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# Sorption methods in marine radiochemistry

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The review presents the general methodology of using sorption methods to solve problems of marine radiochemistry, including sampling, preconcentration and radiochemical preparation and methods for measuring the activity of radionuclides. The possible methodological errors at various stages of sampling and sample concentration are discussed. The most widely used artificial ($^{90}$Sr, $^{134}$Cs, $^{137}$Cs, $^{239}$Pu, $^{240}$Pu), natural ($^{210}$Pb, $^{210}$Po; radium quartet: $^{223}$Ra, $^{224}$Ra, $^{226}$Ra, $^{228}$Ra; thorium isotopes, mainly $^{234}$Th) and cosmogenic ($^{7}$Be, $^{32}$P, $^{33}$P) radiotracers are considered. The sorption of uranium from seawater is not addressed, since its concentration in seawater is usually calculated from the known dependence of uranium concentration on seawater salinity.
The bibliography includes 200 references.

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## 1. Introduction

Seawater is a complex chemical system characterized by a high content of salts (up to 36%), the presence of particulate matter and variability of characteristics, which depend on the place, time and depth of sampling. All these features, in combination with low concentrations of most radionuclides, make seawater a highly sophisticated object of radiochemistry; the sample volumes for determining the contents of some radionuclides can reach a few cubic metres. Marine radiochemistry is the field of science that studies the radioactivity of seawater to solve problems of oceanography and radioecology. Oceanographic processes are often studied using radiotracer techniques. Currently, sorption is used most often to concentrate radionuclides from water. The benefits of sorption methods include the possibility of obtaining large data arrays, which is important in marine expeditions, and using mathematical modelling methods to solve problems of oceanography.

The third decade of the 21st century was proclaimed a Decade of Ocean Science by the United Nations.[1] The discovery of radioactivity in the 19th century and its wide use for both military and civil purposes resulted in contamination of the Global Ocean by artificial radionuclides.[2] This was caused, to a large extent, by the global precipitation of radionuclides as a result of nuclear weapon testing and by disposal of radioactive waste in seas and oceans.[3] The Chernobyl power plant disaster (1986, Ukraine) resulted in considerable contamination of the Barents, Black, Azov and Mediterranean seas;[4] the recent accident at the Fukushima-1 nuclear power plant (2011, Japan) made a contribution to the contamination of the Pacific Ocean;[5] the operation of the plant producing weapons-grade plutonium (Sellafield, UK) resulted in contamination of the Irish Sea and in the transport of radioactive pollutants by sea currents to the Arctic Ocean.[6] Furthermore, there are numerous local sources of contamination in the Arctic:

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unsafe repository of spent nuclear fuel in the Andreev Bay,[7] sites of underwater nuclear testing[8] and radioactive waste disposal at Novaya Zemlya.[9] The melting of glaciers also releases radioactive elements into the ocean.[10] This brings about the need to check the contamination level of the Global Ocean.

Most methods used to concentrate radionuclides from seawater are based on sorption processes, which allow selective recovery of one or several elements and are highly productive, which is necessary for processing large numbers of samples in marine expeditions.[11]

The first publications on sorption of radionuclides from seawater date back to the 1960s. A number of scientists proposed $^{7}$Be as a tracer for studying the vertical mixing in the ocean surface layer.[12] Considering the variability of $^{234}$Th concentration and disruption of its equilibrium with $^{238}$U, it was suggested that $^{234}$Th is adsorbed on the particulate matter.[13]

The discovery of spatial variability of radionuclide concentrations in seawater initiated studies of the processes and parameters of the marine environment that account for this variability. The applicability of radionuclides was investigated in a number of international projects under the auspices of the IAEA such as WOMARS (Worldwide Marine Radioactivity Studies),[14] projects on the use of nuclear and isotope techniques to study submarine groundwater discharge in coastal zones[15] and modelling of the evolution of radioactive contamination,[16] which were implemented by SCOR (Scientific Committee on Ocean Research) working groups: group 146 Radioactivity in the Ocean, (5 decades later RiO5), group 116 SCOR WG 116 on Sediment Trap and $^{234}$Th Methods for Carbon Export Flux Determination, group 20 Radiocarbon Estimation of Primary Production and group 1 Radioactivity in the Ocean.[17] Among other results, group RiO5 created a public catalogue of the procedures used to analyze radionuclides in seawater[18] and developed a course of lectures on the fundamentals of marine radiochemistry.[19 – 21] One more international project, GEOTRACES,[22] presents data on the distribution of heavy metals and radionuclides in the ocean collected in numerous marine expeditions.

The application of radionuclides for studying the processes in the ocean is considered in monographs;[23, 24] however, the monographs do not address the methods used to concentrate the elements. The recovery from seawater is briefly described in radiochemistry textbooks.[25, 26] Among Russian textbooks, note a study guide[27] which gives numerous useful data and recommendations for measuring the concentrations of radionuclides in environmental objects, including seawater.

In Russia, many scientific and educational organizations carried out systematic research in the marine radiochemistry. The results of studies at the Murmansk Marine Biological Institute under the supervision of Academician G.G.Matishov are summarized in a book;[28] studies of the Institute of Biology of the Southern Seas on the influence of the Chernobyl accident are described in several monographs[29 – 31] and the works by the Marine Hydrophysical Institute are reflected in a book by Batrakov.[32] Large-scale research was carried out at the M.V.Lomonosov Moscow State University[33] and at the V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry.[34, 35]

The purpose of this review is to analyze and summarize the available data on the application of sorption processes for the concentration of the most important artificial, natural and cosmogenic radionuclides. The benefits and drawbacks of the materials applied to recover a particular radionuclide are considered; the possible implementations of the sorption technique and the possible procedural errors during sampling and concentration of elements are described.

