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Sorbents based on crown ethers: preparation and application for the sorption of strontium

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The key approaches to the synthesis of crown ether-based sorbents, including immobilization both with and without covalent bonding, are reviewed. Examples of sorbent preparation using anodic oxidation, chemical modification of polymers, polycondensation reactions, chemical modification of inorganic supports and radiochemical synthesis for covalent bonding of crown ether moieties are considered. Immobilization methods without covalent bonding including support synthesis in the presence of crown ethers, impregnation of supports with a crown ether solution and the use of powdered crown ether as a sorbent are presented. The applications of sorbents for selective removal of strontium from solutions of radioactive waste and spent nuclear fuel, for radiochemical analysis (determination of strontium in water, soil and biological materials) and for separation of strontium and yttrium isotopes are discussed.
The bibliography includes 114 references.

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I. Introduction

Currently, thousands of tons of radioactive waste (RW), including high level waste (HLW), have been accumulated in waste repositories;[1–4] therefore, processing of these wastes to reduce the overall activity becomes important. A solution to this problem is the selective extraction of particular radionuclides from the mixture. Purification of process media from radionuclides is also a topical scientific and engineering problem considered in numerous publications.[5–18] Scientists from different countries have accumulated a lot of experimental and theoretical experience in isolation of radionuclides from process media. Spent nuclear fuel (SNF) and RW have high activity owing to the presence of long-lived isotopes, in particular, strontium (^{90}Sr), the half-life ($\tau_{1/2}$) of which is 28.7 years.[19] The high activity of ^{90}Sr and ^{137}Cs is the key factor of the environmental hazard of RW due to the ability of these nuclides to be accumulated in biological tissues.[20, 21] The ^{90}Sr isotope is most hazardous as there is no reliable geochemical barriers for it.[22]

The behaviour of strontium resembles that of calcium and, hence, it can be incorporated into the organo-mineral base of bones and bring about high radiation exposure due to the internal irradiation. It is also important that the daughter radionuclide of ^{90}Sr is ^{90}Y, which has a high maximum β-particle energy (2.27 MeV).[23]

The selective extraction of ^{90}Sr can markedly reduce the radioactivity of waste, which makes easier the subsequent processing and storage.[4, 16] Furthermore, ^{90}Sr is widely used as a source of β-radiation [5] and ^{90}Y finds use in biology and radiotherapy owing to the short half-life (64 h) and stability of the daughter ^{90}Zr radionuclide.[20, 21]

The closed nuclear fuel cycle concept accepted in Russia implies processing of spent nuclear fuel in order to isolate and reuse fissile materials.[24] The fission products and transplutonium elements remain in the HLW, which is vitrified and sent to controlled disposal. For ultimate removal of environmentally hazardous radionuclides, promising methods are disposal into geological formations and nuclear transmutation. Both methods require preliminary fractionation, *i.e.*, separation of radionuclides into groups with similar properties. The necessary degree of fractionation is still a debated issue, but the expediency of isolation of the

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most radiotoxic transplutonium elements and the main heat-generating radionuclides (^{90}Sr and ^{137}Cs) from the HLW is beyond doubt.[25]

Polyether macrocycles possess high complexing ability towards alkali and alkaline earth metal cations including radioactive ones. Sorbents based on crown ethers, which are selective to certain metals, have long been proposed for removing these components from RW.[26] These sorbents are also promising for the separation of strontium isotopes and daughter radionuclides.

Crown ethers are macrocyclic compounds with a regular arrangement of oxygen atoms in a ring of a specified size.[27] They can comprise 9–60 atoms out of which 3–20 atoms are oxygens separated by ethylene bridges.[28] The intense development of crown ether chemistry was initiated in 1967 by the paper of Pedersen;[29] currently, quite a number of compounds of this type have been studied.[30–39]

The first process that made use of macrocyclic compounds for selective recovery of metals was solvent extraction.[40–43] The complexation of macrocycles with metals has been considered in reviews.[44,45]

The sorbent extraction of radionuclides for processing of RW and SNF has a number of advantages over solvent extraction including a lower consumption of the crown ether, decrease in the amount of secondary liquid radioactive waste (LRW), no need to handle flammable liquids and, as a consequence, higher safety of the process. The preparation of sorbents based on crown ethers was considered in reviews[46,47] and papers.[48,49] The use of crown ethers in radiochemistry and radiochemical technology was surveyed in a review,[50] which summarized the data on the sorbent preparation, radiation stability and the use for extraction and sorption of metals. However, owing to accumulation of a huge amount of experimental data, detailed discussion of both methods for extraction of key SNF radionuclides within one review is a fairly complicated task. Therefore, it is expedient to integrate the published data for particular methods of extraction of certain radionuclides.

The sorption of strontium is a rather well-studied scientific problem; however, the extensive literature data have not been summarized so far. Our review gives a systematic account of the data on the use of crown ether-based sorbents for the extraction of strontium and the methods of preparation of these sorbents.

II. Methods for the preparation of sorbents

The methods used to produce sorbents containing crown ethers or crown ether moieties developed to date can be classified into two large groups:[46–51]

— immobilization of crown ethers with covalent bonding;

— immobilization of crown ethers without covalent bonding (impregnation).

In both groups of methods, both organic and inorganic supports are used.

II.1. Immobilization of crown ethers with covalent bonding

The principal methods for preparing sorbents in which crown ether moieties are covalently bonded to a solid support (matrix) include

— anodic oxidation;

— chemical modification of polymeric organic sorbents (alkylation of the styrene–divinylbenzene matrix with amino derivatives of crown ethers, alkylation of polyvinyl alcohol, catalytic oxidation of polysiloxanes, *etc.*);

— polycondensation reactions (azacrown ethers with dicarboxylic acids, benzocrown ethers with formaldehyde);

— chemical modification of inorganic sorbents (mainly silica gel);

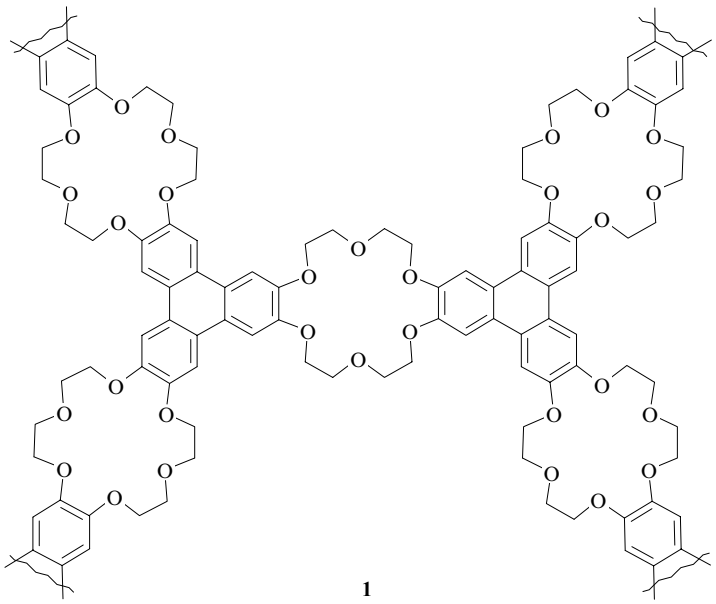
— radiation chemical synthesis.

Examples of sorbent preparation by the listed methods are presented below.

A promising method for the synthesis of crown ether polymers is anodic oxidation of dibenzocrown ethers on the surface of an electrode.[52] This gives in one step crown-containing polymers [for example, poly(dibenzo-18-crown-6), **1**], which possess satisfactory electrochemical and complexing properties.

Currently, most of polymers used for chemical modification are styrene–divinylbenzene matrices or their chloromethyl derivatives (chloromethylated copolymer, CMC, structure **2**, the divinylbenzene moiety is omitted). The

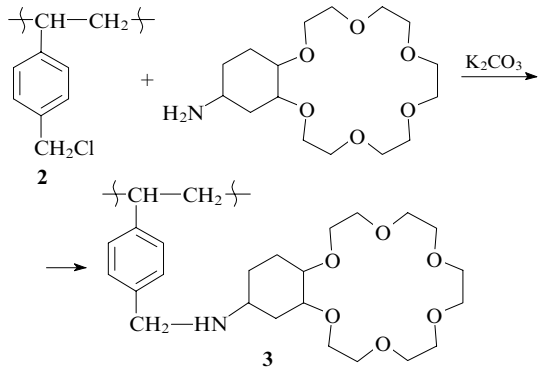
Structure 1



1

method for immobilization of aminocycloaliphatic crown ether derivatives on polymer matrices proposed by Yakshin *et al.*[53] results in the formation of solid grained sorbents bearing both active cyclic polyether moieties and amino groups in rather high concentrations. The synthesis was carried out by the reaction of CMC with an aminocyclohexane derivative of 18-crown-6 (Scheme 1).

