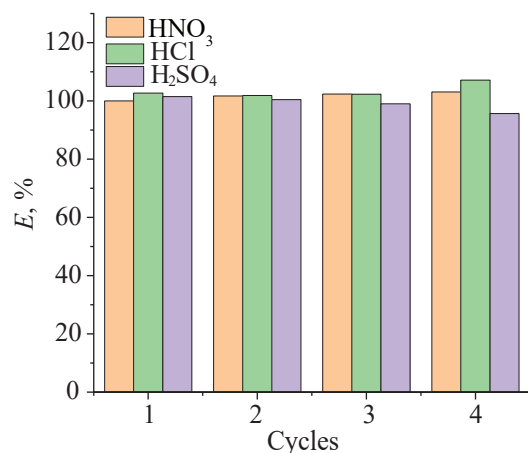
**Fig. 4.** (a)  $\log SF_{Y/Sr}$  and (b)  $\log D$  vs. pH when extracted from an aqueous solution containing  $4 \times 10^{-6}$  M yttrium and  $1 \times 10^{-6}$  M strontium in 1 M  $(Na_2CO_3 + NaOH)$  using mixture of 0.001 M 2,3DHN and 0.0015 M MTOAC in butyl acetate and toluene.

of inorganic acids:  $HNO_3$ ,  $HCl$ , and  $H_2SO_4$  is sufficient (the equilibrium pH of the strip is not higher than 1). The extractant after stripping of yttrium with acids retains its properties. Figure 5 shows the results of experiments on multiple extraction/stripping of yttrium using a mixture of 0.01 M 2,3DHN with 0.015 M MTOAC in toluene as an extractant and 0.05 M  $HNO_3$ ,  $HCl$ , and  $H_2SO_4$  solutions as strips. It can be seen that a slight decrease

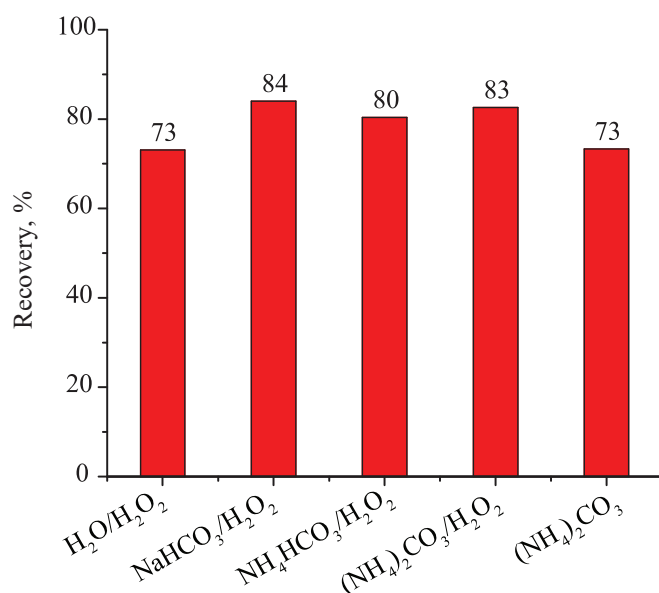
in the extraction capacity after 4 extraction/stripping cycles is observed only in the case of using sulfuric acid (Fig. 5).

Experiments on the leaching of yttrium from sand were carried out with leaching solutions of five different compositions. The percentage of extraction separation of yttrium from sand after carbonate sintering, leaching





**Fig. 5.** Multiple extraction–stripping of yttrium (0.001 M) with a solution of 0.01 M 2,3DHN and 0.015 M MTOAC in toluene from an aqueous phase with pH 12.6. Stripping agents: 0.05 M HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub> solutions.



**Fig. 6.** Extraction of yttrium from sand after carbonate sintering, leaching, and extraction.

and extraction of yttrium into the organic phase is shown in Fig. 6.

As can be seen from the data in Fig. 6, in all the systems studied, there is a high percentage of yttrium extraction (70–80%), therewith aqueous phases consisting of ammonium carbonate or sodium bicarbonate with the addition of hydrogen peroxide proved to be more effective. The introduction of hydrogen peroxide into the leaching solution was proposed for further oxidizing possible organic residues.

Table 1 presents data on carbonate penetration and separation of yttrium from a soil sample containing the <sup>90</sup>Y/<sup>90</sup>Sr radioactive label and stable yttrium with strontium. Based on the measurement results, the percentage of <sup>90</sup>Y extraction from the soil was calculated (final value after all operations).

The data obtained show that leaching from a soil sample is less efficient than from pure sand, which may be due to the high content of mineral acid salts in the soil, which pass into the aqueous phase during leaching and interfere with the complete extraction of yttrium, as well to the possibility of mechanical retention of yttrium by microdispersed particles.

## CONCLUSIONS

Recovery of <sup>90</sup>Y and its separation from <sup>90</sup>Sr are effectively carried out in carbonate media using synergistic extraction mixtures of aromatic dihydroxy compounds with methyltrioctylammonium carbonate. In the presence of MTOAC, the distribution coefficients of both the extractant itself and its solvate with yttrium increase. In alkaline carbonate media with pH 12–13.5, mixtures of 0.01 M 2,3-dihydroxynaphthalene and 0.015 M MTOAC in toluene and butyl acetate extract yttrium with distribution coefficients of more than 80 and <sup>90</sup>Y/<sup>90</sup>Sr separation factors of more than 10<sup>5</sup>. Yttrium is easily stripped with dilute inorganic acids.

Leaching of yttrium from sand samples showed that ammonium carbonate with the addition of hydrogen

**Table 1.** Extraction of <sup>90</sup>Y and stable yttrium from soil (initial sample and strip after leaching, extraction and subsequent stripping with acid)

Method of measurement	Introduced yttrium	Defined by yttrium	% of recovery
Spectrophotometric	40 mg/L	24 mg/L	60
Radiometric	280 pulses/300 s	152 pulses/300 s	54

peroxide has the best properties: the degree of yttrium extraction was over 80%, while the results of carbonate leaching of yttrium from a soil sample are slightly lower, 50–60%, which may be due to the use of water as a leaching agent as well to a more complex sample composition.

#### ACKNOWLEDGMENTS

The studies were carried out using the equipment of the resource centre of St. Petersburg State University “Chemical analysis and Material Research Centre” and the resource centre of St. Petersburg State University “Magnetic resonance research centre.”

#### FUNDING

The study was financially supported by the Russian Science Foundation grant no. 20-63-46006.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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