## 2. Characteristics of the most important radionuclides and processes they undergo; behaviour of radionuclides in seawater

The most important artificial radionuclides that are extensively studied in the marine environment include $^{90}$Sr, $^{134}$Cs, $^{137}$Cs and also $^{238}$Pu, $^{239}$Pu, $^{240}$Pu. The presence of $^{134}$Cs in seawater attests to a fresh source of radioactive contamination, since this isotope has a short half-life. For determining the accumulation factors of these radionuclides in aquatic organisms, it is necessary to know the content of radionuclides in seawater. The $^{137}$Cs radionuclide, similar to potassium in the properties, is accumulated in the muscle tissue; $^{90}$Sr, which resembles calcium, is concentrated in the bone tissue and thus causes long-term irradiation of the body. Plutonium isotopes, most of which are α-emitters, are among the most hazardous radionuclides.[36] Apart from applications in radioecology, $^{137}$Cs is used to study the thermohaline circulation.[37] In the absence of a fresh source of the radionuclide, the distribution of $^{137}$Cs and $^{90}$Sr in the surface layer is uniform, and so is the distribution of the stable strontium isotopes (Fig. 1),[38, 39] since these radionuclides are barely adsorbed by the particulate matter. The main method for analysis of $^{137}$Cs is γ-spectrometry. In the region of the peak at 661.7 keV ($^{137m}$Ba), which is used to measure the activity of $^{137}$Cs, there are virtually no peaks of other radionuclides; therefore, this isotope can be detected rather easily. Currently, the limit of detection of $^{137}$Cs isotope is 0.1 mBq.[40] The $^{90}$Sr isotope is determined by β-spectrometry using the daughter $^{90}$Y radionuclide after preconcentration of the sample.[41, 42] The major isotopes of plutonium ($^{236}$Pu, $^{238}$Pu, $^{239}$Pu, $^{240}$Pu, $^{242}$Pu) are determined by α-spectrometry.[42]

The natural $^{210}$Pb and $^{210}$Po radionuclides are members of the $^{238}$U decay series. They are used to evaluate biogeochemical processes and particulate matter fluxes in the ocean.[43] Unlike another classical pair, $^{238}$U/$^{234}$Th,

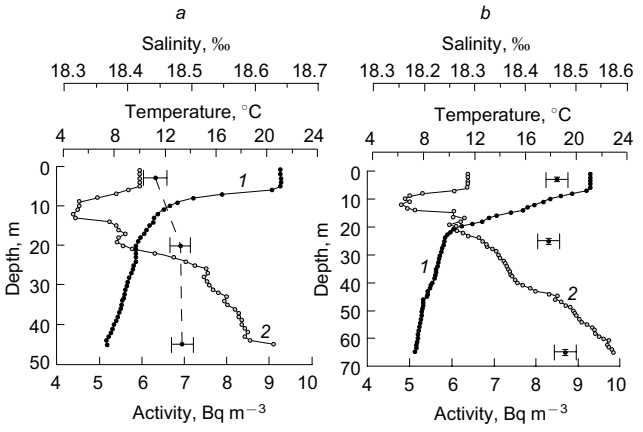



**Figure 1.** Distribution of $^{137}$Cs (*a*) and $^{90}$Sr (*b*) in the surface layer of the Black Sea.[38, 39] (*1*) temperature, (*2*) salinity.

which provides information about the flux of particulate organic carbon (POC) on a time scale of 2 – 3 weeks, study of the distribution of the $^{210}Pb/^{210}Po$ concentration provides information on the seasonal characteristics of the flux (time scale of 2 – 3 months).[44] The activity of $^{210}Po$ is determined by α-spectrometry, that of $^{210}Pb$ is measured by β-spectrometry on the basis of $^{210}Bi$ daughter isotope [43] and by γ-spectrometry.[45] The samples concentrated from seawater by co-precipitation are analyzed, most often, by β-spectrometry. To solve geochronology problems, in the case of direct sorption preconcentration and analysis of bottom sediment samples by means of $^{210}Pb$ isotope, γ-spectrometry at the 46.3 keV line is used. The $^{238}U/^{234}Th$ pair is employed more widely to study the POC fluxes, which is caused by several factors. First, high concentration of these radionuclides in seawater provides easy determination (currently, $^{234}Th$ is analyzed using 2 – 8-litre samples).[46] Second, in most studies, the $^{238}U$ concentration is not determined experimentally, but is calculated from the water salinity.[47] The activity of $^{234}Th$ is measured, most often, by β-radiometry; in addition, $^{234}Th$ is the predominant short-lived β-radionuclide. To determine the residual activity of the concomitant long-lived radionuclides, the sample is measured once again after six months. The modern low-background alpha-beta-radiometers such as Riso GM 25 – 5 or LB 770 can be used to analyze 5 – 10 samples simultaneously.[48] It is also possible to use γ-spectrometry.[49] The data on the contents of $^{234}Th$ and its relationship with POC collected in the studies all over the world are summarized in a database.[50]

The radium isotopes $^{223}Ra$, $^{224}Ra$, $^{226}Ra$ and $^{228}Ra$, which are often called radium quartet, are widely used to study the interaction between sea and underground water in coastal areas.[15] Increased concentrations of radium isotopes are observed at the sites of freshwater discharge: municipal water, river mouths and submarine groundwater discharges (Fig. 2).[51]

The long-lived $^{226}Ra$ isotope is quantified by γ-spectrometry by measuring the amount of accumulated daughter isotopes, $^{214}Pb$ or $^{214}Bi$. In this case, the counting sample should be sealed, as the accumulation proceeds *via* the formation of gaseous $^{222}Rn$.[52] The counting sample (the sorbent or the residue after the sorbent incineration) is

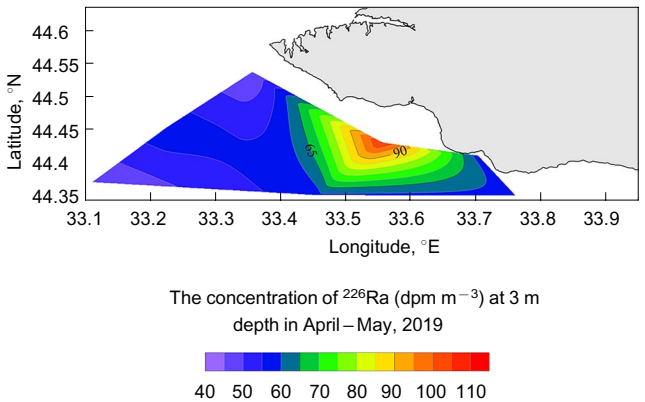



**Figure 2.** Distribution of $^{226}Ra$ in the Black Sea near the South Western coast of the Crimean peninsula. Published with permission from Akademiai Kiado Zrt.[51]