Scheme 1



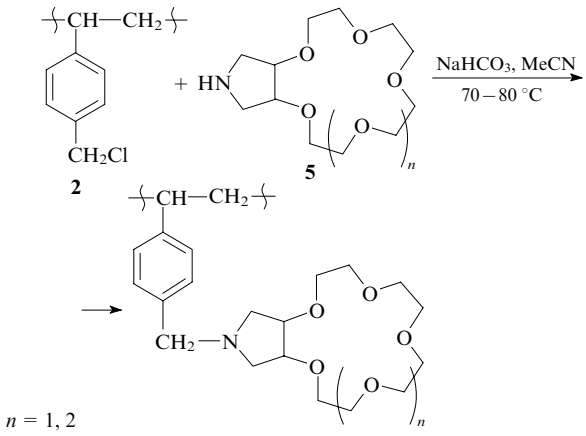
The resulting polymer **3** with side crown ether groups mainly contains secondary amino groups. The simultaneous formation of tertiary amino groups upon the reaction of two adjacent chloromethyl groups with a nitrogen atom cannot be ruled out either.

Di(aminocyclohexano)crown ethers **4** can also be introduced in such reaction (Scheme 2). Depending on the component ratio and reaction conditions, the crown ether polymers thus obtained can contain primary amino groups, apart from secondary and tertiary ones.

The reaction of amino derivatives of cycloalkano-crown ethers with CMC was conducted in dioxane or DMF in the presence of K_2CO_3 at 90 – 100 °C. A macroporous CMC (10% divinylbenzene) with a grain size of 0.3 – 0.6 mm containing 18.1 mass % Cl was used. A stoichiometric amount of crown ether **4** in dioxane was added to a mixture of CMC and K_2CO_3, and the reaction mixture was stirred at 90 °C for 8 h. After cooling, the grains were filtered off, washed with acetone and water (until chloride ions were no longer detected in wash water) and dried to a constant mass. This gave a crown ether polymer containing 17% primary, 61% secondary and 22% tertiary amino groups.

Watanabe *et al.*[54] reported grafting of crown ethers containing a fused pyrrolidine ring (compound **5**) to a chloromethylated styrene – divinylbenzene copolymer. The process was carried out for 5 days at 70 – 80 °C (Scheme 3).

Scheme 3

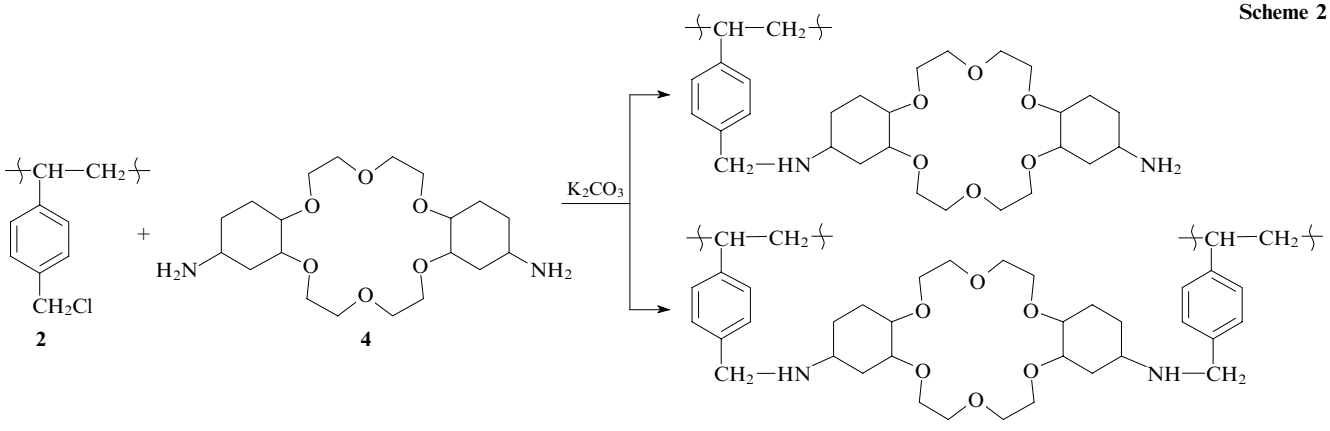


Kurmanaliev[55] pursued the preparation of polymers with a definite swelling capability and sorption capacity. For this purpose, the initial chloromethylated copolymer of styrene and divinylbenzene as yellow grains was first kept in DMF for 24 h. After polymer swelling, 1,10-diaza-4,7,13,16-tetrathia-18-crown-6 was added and the reaction mixture was vigorously stirred for 6 – 8 h at 90 °C. Then the mixture was cooled and the reaction product was filtered off, washed with water and dried to a constant mass.

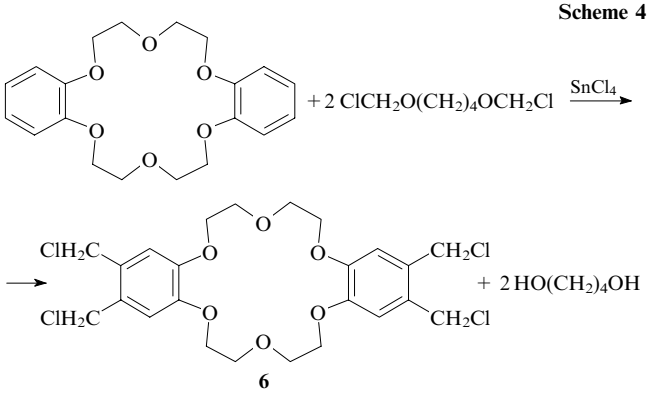
A method for immobilization of dibenzo-18-crown-6 (DB18C6) on cross-linked polyvinyl alcohol (PVA) has been described.[56] The process comprised several stages. The first one was cross-linking and formation of PVA grains; this was done by mixing an aqueous solution of PVA with a solution of glutaraldehyde [$OHC(CH_2)_3CHO$] and pouring the mixture into the organic phase comprising a solution of sorbitan monostearate in paraffin oil. Hydrochloric acid was used as the catalyst; the cross-linking and grain formation took place at 65 °C over a period of 7 h. This gave semitransparent microspheres of cross-linked PVA (c-PVA). The second stage was chloromethylation of DB18C6 with 1,4-bis(chloromethoxy)butane in chloroform at room temperature catalyzed by the Lewis acid $SnCl_4$ (Scheme 4).

In the third stage, the resulting chloromethylated DB18C6 was immobilized on microspheres of cross-linked PVA. The nucleophilic substitution reaction between the chloromethyl groups of crown ether **6** and the hydroxy groups of PVA microspheres was carried out in DMF in the presence of Na_2CO_3, which served as the acceptor for the

Scheme 2



Scheme 4



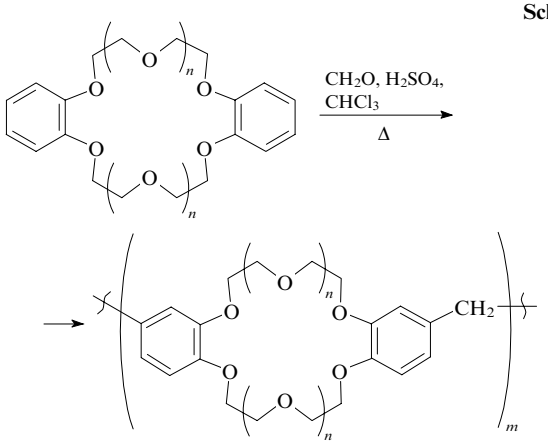
6

acid, for 9 h at 70 °C. Finally, sorbent **7** was obtained (Scheme 5).

Nitration followed by reduction of nitrated DB18C6 afforded diaminodibenzo-18-crown-6 (DADB18C6), which was made to react with an epoxy compound on the surface of a solid support.[35] This gave a crown ether-based resin coating firmly attached to the solid support.

Chauhan and Boudjouk[57] described a one-stage synthesis of polysiloxanes containing unsubstituted crown ether moieties and the corresponding model oligomer. The reaction was conducted in deuterated benzene in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ at 78 °C. The colour of the reaction mixture changed during the reaction: the red colour of the catalyst disappeared after 15 min of heating, the reaction mixture became yellow and homogeneous, and then the yellow colour was replaced by orange and then again by red when the reaction was completed (most often, in 24 h) (Scheme 6).