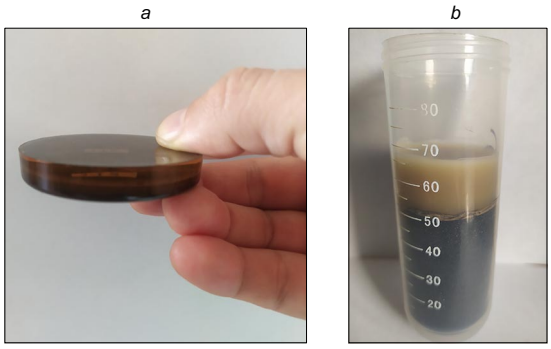



**Figure 3.** Counting samples embedded in epoxy resin (*a*) and wax (*b*) for measurement of $^{226}Ra$ isotopes. Reproduced from archive materials for the study by Dovhyi *et al.*[51]

sealed in different ways: embedded into epoxy resin or wax in Petri dishes if planar detectors are used (Fig. 3 *a*) [51] or in test tubes if a well type detector is used (Fig. 3 *b*),[51] pressed with sugar powder,[53] *etc*. It takes approximately three weeks for the equilibrium between $^{226}Ra$ and daughter isotopes to establish (five half-lives of $^{222}Rn$).

In addition, $^{226}Ra$ is determined by counting accumulated $^{222}Rn$ (Ref. 54) and also by α-spectrometry.[55] The long-lived $^{228}Ra$ isotope is determined by γ-spectrometry.[52] The short-lived $^{223}Ra$ and $^{224}Ra$ isotopes are determined using the RaDeCC system (radium delayed coincidence counter).[56] Data on the methods of analysis of radium isotopes in environmental objects are summarized in an IAEA report.[57]

The cosmogenic $^{7}Be$ isotope is widely used to study the vertical mixing in the ocean surface layer.[58] The application of phosphorus isotopes, $^{32}P$ and $^{33}P$, for this purpose was also considered;[59] however, this method has not gained popularity because of low activity in seawater and complex analysis. The results of numerous studies demonstrated that the vertical distribution of $^{7}Be$ generally reflects the temperature profile: the $^{7}Be$ concentration is constant in the mixed layer and decreases exponentially in the layers below the

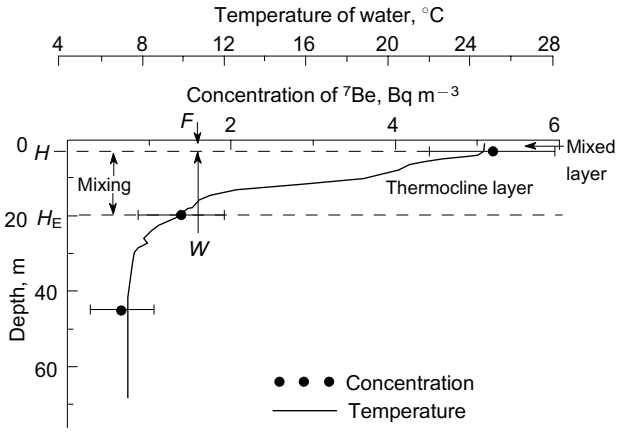



**Figure 4.** Vertical distribution of $^{7}Be$ isotope. $F$ is the $^{7}Be$ flux from atmosphere, $H$ is the depth of the mixed layer, $H_E$ is the depth of the euphotic zone, $W$ is the rate of upwelling. The figure was created by the authors using the data of Refs 60 and 61.

**Table 1**. Characteristics of the most important radionuclides (according to publications [40 – 43, 48, 52, 56, 62, 65 – 74]).

| Radionuclide | Half-life (years) [66] | The major form of existence in seawater | Main method of measurement | Use |
|---|---|---|---|---|
| $^{134}$Cs<br>$^{135}$Cs<br>$^{137}$Cs | 2.07<br>$2.3 \times 10^6$<br>30.2 | Mainly dissolved ($Cs^+$) [67] | γ-Spectrometry [40] | Radioecological monitoring, thermohaline circulation [a] |
| $^{90}$Sr | 29.0 | Mainly dissolved ($Sr^{2+}$) [67] | β-Spectrometry [41, 42] | Radioecological monitoring |
| $^{239}$Pu<br>$^{240}$Pu | $2.41 \times 10^4$<br>$6.56 \times 10^3$ | Mainly adsorbed on particulate matter ($PuO_2$), dissolved species ($PuO_2^+$) [68] | α-Spectrometry [42] | Radioecological monitoring |
| $^{210}$Pb | 22.2 | Distributed between seawater and particulate matter (more than 90% are chloride complexes; mainly $PbCl_2$, 60%) [69] | β-Spectrometry [43] | Determination of POC fluxes |
| $^{210}$Po | 138.4 days | Distributed between seawater and particulate matter (hydrolyzed $Po^{4+}$ species) [70] | α-Spectrometry [43] | Determination of POC fluxes |
| $^{223}$Ra<br>$^{224}$Ra | 11.4 days<br>3.66 days | Mainly dissolved ($Ra^{2+}$) [71] | RaDeCC [56] | Determination of groundwater flow to the ocean |
| $^{226}$Ra<br>$^{228}$Ra | 1600<br>5.75 | Mainly dissolved ($Ra^{2+}$) [71] | γ-Spectrometry [52] | Determination of groundwater flow to the ocean |
| $^{234}$Th | 24.1 days | Distributed between seawater and particulate matter (hydrolyzed $Th^{4+}$ species) [72] | β-Radiometry [48] | Determination of POC fluxes |
| $^{7}$Be | 53.3 days | Distributed between seawater and particulate matter (hydrolyzed $Be^{2+}$ species) [73] | γ-Spectrometry [62] | Determination of vertical transfer |
| $^{32}$P<br>$^{33}$P | 14.3 days<br>25.3 days | Distributed between seawater and plankton (organic and inorganic $PO_4^{3-}$ species) [74] | β-Spectrometry [65] | Determination of vertical transfer and biodynamics of phosphorus |

[a] Thermohaline circulation is the circulation caused by differential of water density arising in the ocean due to non-uniform distribution of salinity and temperature.

thermocline (Fig. 4).[60, 61] Like the $^{137}$Cs radionuclide, $^{7}$Be is analyzed rather easily by γ-spectrometry using an isolated peak at 477 keV energy.[62]

The major application of the short-lived $^{32}$P and $^{33}$P isotopes is to study the biodynamics of phosphorus in the ocean.[63] These isotopes have different half-lives: the half-life of $^{33}$P is longer than that of $^{32}$P; therefore the $^{33}$P : $^{32}$P ratio increases in the series wet atmospheric precipitation — seawater — particulate matter (including various species of microorganisms). According to the model proposed by Lal and Lee,[64] this ratio in the source and in the investigation object can be used to estimate the cycling time for various species of stable phosphorus:

$$t = \ln\left(\frac{R_p/R_s}{\lambda_{32} - \lambda_{33}}\right) \quad (1)$$

where $t$ is the cycling time (phosphorus age); $R_p$ are $R_s$ are the $^{33}$P : $^{32}$P activity ratios in the object and in the source; $\lambda_{32}$, $\lambda_{33}$ are the radioactive decay constants of $^{32}$P and $^{33}$P, respectively. The activity of samples containing $^{32}$P and $^{33}$P is measured by β-spectrometry.[65]

Table 1 shows the key characteristics of the considered radionuclides.[40 – 43, 48, 52, 56, 62, 65 – 74]

## 3. Features of sampling and sample concentration

Sampling is an important part of the procedure of analysis of radionuclides in seawater.† While planning the sampling procedure, one should bear in mind several points that would help to avoid mistakes. The distribution of some radionuclides between seawater and particulate matter necessitates the stage of filtration. Without filtration, methodological errors occur, since it is needed to determine the total concentration of the radionuclide in seawater, but not the content of only soluble part. In hydrochemistry, seawater filtration is performed, most often, using membrane filters with 0.45 μm pores. However, in marine radiochemistry, samples of large volume are very rarely filtered through membrane filters, because due to the presence of suspended particulate matter and highly dispersed colloids, these filters can process at best up to 10 litres (on average, 5 litres) of seawater at a very modest rate (the rate of filtration with the most commonly used filter 47 mm in diameter with 0.45 μm pores is 50 mL min$^{-1}$).[46] In the case

† In the Russian Federation, sampling is regulated by a guideline document,[75] however, this document does not adequately address the number of determined radionuclides and the materials and equipment needed for their concentration.

of slow filtration, the separated particulate matter serves as the adsorbent for the radionuclides dissolved in water, which distorts the distribution. The sample volume often ranges from tens to hundreds of litres, and in some cases, it reaches several cubic metres. Therefore, industrial filters for mechanical removal of the suspended material are used for sampling. They represent 5- or 10-inch high polypropylene cartridges with a pore size of 0.5, 1, 5, 10 or 25 μm (Ref. 76) and are able not only to collect most of the suspended particulate matter (when filters with the smallest pore size are used), but also to separate particulate matter into fractions. The filtration rate of samples through 10-inch high polypropylene cartridges is much higher (up to 20 L $min^{-1}$).

For collecting large samples, it is recommended to use stainless steel well pumpls (Fig. 5)[77] and vibratory pumps. To force samples through a sorbent, peristaltic pumps (capable of processing up to four samples simultaneously, Fig. 6)[38] and membrane pumps are employed.

One of the mistakes in the sampling procedure is a wrong choice of the rates of filtration and forcing water through the column. The upper limit of the filtration rate is determined by the characteristics of the polypropylene cartridges and amounts to 20 L $min^{-1}$ for cartridges of 10 inch height. Filtration at low rates with a parallel conduction of sorption is fraught with the risk of obtaining distorted data due to concentration of radionuclides from seawater on the prefilter. Highly dispersed suspended particles collected on a prefilter act as a sorbent for some radionuclides. The dependence of radionuclide sorption on the particulate matter collected on a filter on the filtration rate has not been studied, but the existence of this dependence is confirmed by our practical experience and by the known ability of many radionuclides to be actively adsorbed on suspensions (for example, the distribution constant of plutonium on a suspended matter can reach $10^6$ mL $g^{-1}$).[27] Therefore, samples are usually filtered at a rate that is maximum possible for the given equipment.




**Figure 5.** Photographs illustrating sampling (*a*) with a well pump and positions of sampling tanks (eight 1 $m^3$ tanks) (*b*) on the forecastle of the research vessel Professor Vodyanitskii (106th cruise, April 18 to May 13, 2019).[77]



**Figure 6.** Facility for parallel pumping of four samples through the sorbent by a peristaltic pump. Reproduced from archive materials for the study by Dovhyi *et al.*[38]

## 4. Implementation methods of sorption

Currently, there are two most popular concertation procedures that allow determination of the efficiency of radionuclide sorption from seawater: (i) the use of two adsorbers (Fig. 7);[38] (ii) and the use of one adsorber (Fig. 8)[77] with addition of natural or radioactive isotopes as tracers of sorption efficiency. Below we consider the benefits and drawbacks of these procedures.

When two adsorbers are used, the collection efficiency is determined from the formula[78]

$$E = 1 - \frac{B}{A} \qquad (2)$$

where $A$ and $B$ are the radionuclide activity on the sorbent in the first and second adsorbers, respectively.

Then the radionuclide activity in the probe

$$C = \frac{A}{E} \qquad (3)$$

In this method, additional tracers are not needed for determination of the collection efficiency. However, it has a number of drawbacks. First, the number of operations involved in sample preparation and counting to determine the concentration of one radionuclide doubles. Second, the



**Figure 7.** System of two adsorbers for the recovery of $^{137}Cs$ from seawater samples with the ferrocyanide silicate (FSS) sorbent using a two-column method (adsorber volume of 700 mL; volume of seawater samples of 2 – 8 $m^3$). Reproduced from archive materials for the study by Dovhyi *et al.*[38]



**Figure 8.** Photograph of adsorbers for the recovery of $^{32}P$ and $^{32}P$ from seawater samples with aluminium oxide by a single-column method (adsorber volume of 700 mL; volume of seawater samples of 2 – 3 $m^3$). Reproduced from archive materials for the study by Dovhyi *et al.*[77]

activity of the second adsorber is most often relatively low and, therefore, the error of determination increases.