Scheme 7

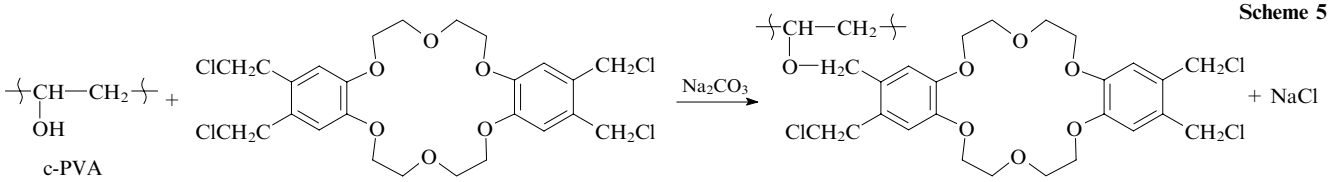


$n = 1, 2$

The synthesis of crown ether polymers **8a – c** and **9** by polycondensation of diaza-18-crown-6 (DA18C6) with sebacic or terephthalic acid chloride, toluylene diisocyanate and diglycidyl ether of bisphenol A was reported.[58]

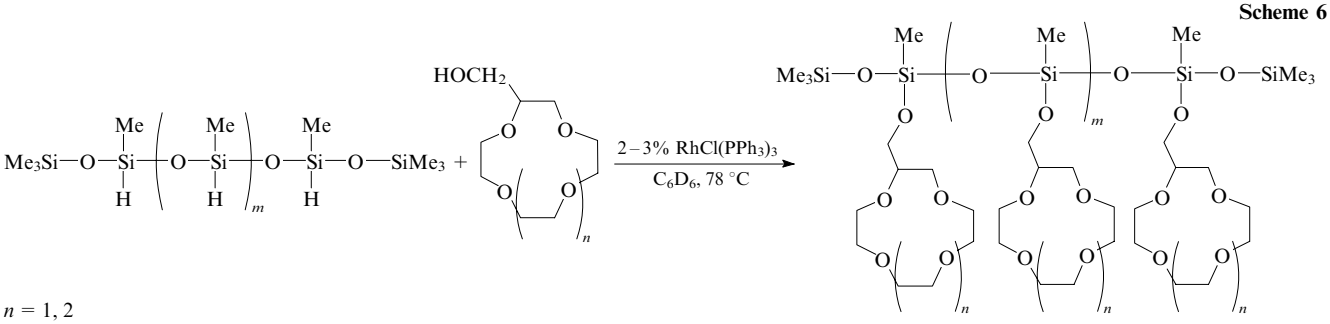
A known method[59] for the polymer preparation includes the reaction of DB18C6 or dibenzo-24-crown-8 (DB24C8) with formaldehyde in chloroform catalyzed by sulfuric acid. The crown ether, a 30% aqueous solution of CH_2O (4 equiv.), $CHCl_3$, water and H_2SO_4 were mixed and the mixture was heated until $CHCl_3$ was removed. This gave a brown powder (Scheme 7).

Scheme 5



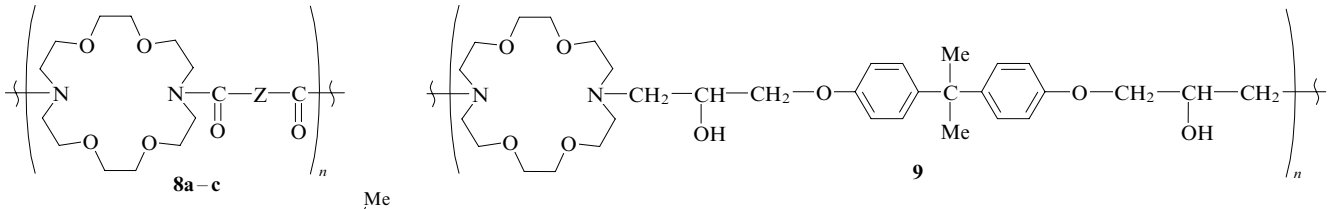
6 **7**

Scheme 6

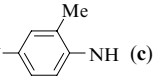


$n = 1, 2$

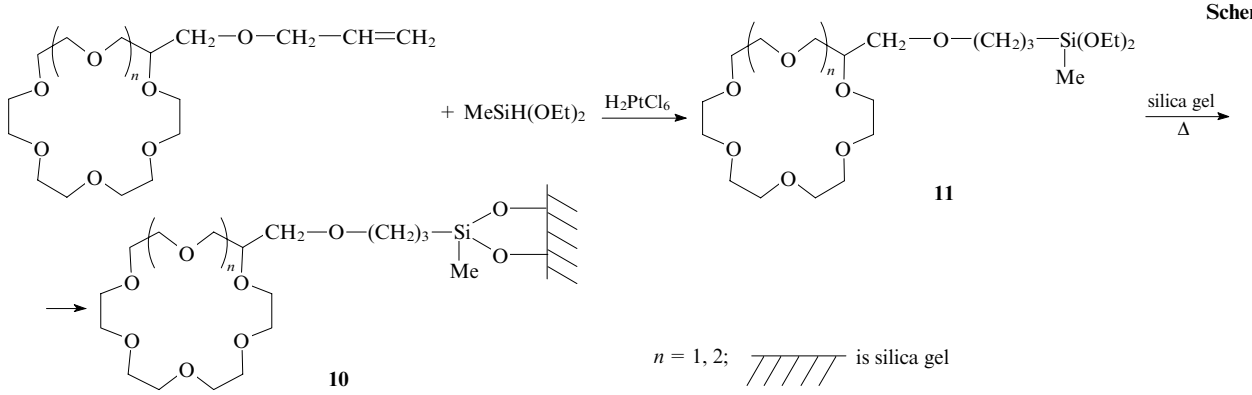
Structures 8, 9



8a – c **9**

Z = $(CH_2)_8$ (**a**), 1,4-C_6H_4 (**b**),  (**c**)

Scheme 8



Al'tshuler *et al.*[60–62] prepared crown-containing sorbents by emulsion polycondensation of crown ether (DB18C6 or DB24C8) with formaldehyde in the presence of a strong electrolyte. The polymer was formed as spheres of controlled size. The average particle diameter for the sorbent sample found as the arithmetic mean of the sizes of 1000 spheres was 0.11 mm.

Modified silica gel **10** was prepared by refluxing allyloxymethyl-substituted macrocycle, a catalytic amount of chloroplatinic acid and excess methyldiethoxysilane in benzene for 16 h.[63] The intermediate product **11** thus formed was added to silica gel (in 1 : 10 ratio). After removal of the solvent, the residue was heated at 120 °C for 16 – 24 h for completion of the addition reaction (Scheme 8).

The use of radiation chemical synthesis for the preparation of sorbents based on crown ethers allows selective one-step generation of radical active sites in the polyether ring; the active sites can add to the reactive groups of the support or monomer.[50] For example, Zakurdaeva *et al.*[64] obtained sorbent **12** from polyethylene oxide (PEO) and dicyclohexano-18-crown-6. A mixture of solutions of dicyclohexano-18-crown-6 (DCH18C6) isomers in a 1 M solution of KCl and PEO in water or in 1 M KCl taken in definite proportions were placed in glass tubes and, after the removal of oxygen, exposed to γ-radiation from ^{60}Co at room temperature (the dose rate was 10 kGy h^{-1}) (Scheme 9). After irradiation, the insoluble gel fraction, which was the useful product of radiolysis, was isolated. The content of this product increased with a decrease in the crown ether concentration in the solution. At a concentration of 1%, the mass fraction of the insoluble material reached ~75%.

Scheme 9

Chain initiation

$H_2O \longrightarrow {}^{\bullet}OH, H^{\bullet}$, *etc.*

Chain propagation

$-CH_2-CH_2-O- + {}^{\bullet}OH \longrightarrow -CH_2-\dot{C}H-O- + H_2O$

$CE + {}^{\bullet}OH \longrightarrow R^{\bullet}_{CE} + H_2O$

Chain termination

$-CH_2-\dot{C}H-O- + R^{\bullet}_{CE} \longrightarrow -CH_2-\underset{\displaystyle R_{CE}}{\underset{|}{CH}}-O-$ **12**

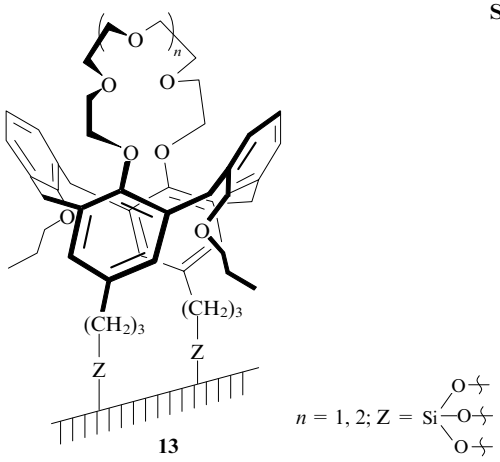
$2\ -CH_2-\dot{C}H-O- \longrightarrow -CH_2-\underset{\displaystyle -CH_2-CH-O-}{\underset{|}{CH}}-O-$

$R^{\bullet}_{CE} \longrightarrow$ recombination, disproportionation, *etc.*

CE is crown ether, $R^{\bullet}_{CE}$ is the crown ether radical

Calix[4]arene-crown-5 and calix[4]arene-crown-6 (macrocycle : silica gel = 1 : 10 by mass; structures **13**) were synthesized and grafted to silica gel.[67] The sorbents were obtained by heating calixcrown ethers containing allyl groups with triethoxysilane and H_2PtCl_4 as a catalyst in anhydrous toluene with stirring of the heterogeneous mixture for 30 h.

Structures 13



13

II.2. Immobilization of crown ethers without covalent bonding

The key methods for the preparation of sorbents in which crown ether moieties are not covalently bonded to the solid support (matrix) are as follows:

— preparation of an organic (either polymer or crystalline) matrix in the presence of crown ether (note that this approach is applicable only when the organic part is devoid of functional groups capable of binding to crown ethers);

— impregnation of the ready organic polymer matrix with a solution of crown ether;

— impregnation of the ready inorganic sorbent matrix with crown ether;

— preparation of the inorganic sorbent matrix in the presence of crown ether;

— utilization of powdered crown ether as the sorbent.