One more problem associated with the use of two adsorbers is leaching of the active component from the sorbent. This process is often underestimated by researchers; however, it can significantly deteriorate the collection efficiency.

The use of a single adsorber for collection is possible in the following cases: when it is known for certain that the radionuclide is recovered quantitatively under the conditions used or when a tracer (stable or radioactive) is added to the sample. This procedure has a number of benefits. When a single adsorber is used, the radiochemical sample preparation and counting should be carried out for only one sample. The sorption efficiency is determined more accurately when a stable or radioactive tracer is used than by using the ratio of radionuclide activities in the first and second adsorbers. The concentration of stable elements in the initial and final samples can be determined rather easily and quickly by atomic absorption spectrophotometry, flame emission photometry for alkali (caesium) and alkaline earth (strontium) elements or inductively coupled plasma mass spectrometry. For this purpose, one sample is collected and the final concentration of the radionuclide in this sample is determined,[79,80] or samples are taken every time as a definite solution volume has been passed; this makes it possible to construct a sorption curve.[81] Of course, leaching of the active component does not play any role in this case.

The physical loss of the sorbent also introduces an error into the results of measurements, especially in the case of highly dispersed sorbents. As the particle size of the sorbent decreases, the sorption efficiency increases; however, the flow resistance and sample pumping time also increase. The known sorbents considerably differ in the particle size range, which is indicated in their specification; for example, the particle size of the Anfezh sorbent amounts to 0.01 – 2.5 mm. Pumping of large samples through the sorbent takes a lot of time; meanwhile, in marine expeditions, it is often necessary to collect and process a multitude of samples. Furthermore, due to compaction of the sorbent, the flow rate of the solution can significantly decrease. To prevent this, it is recommended to screen out the fine fraction.

The variants of sorption processes are considered below in relation to concentration methods of particular radionuclides. For artificial $^{137}$Cs and $^{90}$Sr, direct recovery from seawater has been studied in most detail. No studies of this type are available for other radionuclides for a number of reasons. For example, according to some procedures, prior to the sorption and purification, the radionuclide is co-precipitated with a collector, for example, iron(III) hydroxide or calcium phosphate. The precipitate is then washed, separated from the solution and dissolved in an acid for the subsequent selective concentration of the radionuclide. This scheme is used for analysis of $^{210}$Pb, $^{210}$Po, $^{239,240}$Pu and, in some procedures, $^{90}$Sr. In the case of short-lived radionuclides (for example, $^{7}$Be, $^{32}$P and $^{33}$P), the use of this method for gaining quantitative characteristics of sorption is difficult; therefore, these nuclides are recovered by a single-column method using stable isotopes or by a two-column method, with the sorption efficiency (the degree of radionuclide recovery from seawater) being used as the characteristics.

## 5. Sorption of artificial radionuclides

### 5.1. Sorption of $^{137}$Cs from seawater

During the last ~40 years, methods of sorption from seawater and concentration have been actively used to determine $^{137}$Cs. The use of selective sorbents allows for fast collection and concentration of $^{137}$Cs from large volumes of natural water, which markedly facilitates the analytical procedure in comparison with the co-precipitation procedure. The sorbents based on ammonium molybdophosphate[82] and transition metal hexacyanoferrates (TM-HCFs) are used most commonly.[82,83]

Transition metal hexacyanoferrate powders in a pure state can be used to collect $^{137}$Cs from seawater. For this purpose, Roger and Wilson[84] proposed to use relatively small-sized columns. However, composite sorbents based on TM-HCFs supported on inert materials are used most often. The immobilization of TM-HCFs on an inert support prevents them from leaching and gives materials with high mechanical and hydromechanical strength.[85]

Specific features of immobilization of TM-HCF-based sorbents are determined by their physical and chemical characteristics, one of which is the presence of exchangeable functional groups. Immobilization of the sorbent phase on the supports that have no ion exchange properties is due to adhesion or physical attachment of TM-HCF crystals. If the support has grafted functional groups, there is additional electrostatic interaction between these groups and TM-HCF particles.[86]

Modification of ion exchange resins is one of the earliest methods for the synthesis of composite sorbents. The filled ion exchange resins obtained in this way are widely used to determine the concentration of $^{137}$Cs in seawater.[78,87,88] A specific feature of the synthesis of these materials is the need for the successive treatment of the ion exchange resin with solutions of transition metal salt and potassium HCFs.

The materials that are obtained by immobilization of TM-HCFs on supports containing no exchangeable functional groups can be conventionally assigned to another type. Such sorbents can be obtained by either successive treatment of supports with solutions of transition metal salt and HCF-$K^+$ (Refs 89 – 91) or direct modification of TM-HCF suspensions,[92 – 95] which simplifies the procedure. The use of natural, particularly renewable, raw materials as supports can reduce the cost of industrially manufactured sorbents. Most often, cellulose-based raw materials and aluminosilicates are employed. Materials manufactured in this way include the commercial sorbents NIKET[96,97] and ANFEZH.[98 – 107] Besides this, the use of a sorbent based on potassium nickel ferrocyanide supported on silica gel (FSS) was described. This sorbent proved to be efficient for the recovery of $^{137}$Cs from seawater.[38] Many publications are devoted to the practical application of cellulose-supported HCF sorbents.[99 – 104, 108 – 111]

Worthy of note are new promising supports including zeolite imidazole frameworks,[112] mesoporous silica gels,[113] aerogels[114] and hydrogels.[115] These materials exhibit high sorption characteristics in the recovery of caesium from seawater, but their wide use is hindered by the lack of commercial availability. Under dynamic conditions, nanosorbents possess rather high hydrodynamic resistance and, therefore, it is impossible to attain high flow rates of solutions.