Typical representatives of crown ether-based sorbents are solid phase extraction systems (SPES) and solid phase extraction solutions (SPESL).

Yakshin *et al.*[68–70] proposed preparing SPESL as solid grained materials formed on cooling of molten mixtures of liquid or readily melting extractants with solid inert diluents.

The extractants used included DB18C6, di-*tert*-butyldibenzo-18-crown-6 (DTBDB18C6), diisooctyldibenzo-18-crown-6 (DIODB18C6), dicyclohexano-18-crown-6 (isomer A, DCH18C6 A), di-*tert*-butyldicyclohexano-18-crown-6 (DTBDCH18C6), diisooctyldicyclohexano-18-crown-6 (DIODCH18C6), octyl-18-crown-6 (O18C6), dodecyl-18-crown-6 (DD18C6), benzo-15-crown-5 (B15C5), dibenzo-21-crown-7 (DB21C7), dicyclohexano-21-crown-7 (DCH21C7), DB24C8, dicyclohexano-24-crown-8 (DCH24C8), dibenzo-30-crown-10 (DB30C10).

Organic compounds that crystallize to form systems in which the intercrystalline voids accommodate the discrete phase of the extractants served as the matrices. Such compounds include aromatic hydrocarbons (naphthalene, biphenyl, phenanthrene, *etc.*), polyhalogenated higher aromatic and aliphatic hydrocarbons, nitroalkanes, ethers and esters (diphenyl oxide, phenyl esters of higher carboxylic acids).

In order to enhance the sorption capacity of SPESL, an additional third component was introduced, namely, a source of organic anions (carboxylic acids, alkylsulfonic acids, organic phosphorus acids, *etc.*), a source of bulky inorganic anions (polymolybdates, polytungstates, hexachlorostibates, *etc.*), an additional stabilizing solvent (polyhalogenated hydrocarbons, nitroalkanes, *etc.*).

For example, in a study of Yakshin *et al.*,[70] a mixture of biphenyl and DTBDCH18C6 was heated to 70 °C, the resulting homogeneous melt was dispersed with stirring at 70 °C in a 1% aqueous solution of starch during 10 min and cooled down to room temperature with stirring. The resulting grains were filtered off, washed with water and dried in air. This gave SPESL with a DTBDCH18C6 content of 20%; the size of spherical grains was 0.1 – 1 mm (63% had 0.3 – 0.6 mm size). The appearance of the solid spherical grains is shown in Fig. 1.[68]

Preetha and Prasada Rao [71] prepared SPESL by dissolving a mixture of DCH18C6 and benzophenone (1 : 100) in a minimum amount of acetone, and the resulting acetone solution was poured into demineralized water with continuous stirring at room temperature. The mixture was stirred for 3 h, allowed to stand for settling down for 10 min and filtered. The precipitate was washed and dried at 40 °C for several hours.

Currently, several dozens of SPES are known.[72–89] The initial crown ethers used included DB18C6, DTBDB18C6, DIODB18C6, DCH18C6 A, DTBDCH18C6, O18C6, DIODCH18C6, DD18C6, B15C5, DB21C7, DCH21C7, DB24C8, DCH24C8 and DB30C10.

It is possible to distinguish two approaches to the design of SPES. According to one approach, SPES based on liquid or readily melting crown ethers (DCH18C6 A, DTBDB18C6, DIODB18C6, DTBDCH18C6, O18C6, DIODCH18C6, DD18C6, DCH21C7 and DCH24C8) were synthesized by adding a homogeneous mixture of styrene (58%), divinylbenzene, azobis(isobutyronitrile) (AIBN) and

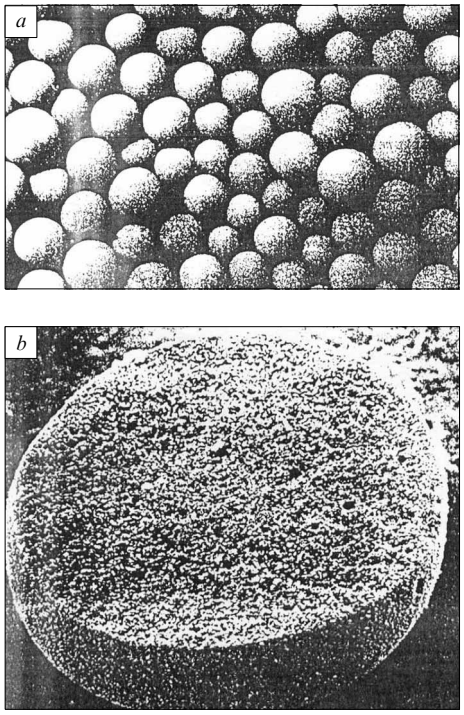


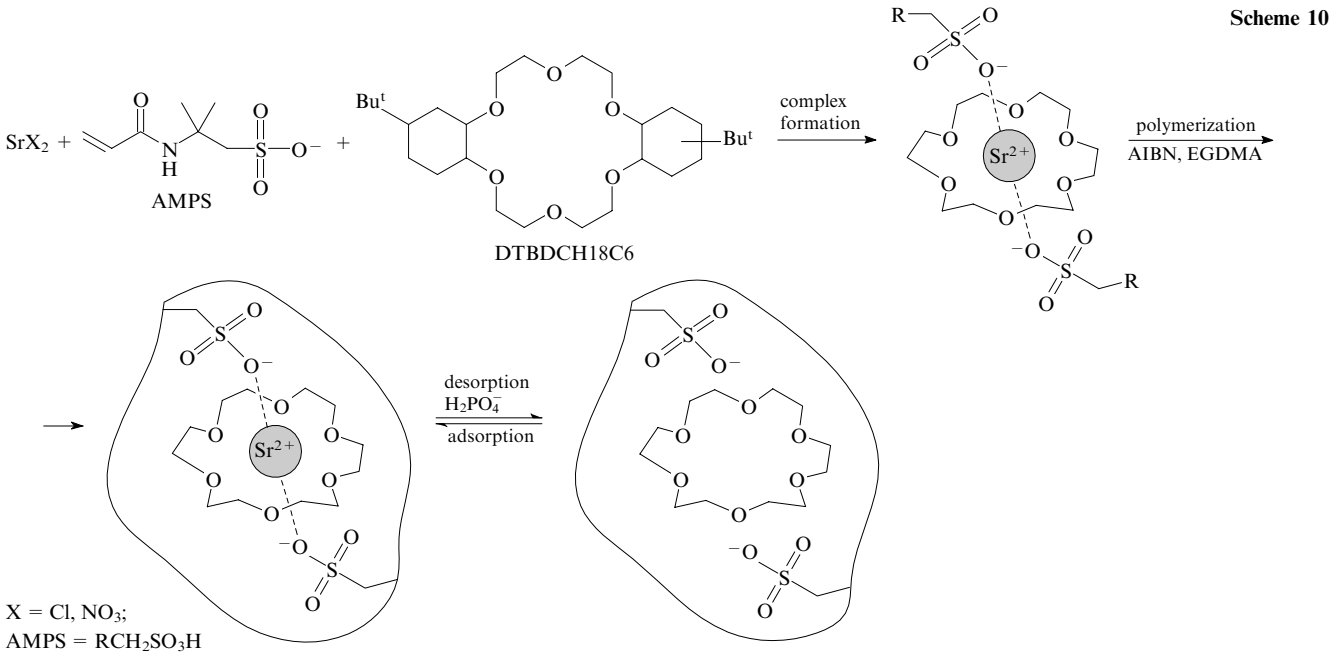
Figure 1. Grains of the solid phase extraction solution based on biphenyl and di-*tert*-butyldicyclohexano-18-crown-6.[68] (*a*) 10 : 1 magnification; (*b*) 100 : 1 magnification.

crown ether to a 0.75% aqueous solution of starch. The polymerization mixture was dispersed with intense stirring, and polymerization was performed under the following temperature conditions: heating to 80 °C in 1 h, maintenance at 80 °C for 3 h, heating to 90 °C in 1 h and maintenance at 90 °C for 1 h. After cooling, the resulting grains were filtered off, washed with water and dried in air. This gave SPES with a crown ether content of 40% – 43% as solid spherical grains.[73]

In the synthesis of SPES based on solid poorly soluble crown ethers (DB18C6, B15C5, DB21C7, DB24C8 and DB30C10), a solution of crown ether in tetrachloroethane was used.[72] This procedure with variable amounts of the cross-linking agent, the crown ether and the solvent furnished SPES with different contents of the active component.

The synthesis of a group of sorbents based on an acrylamide derivative with insertion of a metal cation, which is then removed by desorption, has been reported.[74] The 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS) monomer was dissolved in methanol with continuous stirring, and DTBDCH18C6 and strontium nitrate were added to the reaction mixture (Scheme 10, the cyclohexane moieties in the intermediate and final products are omitted for the sake of simplicity). The solution was heated to 40 °C and stirred for 5 h for the formation of a strontium complex with the crown ether and AMPS. Then the cross-linking agent, [ethylene glycol dimethacrylate (EGDMA)] and the radical polymerization initiator (AIBN) were added. Polymerization was carried out without oxygen in order to prevent trapping of the radical and retardation of the process. The reaction ampoule was sealed and heated to 60 °C for 24 h. The resulting white polymer was dried to remove the remaining solvent, ground and washed several

Scheme 10



times with 3 M HNO_3 and then with 0.1 M NaH_2PO_4 for desorption of Sr^{2+} cations.