Analysis of publications devoted to HCF sorbents shows that sorption characteristics considerably depend on

the type of transition metal contained in the inorganic phase. In particular, Pekárek and Veselý [116] noted that the sorption capacity of various HCFs towards caesium decreases in the series

$$HCF\text{-}Co^{2+} > HCF\text{-}Ni^{2+} > HCF\text{-}Zn^{2+} > HCF\text{-}Cu^{2+} > HCF\text{-}Fe^{3+}$$

The series of decreasing capacity of HCF sorbents towards caesium reported later by Vincent *et al.*[117] and Nilchi *et al.*[118] differed from each other. The authors attributed this difference to details of the formation of the active phase of the sorbents, the properties of which depend on the method of preparation of the composite sorbent.[85, 117] The exchange capacity was also inconsistent with the distribution constant ($K_d$).[117] Indeed, despite low exchange capacity, the distribution constant of $^{137}Cs$ found for $HCF\text{-}Fe^{3+}$ sorbents was inferior only to those found for $HCF\text{-}Co^{2+}$ sorbents. These facts complicate the prediction of the sorption characteristics of HCF sorbents; therefore, real evaluation of the efficiency of these materials requires comparative experiments.

The next stage of development of HCF sorbents is production of fibrous materials. Owing to their large specific surface area, fibrous composite sorbents impregnated with HCF or another active ingredient can provide a high rate of ion exchange, which ensures more complete recovery of radionuclides at increased flow rates of seawater. Therefore, this type of material can be considered most promising. Fibrous sorbents can be obtained by preliminary grafting of functional groups on the fibre surface, which ensures attachment of TM-HCF during modification.[86, 119 – 122] Despite the obvious advantages of this method, grafting of functional groups on the fibre complicates the synthesis; therefore, an original method for the production of fibrous sorbents was developed.[123, 124] The essence of the method is to treat a polyether fibre with a chitosan solution containing a suspension of $HCF\text{-}Zn^{2+}$ and subsequent treatment of the product with a dilute solution of NaOH. These materials were successfully tested in marine expeditions. Unfortunately, fibrous sorbents are currently unavailable due to the absence of established industrial production.

Veleshko *et al.*[125] proposed to fabricate a composite material by modification of freshly formed chitosan granules with potassium copper ferrocyanide. This material was successfully tested in marine expeditions on radioecological monitoring of the Kara and Barents Seas.

Selective resorcinol formaldehyde resin was reported to be applicable for the sorption of $^{137}Cs$ from seawater.[126 – 128] A benefit of this ion exchanger is reusability after elution and regeneration.

A composite material based on resorcinol formaldehyde resin with various contents of barium silicate was fabricated. Testing of the material showed that an increase in the concentration of barium silicate resulted in a decrease of distribution constants of caesium.[129]

High caesium distribution constants were also obtained by using sodium titanosilicate (STS) $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$.[130] A number of reported sorbents [131 – 133] showed low characteristics of $^{137}Cs$ recovery from seawater.

The published data are summarized in Table 2 (Refs 88, 90, 91, 93, 102, 110 – 115, 120, 124 – 127, 129 – 131), which presents the results of sorption of $^{137}Cs$ from seawater and liquid radioactive waste (LRW) containing seawater under static conditions, and in Table 3 (Refs 82, 83, 88, 89, 100,

**Table 2**. Parameters of sorption of $^{137}Cs$ from seawater under static conditions (according to publications [88, 90, 91, 93, 102, 110 – 115, 120, 124 – 127, 129 – 131]).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| Copper ferrocyanide – Amberlite IRA-904 (National Institute of Radiological Sciences, Japan) | Ocean water | 100 | $9.99 \times 10^4$ | 88 |
| | | 200 | $9.98 \times 10^4$ | 88 |
| | | 1000 | $1.10 \times 10^5$ | 88 |
| | | 2000 | $1.16 \times 10^5$ | 88 |
| NPF – HTD: nickel potassium ferrocyanide based on hydrated titanium dioxide (UrFU, RF) | Artificial seawater | 2500 | $4.1 \times 10^4$ | 90, 91 |
| NPF – CL: nickel potassium ferrocyanide based on clinoptilolite, Shivertuyskoye deposit, Transbaikal Region, Russia (UrFU, RF) | Artificial seawater | 2500 | $3.0 \times 10^4$ | 90, 91 |
| NPF – GL: nickel potassium ferrocyanide based on quartz glauconite concentrate of the Karinskoye deposit, Chelyabinsk Region, Russia (UrFU, RF) | Artificial seawater | 2500 | $5.0 \times 10^4$ | 90, 91 |
| Termoxid-35: potassium nickel ferrocyanide supported on hydrated zirconium dioxide (JSC Scientific Production Company Termoxid, RF) | Artificial seawater | 2500 | $6.1 \times 10^4$ | 90 |
| | Seawater | 200 | $(3.1 \pm 0.7) \times 10^4$ | 110 |
| Termoxid-3A: zirconium phosphate (JSC Scientific Production Company Termoxid, RF) | Artificial seawater | 2500 | 750 | 90 |
| | Seawater | 200 | $(1.2 \pm 0.2) \times 10^3$ | 110 |
| Mikoton-Cs: potassium copper ferrocyanide supported on chitin-containing fibrous material Mikoton (National Research Center Kurchatov Institute, RF) | Seawater | 100 | $(1.8 \pm 0.8) \times 10^4$ | 93 |
| | | 500 | $(3.1 \pm 1.4) \times 10^4$ | 93 |
| | | 1000 | $(3.4 \pm 1.5) \times 10^4$ | 93 |
| | | 10 000 | $(4.8 \pm 2.2) \times 10^4$ | 93 |
| ANFEZH: cellulose-supported iron potassium ferrocyanide (LLC Research and Production Enterprise Eksorb, RF) | Seawater | See [a] | $(9.4 \pm 0.7) \times 10^5$ | 102 |
| | | 200 | $(6.8 \pm 0.6) \times 10^4$ | 110 |
| | Artificial seawater | See [a] | $(1.1 \pm 0.8) \times 10^6$ | 102 |
| | | 1000 | $8.1 \times 10^3$ | 111 |

**Table 2** (continued).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| NIKET: cellulose-supported nickel potassium ferrocyanide (LLC Research and Production Enterprise Eksorb, RF) | Seawater | 200 | $(1.6 \pm 0.2) \times 10^4$ | 110 |
| UNIKET: cellulose-supported iron potassium ferrocyanide (LLC Research and Production Enterprise Eksorb, RF) | Seawater | 200 | $(2.7 \pm 0.7) \times 10^4$ | 110 |
| FSS: nickel potassium ferrocyanide supported on silica gel (Institute of Physical Chemistry and Electrochemistry, RAS) | Seawater | 200 | $(1.1 \pm 0.3) \times 10^4$ | 110 |
| FD-M: copper potassium ferrocyanide supported on phosphorylated wood (Institute of Physical Chemistry and Electrochemistry, RAS) | Seawater | 200 | $(6.1 \pm 0.4) \times 10^4$ | 110 |
| Axionit RCs: resorcinol formaldehyde polymer supported on sulfonated styrene divinylbenzene (JSC Axion — Rare and Noble Metals, RF) | Seawater | 200 | $(2.4 \pm 0.8) \times 10^2$ | 110 |
| NKF-C: nickel potassium ferrocyanide supported on cellulose material (UrFU, RF) | Seawater | 200 | $(4.4 \pm 0.2) \times 10^4$ | 110 |
| Anion exchange resin Biorad AG 1-X4 Cl impregnated with $MnO_2$ (Texas University A&M, USA) | Artificial seawater | 1000 | 7.59 | 111 |
| Nanostructured mesoporous $MnO_2$ (Texas University A&M, USA) | Artificial seawater | 1000 | 51.3 | 111 |
| Biogenic $MnO_2$ (Texas University A&M, USA) | Artificial seawater | 1000 | 9.77 | 111 |
| Self-assembled monolayers with $Mn^{3+}$ on a mesoporous support (Texas University A&M, USA) | Artificial seawater | 1000 | 6.46 | 111 |
| Self-assembled monolayers with $Mn^{4+}$ on a mesoporous support (Texas University A&M, USA) | Artificial seawater | 1000 | 12.3 | 111 |
| Wet $MnO_2$ (Texas University A&M, USA) | Artificial seawater | 1000 | 339 | 111 |
| ZIF-8-FC: potassium ferrocyanide supported on a zeolite imidazole framework (Pusan National University, Republic of Korea) | Artificial seawater | 1000 | $4.3 \times 10^4$ | 112 |
| CoFC: crystalline cobalt ferrocyanide (Institute for the Separation Chemistry in Marcoule, France) | Seawater | 2000 | $6 \times 10^5$ | 113 |
| CoFC@Silica-Py: cobalt ferrocyanide impregnated into silica-based porous nanocomposite (Institute for the Separation Chemistry in Marcoule, France) | Seawater | 2000 | $8 \times 10^5$ | 113 |
| CoFC@Glass-Py: cobalt ferrocyanide impregnated into glass-based porous nanocomposite (Institute for the Separation Chemistry in Marcoule, France) | Seawater | 2000 | $3 \times 10^5$ | 113 |
| Composite aerogels based on titanium carbide encapsulated into sodium alginate (Kyungpook National University, Republic of Korea): | Artificial seawater | | | |
| PBMX-I$_{sphere}$ | | 1000 | $1.06 \times 10^4$ | 114 |
| PBMX-II$_{sphere}$ | | 1000 | $7.70 \times 10^4$ | 114 |
| PBMX-III$_{sphere}$ | | 1000 | $1.03 \times 10^5$ | 114 |
| Composite hydrogels containing HCFs (Leeds University, UK): | Seawater | | | |
| DG(Cu) | | 1000 | $7.75 \times 10^2$ | 115 |
| DHG(Cu) | | 1000 | $9.78 \times 10^4$ | 115 |
| DHG(Fe) | | 1000 | $2.26 \times 10^4$ | 115 |
| DHG(step-Fe) | | 1000 | $3.19 \times 10^4$ | 115 |
| DHG(step-Cu) | | 1000 | $2.38 \times 10^4$ | 115 |
| VBTAC-Co-FC: cobalt ferrocyanide supported on nylon fibres with grafted vinylbenzyltrimethylammonium chloride $CH_2{=}CHC_6H_4CH_2N(CH_3)_3Cl$ (Chiba University, Japan) | Ocean water | 100 | $4.9 \times 10^3$ | 120 |
| SSS-Co-FC: cobalt ferrocyanide supported on nylon fibres with grafted sodium *p*-styrenesulfonate $CH_2{=}CHC_6H_4SO_3Na$ (Chiba University, Japan) | Ocean water | 100 | $4.9 \times 10^3$ | 120 |