The preparation of polymer nanoparticles was reported.[75,76] For this purpose, 0.5 mmol of DB24C8 was added to an acetonitrile – DMSO mixture (2 : 1) used as the pore-forming system. Polymerization was carried out using methacrylic acid (30 mmol), EGDMA (600 mmol) and AIBN as the functional monomer, cross-linking agent and free radical initiator, respectively. Then the reaction vessel was plugged and stirred for 36 h with heating at 60 °C to complete the polymerization. After polymerization, the excess of the solvent was removed by centrifugation. The nanoparticles thus obtained were washed with ethanol and then with distilled water to neutral pH. Then they were dried in a vacuum at 70 °C. The procedure gave nanoparticles of 50 – 90 nm size.

A drawback of SPES is the loss of the extractant during sorption and desorption. Indeed, SPES based on DCH18C6 A, DTBDCH18C6, O18C6, DD18C6, B15C5, DCH21C7 and DCH24C8 lose up to 90% of the crown ether, SPES based on DB18C6, DTBDB18C6, DB21C7, DB24C8 and DB30C10 lose from 10% to 30% of the crown ether and, finally, the loss of DIODB18C6 and DIODCH18C6 does not exceed 5 mass % – 10 mass %. The loss of crown ethers can be sharply reduced by keeping the initial aqueous phase for 48 h in contact with the corresponding crown ether.[72] The loss of the extractant in SPES can be fully made up for by impregnating the sorbent with a fresh portion of crown ether; as a result, the initial properties of the SPES are completely restored.

According to the second approach to the synthesis of SPES, a solid polymer matrix is filled with a crown ether by different methods: in an excess of the extractant,[72,77,78] in a solution of the crown ether in chloroform or tetrachloroethane,[72,79–81] or in the presence of an aqueous phase.[72,77,78] The best procedure for impregnation of a ready polymer matrix with an extractant is impregnation in the presence of an aqueous phase (water, aqueous solution of starch).[72]

Yakshin *et al.*[72] added DIODB18C6 and water to a polymer matrix and stirred the mixture for 5 h at 80 °C. On cooling, the grains were filtered off, washed with water and dried in air. This gave a SPES with a DIODB18C6 content of 43%.

A facile and efficient method for the preparation of a crown-containing sorbent with an inert porous support (Amberlite XAD-7 or Amberchrom CG-71 ms resin) was described.[82–84] The prepared resin was stirred in methanol together with a 1 M octan-1-ol solution of DTBDCH18C6. After removal of methanol, a resin with a crown ether content of ~23% was obtained. The presence of hydrophobic *tert*-butyl substituents in a crown ether molecule ensures a good attachment of the macrocycle to the support surface on contact with aqueous solutions. This sorbent is marketed by the European company TrisKem Int. (before 2008, Eichrom Environment) under the trade name Sr Resin. This company has developed a series of sorbents for selective recovery of radionuclides, in particular, crown ether-based sorbents. Among these, there are the sorbents TK100 and TK101[85,86] on the basis of DTBDCH18C6 and di(2-ethylhexyl) phosphate, which are able to extract strontium radioisotopes together with ^{210}Pb.

El-Dessouky and Borai[87] pretreated the Amberlite XAD-7 resin with a mixture of ethanol, hydrochloric acid and water (2 : 1 : 1) in order to remove the preservative and the residual monomer and then washed to neutral pH and dried. The resin pretreated in this way was saturated with the impregnating solution during 4 h at room temperature. The impregnating solution was a 1 : 1 mixture of a 0.03 M solution of the Cyanex-310 extractant and a 0.04 M solution of crown ether [15-crown-5 (15C5), 18-crown-6 (18C6) or DB18C6] in chloroform.

The non-ionogenic sorbent Porolas-T manufactured by the enterprise 'Pitches' (Dneprodzerzhinsk), resulting from suspension polymerization of divinylbenzene in the presence of a pore-forming agent followed by conditioning for imparting hydrophilic properties to the surface, has been used as an inexpensive commercially available polymer matrix. The preliminarily washed and dried Porolas-T

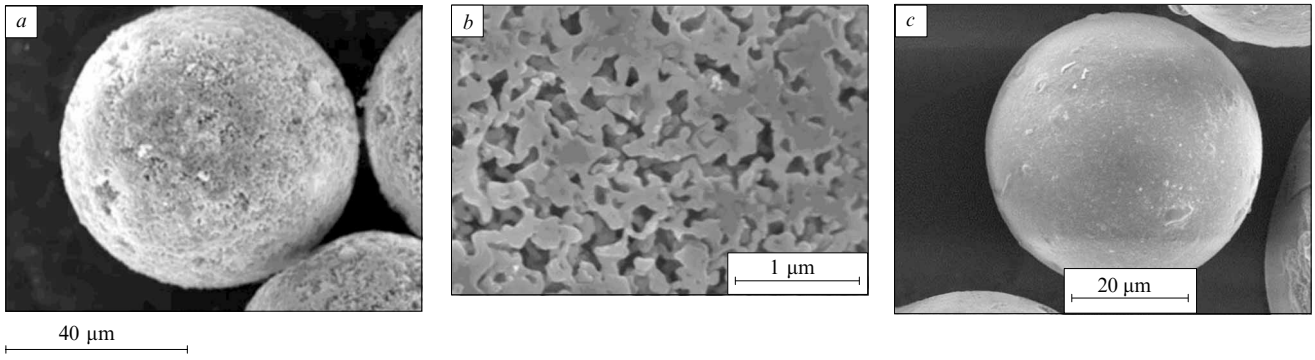


Figure 2. Sorbents (DTBDCH18C6 + M)/SiO_2-P: appearance of the grains (*a*) and inner structure (*b*) of the sorbent (DTBDCH18C6 + ooctanol)/SiO_2-P;[96] grains of (DTBDCH18C6 + dodecanol)/SiO_2-P (*c*).[98]

resin was impregnated with different amounts of DB18C6. This gave a new sorbent, Porolas-DB18C6-Sr,[88,89] with DB18C6 contents of 2.3%, 3.9%, 5.5% and 6.5%. It was found that the obtained sorbent was a SPES with liquid (a saturated solution of crown ether in chloroform) and crystalline inclusions of crown ether.

A method for the preparation of polyurethane impregnated with a crown ether has been reported.[90] Dried polyurethane foam cubes were mixed with an aqueous solution of crown ether with effective stirring for 20 min and, after that, the cubes were squeezed out and dried.

The preparation of a sorbent by impregnation of a support based on AMPS – EGDMA and AMPS – divinylbenzene copolymers was reported.[74] The polymeric support was mixed with methanol and a 1 M solution of DTBDCH18C6 in octan-1-ol and sonicated for 30 min. Then methanol was removed and the sorbent was dried.

The advantages of sorbents obtained by immobilization of crown ethers on a porous support without covalent binding (impregnation) include the accessibility of macrocyclic moieties located on the support surface to the contact with metal ions.[50]

Chuang and Lo[91] considered the preparation of a crown-containing sorbent by deposition of DCH18C6 or DB18C6 on silica gel. The pre-dried silica gel was treated with dimethyldichlorosilane to replace free hydroxy groups, washed with anhydrous methanol and dried at 105 °C. Then a solution of crown ether in chloroform was added, and chloroform was slowly removed from the suspension to give a dry sorbent that contained 3.8% crown ether and was rather stable against washing out of the crown ether.

Other methods of non-covalent attachment of a crown ether (DA18C6 or DB18C6) to the surface of silica gel have also been proposed.[92] The silica gel surface was modified with diaza-18-crown-6 ether *via* two stages: first, trimethylsilyl groups were grafted onto the silica gel surface using hexamethyldisilazane. After that, the resulting silica gel was heated with a chloroform solution of DA18C6. The noncovalent attachment of DB18C6 to the silica gel surface was accomplished by stirring dry silica gel with a solution of crown ether in chloroform for 5 h. Excess solvent was removed by filtration and the resulting gel was dried.

A new trend is related to the use of the SiO_2-P composite support, which consists of silica gel particles immobilized in the matrix formed by the formylstyrene – divinylbenzene copolymer,[93,94] for impregnation with various extractants, including crown ethers. A number of papers[66,95–98] describes a method for impregnating this support with DTBDCH18C6. Alcohols (butan-1-ol,[66,97] octan-1-ol[66,95–97] or dodecan-1-ol[66,97,98]) and tributyl phosphate[66,97] were used as modifying agents (M). In the first stage, SiO_2-P particles were treated with methanol and acetone to increase the affinity for DTBDCH18C6 and for modifying agent. Then the crown ether and the modifying agent were dissolved in dichloromethane, and SiO_2-P was added. The mixture thus formed was stirred at room temperature for 1 – 1.5 h, then the temperature was raised to 50 °C, and stirring was continued for 4 h; as a result, crown ether penetrated into the pores of the SiO_2-P particles and was physically attached to the pores. A series of sorbents generally described as (DTBDCH18C6 + M)/SiO_2-P were obtained (Fig. 2).

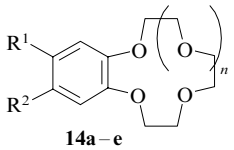
One more polymeric composite, calix[4]arene-R14 + M)/SiO_2-P,[66,97,99] was prepared on the basis of 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene; the modifying agents used included tributyl phosphate, octan-1-ol, butan-1-ol and dodecan-1-ol.

Crown-containing sorbents were also prepared by co-precipitation of 15C5 or 18C6 with phosphomolybdic[51] or phosphotungstic[51,100] heteropoly acid. Luk *et al.*[100] prepared a sorbent by co-precipitation of 15C5 and phosphotungstic acid ($H_3PW_{12}O_{40}\,24\,H_2O$) on mixing a 10^{-2} M solution of the crown ether in dichloromethane with a 10^{-2} M solution of phosphotungstic acid in 2 M nitric acid.

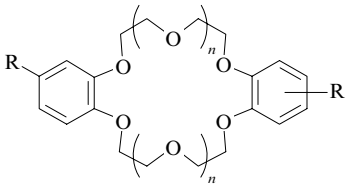
A sol – gel synthesis of sorbents has been proposed.[101] The crown ether B15C5 and ionic liquid ($[C_8mim]^+[PF_6]^-$, $[C_8mim]^+[BF_4]^-$ or $[C_8mim]^+[NTf_2]^-$, C_8mim is 3-methyl-1-n-octylimidazolium, Tf = CF_3SO_2) were added to a mixture of tetraethyl orthosilicate and 0.05 M formic acid. After washing and drying of solid products, the sorbents HF15SG, TF15SG and DF15SG were obtained containing 0.786 mass %, 0.900 mass % and 0.791 mass % B15C5, respectively.

Yalshin *et al.*[102] found for the first time that the introduction of one (benzocrown ethers) or two (dibenzocrown ethers) bromine or iodine atoms into the benzene rings of the macrocycle enhances the sorption capacity of the target bromides and iodides compared with the corresponding unsubstituted crown ethers. The sorbents were prepared by thorough ball milling of benzo- or dibenzocrown ethers as well as halo derivatives **14** and **15**. Compounds **15b**,**d**,**e** were obtained as mixtures of *cis*- and *trans*-isomers.

Structures 14, 15



14a–e



15a–e

Compound **14**	R^1	R^2	*n*	Compound **15**	R	*n*
a	Br	H	1	**a**	H	1
b	H	H	2	**b**	Br	1
c	Br	H	2	**c**	H	2
d	Br	Br	2	**d**	Br	2
e	Br	H	3	**e**	I	2

III. Application of sorbents impregnated with crown ethers for extraction of strontium

This Section summarizes the data on application of sorbents, the preparation of which is discussed in Section II, for the extraction of strontium from radioactive solutions, separation of radionuclides and determination of strontium in environmental samples. The quantitative characteristics of the sorbent extraction (the partition ratios and recoveries) and parameters of the starting solutions and sorption systems are summarized in Table 1 in Section III.1.

III.1. Strontium extraction from spent nuclear fuel and radioactive wastes

Shapovalov *et al.*[103] reported sorption of ^{90}Sr from SNF with 3% depletion and storage for 1 year using the Sr Resin sorbent selective for strontium comprising DTBDCH18C6 immobilized on a polyacrylate matrix. The flow diagram of the process is shown in Fig. 3.

The nuclear fuel elements were cut into parts, the fuel was dissolved in 8 M HNO_3 and, after that, the concentration of the acid in the resulting solution was brought to 3–4 mol litre^{-1}. This solution contained 100–150 g litre^{-1} of uranium and fission products, including 5–10 Ci litre^{-1} of ^{90}Sr.

The solution (350–400 ml) prepared for the extraction procedure was supplied to the first column (30 ml) packed with Sr Resin. In this column, ^{90}Sr was purified from the major amount of active and inactive impurities. The flow rate of the solution was 50–60 ml h^{-1}. The column was washed with a 3.0–3.5 M HNO_3 solution (150 ml) at a flow rate of 120–150 ml h^{-1}. Strontium was desorbed with distilled water (200 ml) supplied at a flow rate of 175–200 ml h^{-1}.

The major part of uranium and fission products remained in the mother solution but after elution form the first column, the solution of ^{90}Sr still contained some impurity radionuclides; therefore, the authors suggested additional purification on a second column.

Prior to the supply onto the second column, the solution desorbed from the first column was concentrated to dryness, and the dry residue was dissolved in 200 ml of 3.0–3.5 M HNO_3; after that, the solution to be purified was passed at a 100–120 ml h^{-1} flow rate through the second Sr Resin column (30 ml). Washing and desorption were the same as in the first column.

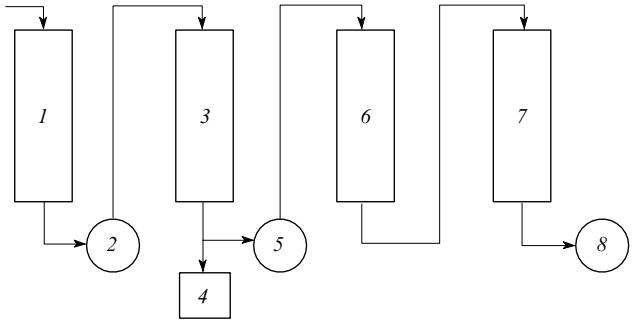


Figure 3. Flow diagram of strontium sorption from spent nuclear fuel.[103]
(*1*) Dissolution of nuclear fuel elements, (*2*) adjustment of the solution acidity, (*3*) primary ^{90}Sr recovery in a column packed with Sr Resin, (*4*) tail solution storage vessel, (*5*) adjustment of the solution volume and acidity, (*6*) secondary recovery of ^{90}Sr in a column packed with Sr Resin, (*7*) purification of the ^{90}Sr solution in a Dowex 50W × 8 column to remove traces of organic compounds, (*8*) adjustment of the solution volume and acidity.

After the second column, the desorbed solution was fed at a 180–200 ml h^{-1} flow rate to a 20 ml column with the Dowex 50W × 8 cation exchanger to remove traces of the crown ether. The cation exchanger was washed with 0.2 M HNO_3 or HCl (200 ml); the flow rate of the wash solution was 150–170 ml h^{-1}. Strontium was desorbed with 4 M HNO_3 or HCl (200 ml) at a flow rate of 150–170 ml h^{-1}.

The last stage was conditioning of the ^{90}Sr solution to adjust the acidity and the volume activity. For this purpose, the desorbed solution was concentrated to dryness, and the dry residue was dissolved in a required volume of HNO_3 or HCl with the specified concentration.

The procedure gave high-purity ^{90}Sr, which was suitable as the raw material for isolation of the daughter fission product — ^{90}Y.

The recovery of strontium from hydrochloric acid solutions was investigated.[69] Sorption was carried out by DB18C6 and DCH18C6 endoreceptors impregnated into a naphthalene matrix. Each experiment made use of 10 ml of the initial solution and 0.1 g of SPESL under static conditions at room temperature, the phase contact time being 48 h. The metal content was determined by inductively coupled plasma atomic emission spectroscopy. The sorption capacity of the obtained SPESL was estimated from the percentages of metals recovered from 0.5–9 M hydrochloric acid solutions containing 1×10^{-3}% of each of the following metals: Al, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Mg, Mn, Na, Ni, Pb, Sb, Sn, Sr, Ti, Zn and Zr. Data on the partition ratios of strontium are summarized in Table 1.

Yakshin *et al.*[73] extracted strontium by means of SPES based on DCH18C6 impregnated into a styrene–divinylbenzene matrix. The initial aqueous solutions contained 10 mg litre^{-1} of each of 25 elements: Al, B, Ba, Bi, Cd, Co, Cr, Cu, Ga, Ge, B, K, La, Li, Mn, Mo, Na, Ni, Pb, Re, Se, Sr, Tl, V and Y and 0.1, 1, 3, 5 or 7 M nitric acid. The sorption was carried out by stirring 0.5 g of the sorbent with 5 ml of the initial solution for 48 h at a temperature of (20 ± 1) °C. As follows from experimental data, an increase in the nitric acid concentration from 0.1 to 7 M causes variation of the partition ratio of strontium, the maximum

Table 1. Crown ether-based sorbent extraction of strontium.

Crown ether	Matrix	Solvent	Crown ether concentration in the sorbent (%)	Medium	Acid concentration /mol litre^{-1}	K_p /ml g^{-1}	R (%)	Ref.
DB18C6	Naphthalene	–	1	HCl	0.5	–	16	69
					9	–	16	69
DCH18C6			10		7	–	23	69
					9	–	23	69
DCH18C6	Styrene–divinylbenzene copolymer	0.75% aqueous solution of starch	1	HNO_3	0.1	2.0	–	73
					1	3.1	–	73
					3	4.6	–	73
					5	3.3	–	73
					7	4.8	–	73
			5	HNO_3	0.1	8.8	–	73
					1	19.5	–	73
					3	31.2	–	73
					5	25.0	–	73
					7	25.3	–	73
			10	HNO_3	0.1	12.4	–	73
					1	34.3	–	73
					3	56.3	–	73
					5	45.0	–	73
					7	34.9	–	73
			20	HNO_3	0.1	14.3	–	73
					1	40.2	–	73
					3	58.0	–	73
					5	45.8	–	73
					7	32.2	–	73
DTBDCH18C6	Amberlite XAD-7 or Amberchrom CG-71 ms	Octan-1-ol	23	HNO_3	0.02	0.43	–	84
					0.05	1.5	–	84
					0.1	3.1	–	84
					0.25	14.6	–	84
					0.5	25.3	–	84
					1	64.7	–	84
					2	135	–	84
					3	145	–	84
					4.1	161	–	84
					5.1	178	–	84
					6.2	188	–	84
					7.3	190	–	84
DTBDCH18C6	Amberlite XAD-7 or Amberchrom CG-71 ms	Octan-1-ol	10	HNO_3	0.1	6	–	104
					0.5	32	–	104
					1	50	–	104
					2	72	–	104
					3	85	–	104
					4	88	–	104
					5	90	–	104
					6	87	–	104
			20	HNO_3	0.1	10	–	104
					0.5	55	–	104
					1	84	–	104
					2	140	–	104
					3	170	–	104
					4	180	–	104
					5	190	–	104
					6	200	–	104
			40	HNO_3	0.1	6	–	104
					0.5	35	–	104
					1	75	–	104
					2	140	–	104

Table 1 (continued).

Crown ether	Matrix	Solvent	Crown ether concentration in the sorbent (%)	Medium	Acid concentration /mol litre^{-1}	K_p /ml g^{-1}	R (%)	Ref.
DTBDCH18C6	Amberlite XAD-7 or Amberchrom CG-71 ms	Octan-1-ol	40	HNO_3	3	170	–	104
					4	200	–	104
					5	240	–	104
					6	270	–	104
DCH18C6	Silica gel	Chloroform	3.8	$C_6H_2(NO_2)_3OH$	10^{-2}	–	98.6	91
DB18C6						–	35.7	91
DTBDCH18C6	SiO_2-P	Dodecan-1-ol		HNO_3	0.5	90	–	98
					1	300	–	98
					2	330	–	98
					3	80	–	98
					4	100	–	98
DB24C8	–	–	100	HCl	1	0.34	–	102, 105
					3	0.44	–	102, 105
					5	0.44	–	102, 105
Dibromo-DB24C8	–	–	100	HNO_3	1	0.16	–	102, 105
					3	0.26	–	102, 105
				HCl	5	0.25	–	102, 105
Diiodo-DB24C8	–	–	100	HCl	3	0.56	–	102, 105
					5	1.3	–	102, 105
DB18C6	Porolas-T	Chloroform	2.3	HNO_3	0.1	8.50	–	106
					1	15.86	–	106
					3	68.79	–	106
					5	111.52	–	106
					7	139.33	–	106
			3.9	HNO_3	0.1	1.33	–	106
					1	28.20	–	106
					3	94.54	–	106
					5	143.32	–	106
					7	174.46	–	106
			5.5	HNO_3	0.1	34.92	–	106
					1	52.87	–	106
					3	135.47	–	106
					5	192.91	–	106
					7	236.67	–	106

Note. K_p is the partition ratio (the solution volume, ml, of the recovered metal in 1 g of the sorbent), R is the recovery (%).

being observed at 3 M HNO_3. The effect of the crown ether content in the polymer matrix (1%, 5%, 10% or 20%) was studied. The highest partition ratio of strontium was achieved by using the polymer matrix with a 20% content of the crown ether (see Table 1).

Chiarizia *et al.*[84] investigated the sorption of strontium from nitric acid solutions of different concentrations with the Sr Resin sorbent. The highest partition ratio was observed for the extraction of strontium from 7.3 M nitric acid solutions. The process parameters and the data on strontium recovery are given in Table 1.

Dietz *et al.*[104] investigated the sorption of strontium with the Sr Resin sorbent containing 10%, 20% or 40% DTBDCH18C6 from solutions containing various concentrations of nitric acid (0.1 – 6 M). It was found that strontium is extracted most efficiently from 6 M nitric acid solutions when the crown ether concentration in the sorbent is 40%. In this paper, sorption kinetics was also measured and the selectivity of strontium sorption with Sr Resin was demonstrated (see Table 1).

The recovery of strontium by extraction chromatography was considered.[97] The solutions used modelled the HLW formed upon processing of SNF. The initial solution with an HNO_3 concentration of 2 mol litre^{-1} containing 5×10^{-3} mol litre^{-1} of Rh^{3+}, Zr^{4+}, Na^+, K^+, Cs^+, Sr^{2+}, Ba^{2+}, Ru^{3+}, Mo^{6+} and Pd^{2+} or 5×10^{-3} mol litre^{-1} of La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Y^{3+}, Sr^{2+} and Lu^{3+} was passed through a column with the (DTBDCH18C6 + M)/SiO_2-P polymer composite. The residual amount of accompanying ions was eluted with 2 M HNO_3 and strontium was eluted with water. It was shown that strontium can be separated from all impurity

ions except for barium; separation from barium requires additional operations.

Sorption of strontium (1 mmol litre^{-1}) from the aqueous phase (5 ml) with different concentrations of nitric acid (0.5, 1, 2, 3 or 4 M) with the (DTBDCH18C6 + dodecan-1-ol)/SiO_2-P sorbent (0.1 g) at different temperatures was described.[98] The strontium concentration before and after sorption was determined on an inductively coupled plasma atomic emission spectrometer. The highest partition ratio of strontium was found for 2 M nitric acid (see Table 1).

The sorbents obtained by ball milling of halo derivatives of benzo- and dibenzocrown ethers[102,105] showed low uptake of strontium (see Table 1).

The applicability of the Porolas-DB18C6-Sr sorbent[88,89] for the selective sorption of strontium from nitric acid solutions was tested. The sorbents (0.1 g portions) with DB18C6 contents of 2.3%, 3.9% and 5.5% were added to 10 ml portions of the test solution of strontium with a concentration of 8 mg litre^{-1} and a nitric acid concentration 0.1, 1, 3, 5 or 7 mol litre^{-1}. The systems thus obtained were kept for 48 h with stirring at intervals (the time needed to reach the equilibrium was found in preliminary experiments). After that, each solution was filtered and measured on an atomic absorption spectrophotometer using air–acetylene flame. It was found that an increase in the acid concentration in the solution or an increase in the crown ether content in the sorbent induce increase in the partition ratio of strontium (see Table 1).[106] The sorbent proved to be selective to strontium;[107] the sorption isotherm[108] and the sorption kinetic curves[109] were constructed; and sorption of strontium from contaminated solutions was analyzed.[110] The obtained results were validated by using radioactive ^{90}Sr and the Porolas-DB18C6-Sr sorbent.[111]

III.2. Determination of strontium in water, soil and biological materials

The sorption of strontium with materials impregnated with crown ethers can be accomplished not only from SNF or RW but also from environmental (water, soil) and biological materials. It is significant to determine the concentration of strontium in various natural samples that can get into the human or animal body. In this case, analysis is complicated by the presence of large excess of interfering ions such as Na^+, K^+, Mg^{2+}, Ca^{2+} and so on.[19]

The sorbents proposed by Hrdina *et al.*,[74] the preparation of which is described in Section II, were used to extract ^{90}Sr from urine. It was found that increase in the pH of the sample from 7.5 to 9 results in increase in the ^{90}Sr recovery from 47.9% to 94.8%; under these conditions, almost 90% of ^{90}Y is separated as the hydroxide.

A method for determination of the content of radioactive strontium in water, soil and agricultural products by extraction chromatography using a sorbent impregnated with DCH18C6 (10%) has been reported.[80] The sample was dried and then annealed at 500–600 °C, the resulting ash was dissolved in HNO_3 or HCl, and the solution was passed through a sorption column to withdraw strontium. After isolation of strontium, its β-activity was measured. The chemical yield was >95% and the purity was >98%.

Burak *et al.*[81] considered two alternative procedures for ^{90}Sr determination using SPES based on DCH18C6. The first procedure was meant for determination of ^{90}Sr in soil, water and milk. The incinerated samples were leached two times with 7.5 M nitric acid, filtered and concentrated to obtain wet salts. Then the nitric acid concentration was corrected to 1.5 M, the solutions were passed through a column with the sorbent, strontium was desorbed from the column and the β-activity of the obtained strontium carbonate precipitate was measured. The second procedure was meant for determination of ^{90}Sr in plant agricultural products. In this case, 'wet' incineration was used for sample preparation: the crushed plant sample was boiled with nitric acid in the presence of perchloric acid for 1–5 h. The resulting solution was passed through a column with the sorbent and then the β-activity was measured. The strontium recovery was ~90%–95%.

The TrisKem Int. company proposed determination of ^{90}Sr in aqueous samples without changing their acidity, which markedly simplifies analysis of environmental objects. One-litre samples were passed through columns with the TK 100 sorbent[85,86] at a flow rate of 5 ml min^{-1}. Potassium and calcium passed through the sorbent without being retained. The breakthrough of strontium started after 600 ml of the initial solution had been passed; thus, it was found that under these conditions, the maximum sample volume for a standard column with 2 ml of the sorbent was 500 ml. Yttrium, lead and uranium were retained in the sorbent even after 1 litre of the initial solution had been passed. Yttrium was removed quantitatively on treatment with 8 M HNO_3. Strontium was eluted with 2 M HCl, and lead and uranium were washed out with 6 M HCl. Lead and uranium can be separated by using the TK 101 resin,[85,86] which readily separates lead from other elements. The studies showed that strontium is recovered from a sample of water in high yield (83.9%–97.7%).

A method for determination of strontium in soil, grass, milk and animal bones by means of the Sr Resin sorbent was proposed.[112] For this purpose, 3 g of Sr Resin was washed for 1–2 h in distilled water and then packed into a glass chromatographic column. Through the column, 100 ml of distilled water and 100 ml of 3 M HNO_3 were passed. The test sample was dissolved in 3 M HNO_3 and passed through the column with the sorbent. Strontium was selectively sorbed, while other ions were eluted in the filtrate. The Sr Resin sorbent can be used many times after washing.

III.3. Separation of strontium and yttrium isotopes

A method for the separation of ^{90}Sr and ^{90}Y by extraction chromatography has been developed.[91] Sorbents based on DCH18C6 and DB18C6 supported on silica gel and 10^{-2} M solutions of picric acid were used. The radiation stability of the prepared sorbent containing 3.8% crown ether was estimated by comparing the uptake of strontium cations by irradiated and non-irradiated samples. In the range of absorbed doses of 0–1.0 MGy, the sorption capacity remained almost invariable, which was indicative of the radiation stability of the sorbent. Yttrium was obtained in 80% yield with >98% purity; the results on the recovery of strontium are given in Table 1.

It was proposed[113] to separate ^{89}Sr and ^{89}Y by means of the strontium-selective Sr Resin sorbent. The yttrium oxide target was irradiated with neutrons to perform the reaction ^{89}Y(n, p)^{89}Sr. Then ^{89}Sr was isolated according to the flow diagram shown in Fig. 4.

The irradiated yttrium oxide grains were dissolved in 4–6 M HNO_3, the volume of the solution was brought to 1–1.5 litres and the concentration of HNO_3 was brought to 3–4 mol litre^{-1}. The solution thus formed was fed to the first 100-ml column packed with Sr Resin. In this column,

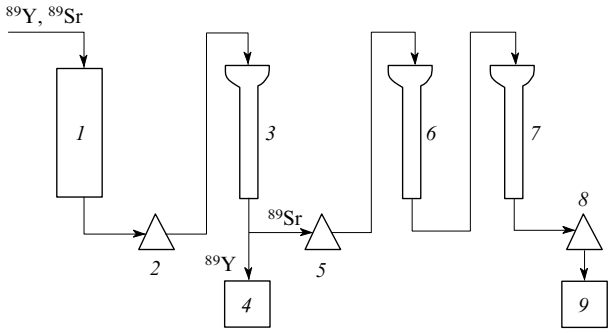


Figure 4. Flow diagram of separation of ^{89}Sr and ^{89}Y.[113] (*1*) dissolution of yttrium oxide grains, (*2*) adjustment of the solution volume and acidity, (*3*) primary purification of ^{89}Sr in a column packed with Sr Resin, (*4*) storage vessel for the solution of ^{89}Y, (*5*) adjustment of the solution volume and acidity, (*6*) secondary purification of ^{89}Sr in the second column packed with Sr Resin, (*7*) purification of the ^{89}Sr solution in the column with the Dowex 50W × 8 cation exchanger to remove traces of organic compounds, (*8*) adjustment of the solution volume and acidity, (*9*) storage vessel for the ^{89}Sr solution.

^{89}Sr was purified from the major amount of ^{89}Y and from active and inactive impurities. The flow rate of the initial solution was 75 – 100 ml h^{-1}. The column was washed with 600 ml of 3 – 4 M HNO_3 supplied at a flow rate of 100 – 120 ml h^{-1}. Desorption of ^{89}Sr was accomplished by distilled water (600 ml) supplied at a flow rate of 100 – 120 ml h^{-1}. Before being supplied to the second column, the desorbed solution from the first column was concentrated to dryness, and the dry residue was dissolved in 50 ml of 3 – 4 M HNO_3. After that, the sample solution was passed through the second 6-ml column packed with Sr Resin at a 20 – 30 ml h^{-1} flow rate in order to remove the residual amounts of radionuclides and non-radioactive impurities. The column was washed with 3 – 4 M HNO_3 (60 ml) at a flow rate of 20 – 30 ml h^{-1}. Desorption of ^{89}Sr was accomplished by distilled water (40 ml) at a flow rate of 20 – 30 ml h^{-1}. After the second column, the desorbed solution was supplied to a 5-ml column with the Dowex 50W × 8 cation exchanger to remove traces of the crown ether. The cation exchanger was washed with 80 ml of 0.2 M HNO_3 or HCl, the wash solution was supplied at a flow rate of 30 – 40 ml h^{-1}. Desorption of ^{89}Sr was carried out by 4 M HNO_3 or HCl (50 ml) supplied at a flow rate of 30 – 40 ml h^{-1}. Then the desorbed solution was concentrated to dryness, and the dry residue was dissolved in an appropriate amount of HNO_3 or HCl of the specified concentration to adjust the acidity and the volume activity of the ^{89}Sr solution.

Fukuda *et al.*[114] studied the isotope effects of strontium in the chromatography using the natural isotope mixture. Silica gel impregnated with B15C5 crown ether and the strontium-specific Sr Resin sorbent based on DTBDCH18C6 were used as chromatographic materials. In experiments with the B15C5-based sorbent, five columns filled with the resin were connected in series. The resin was first washed with a solution of HCl with the same concentration as in the initial solution of strontium in order to maintain a constant HCl concentration throughout the chromatographic system. The initial HCl solution containing $SrCl_2$ was continuously pumped into the upper part of the first column at a constant flow rate using a high-pressure pump. The solution coming out of the lower part of the fifth column was collected and analyzed for the content of strontium and strontium isotopes. Similar experiments were carried out with the DCH18C6-based resin using two columns. The isotope effect was found to be $\sim 10^{-4}$.

IV. Conclusion

The presented published data provide the conclusion that immobilization without covalent bonding is the most facile, effective and cheap method for the preparation of sorbents for the sorption of strontium. These sorbents demonstrate better extraction characteristics at a lower crown ether content than sorbents obtained by copolymerization of the matrix monomers in the presence of crown ether.

The chemical immobilization methods developed to date are based, most often, on alkylation reactions. Many of the proposed methods are too complex, consist of numerous stages and require long time; therefore, they need to be improved. Exception is provided by radiation chemical methods, which enable selective one-step generation of active sites in the polyether ring and addition of the active sites to reactive groups of the monomer; however, these methods are too expensive.

The performed analysis indicates that sorbents based on the DCH18C6 endoreceptors are more effective for selective sorption of strontium; however, this crown ether has a considerable drawback, namely, high water solubility, which leads to leaching of the crown ether from the sorption system; therefore, its derivatives with alkyl groups (in particular, *tert*-butyl groups) in the cyclohexane moieties have found wider application.

Nitric acid solutions are most convenient for sorption and extraction of strontium. For most of the studied sorbents, the optimal concentration of nitric acid is 3 to 7 mol $litre^{-1}$. However, mention should also be made of silica gel-based sorbents with picric acid as the salting-out agent, which provide high strontium recoveries.

The information stated above leads to the conclusion that recovery of strontium from nitric acid solutions of SNF is a promising application for crown ether-based sorbents in chemical engineering, because these solutions have a high content of nitric acid (5 – 6 M) after dissolution of the fuel. The application of such sorbents for the processing of most types of LRW is problematic as it requires the addition of concentrated nitric acid to the initial solution, which considerably increases the volumes of LRW and is inexpedient for industrial use.

Yet another area in which sorbents of this type have already found use is radiochemical analysis. This is caused by the possibility of dissolving solid samples and dry residues obtained upon evaporation of liquid samples in nitric acid followed by sorbent extraction of strontium.

As the principal problem related to the study of the sorbent extraction of strontium and other metals is the lack of integrated approach, namely, there are often no data on the effect of the solution composition, concentration of the salting-out agents, sorption kinetics or isotherm, conditions of metal desorption and sorbent selectivity. The inadequate amount of the data hampers evaluation of the applicability of materials for large-scale laboratory testing.

In view of the specific nature of crown ethers as the base of sorption materials, a topical task is the development of a strategy for the search for particular conditions, including the selection of the macrocycle, for selective sorption of desired metals. Since the isotope effect for ^{90}Sr and the

natural isotope mixture is low, performing the greater part of experiments on the natural isotope abundances with subsequent validation of the results on radioactive samples can be regarded as a good strategy.

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