**Table 2** (continued).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| Chitosan ferrocyanide sorbents (CFS) (Institute of Chemistry, Far Eastern Branch of the RAS): | Ocean water | | | |
| CFS Zn-K | | 1000 | $8.0 \times 10^3$ | 124 |
| CFS Cu-K | | 1000 | $1.55 \times 10^5$ | 124 |
| CFS Ni-K | | 1000 | $5.01 \times 10^5$ | 124 |
| SFCG-$SO_4$-FC: freshly formed chitosan granules modified with potassium and copper ferrocyanide (National Research Center Kurchatov Institute, RF) | Seawater | 1000 | $2.3 \times 10^3$ | 125 |
| Resorcinol formaldehyde resins (Institute of Chemistry, Far Eastern Branch of the RAS): | Ocean water | | | |
| RF130(K) | | 1000 | $1.6 \times 10^3$ | 126 |
| RF160(K) | | 1000 | $2.3 \times 10^3$ | 126 |
| RF190(K) | | 1000 | $3.4 \times 10^3$ | 126 |
| RF210(K) | | 1000 | $4.1 \times 10^3$ | 126 |
| RF130(Na) | | 1000 | $1.5 \times 10^3$ | 126 |
| RF160(Na) | | 1000 | $2.4 \times 10^3$ | 126 |
| RF190(Na) | | 1000 | $3.4 \times 10^3$ | 126 |
| RF210(Na) | | 1000 | $4.5 \times 10^3$ | 126, 127 |
| | | 100 | $1.0 \times 10^4$ | 127 |
| Composite material based on resorcinol formaldehyde resin with various contents of barium silicate, mass % (Institute of Chemistry, Far Eastern Branch of the RAS): | Ocean water | | | |
| – | | 1000 | $2.81 \times 10^3$ | 129 |
| 4.5 | | 1000 | $2.75 \times 10^3$ | 129 |
| 10.9 | | 1000 | $2.94 \times 10^3$ | 129 |
| 15.4 | | 1000 | $1.48 \times 10^3$ | 129 |
| 28.2 | | 1000 | 910 | 129 |
| 100 | | 1000 | 0 | 129 |
| Sodium titanosilicate (STS) $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ (Texas University A&M, USA) | Artificial seawater | 500 | $2.85 \times 10^4$ | 130 |
| | | 1000 | $2.82 \times 10^4$ | 130 |
| | | 2500 | $1.90 \times 10^4$ | 130 |
| | | 5000 | $1.85 \times 10^4$ | 130 |
| | | 7500 | $9.8 \times 10^3$ | 130 |
| | | 10000 | $9.0 \times 10^3$ | 130 |
| Montmorillonite from the Cherkasskoye deposit (A.V.Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences, Ukraine) | Seawater | 500 | 30 | 131 |
| Montmorillonite from the Cherkasskoye deposit with $Fe(OH)_3$ (5 mass %) precipitated on the surface (A.V.Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences, Ukraine) | Seawater | 500 | 45 | 131 |

[a] No data are presented in the source.

101, 104, 105, 122, 123, 126, 127, 132, 133), which presents the radiochemical yields upon sorption of $^{137}Cs$ under dynamic conditions.

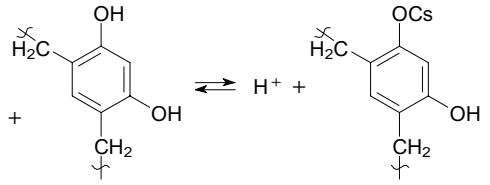
These data provide the conclusion that the use of a single column with addition of stable caesium as a tracer is the most efficient method for the recovery of $^{137}Cs$ from seawater, while KNiFC-PAN, NIKET and UNIKET are the most efficient sorbents.

When the above-considered methods are used, $^{135}Cs$ is concentrated together with other caesium isotopes. It decays by emitting β-particles, the maximum energy of which is 269 keV; however, radiometric determination by counting β-particles is hampered by $^{137}Cs$ isotope, which is also present in the sample and is five orders of magnitude

**Scheme 1**

(*a*) $n\,Cs^+ + K_{1.33}Me^{II}_{1.33}[Fe(CN)_6] \rightarrow n\,K^+ + K_{1.33-n}Cs_nMe^{II}_{1.33}[Fe(CN)_6]$

(*b*) $n\,Cs^+ + (NH_4)_3[PMo_{12}O_{40}] \cdot 2H_2O \rightarrow$
$\rightarrow n\,NH_4^+ + (NH_4)_{3-n}Cs_n[PMo_{12}O_{40}] \cdot 2H_2O$

(*c*) $Cs^+ +$  $H^+ +$ 

(*d*) $2n\,Cs^+ + Zr(HPO_4)_2 \cdot m\,H_2O \rightarrow 2n\,H^+ + Zr(Cs_nH_{1-n}PO_4)_2 \cdot m\,H_2O$

(*e*) $n\,Cs^+ + Na_2Ti_2O_3SiO_4 \cdot 2H_2O \rightarrow n\,Na^+ + Na_{2-n}Cs_nTi_2O_3SiO_4 \cdot 2H_2O$

**Table 3**. Parameters of sorption of $^{137}Cs$ from seawater under dynamic conditions (according to publications [82, 83, 88, 89, 100, 101, 104, 105, 122, 123, 126, 127, 132, 133]).

| Sorbent (manufacturer) | Solution | Sorbent weight or volume in the column | Processed volume, L | Flow rate, mL $min^{-1}$ | Caesium added | Radio-chemical yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| AMP – PAN: ammonium molybdophosphate supported on polyacrylonitrile (PAN) (Triskem Int., France) | Acidified ocean water | 25 mL | 106 | 280 | 25 mg $L^{-1}$ | 88.7 ± 0.3 | 82 |
| | | 25 mL | 93 | 285 | 4 mg $L^{-1}$ | 88.8 ± 0.4 | 82 |
| | | 25 mL | 101 | 319 | 4 mg $L^{-1}$ | 84.9 ± 0.5 | 82 |
| | | 25 mL | 95 | 243 | 4 mg $L^{-1}$ | 94.1 ± 0.3 | 82 |
| | | 25 mL | 98 | 326 | 4 mg $L^{-1}$ | 86.3 ± 0.5 | 82 |
| | | 25 mL | 96 | 298 | 4 mg $L^{-1}$ | 85.7 ± 0.6 | 82 |
| KNiFC – PAN: nickel potassium ferrocyanide supported on PAN (Triskem Int., France) | Acidified ocean water | 25 mL | 97 | 287 | 4 mg $L^{-1}$ | 92.4 ± 0.4 | 82 |
| | | 25 mL | 98 | 288 | 4 mg $L^{-1}$ | 94.4 ± 0.3 | 82 |
| | | 25 mL | 101 | 293 | 4 mg $L^{-1}$ | 93.0 ± 0.4 | 82 |
| | | 25 mL | 102 | 260 | 4 mg $L^{-1}$ | 91.5 ± 0.5 | 82 |
| | | 25 mL | 100 | 293 | 4 mg $L^{-1}$ | 93.2 ± 0.5 | 82 |
| | Ocean water | 25 mL | 102 | 279 | 4 mg $L^{-1}$ | 91.9 ± 0.5 | 82 |
| | | 25 mL | 100 | 250 | 4 mg $L^{-1}$ | 92.7 ± 0.5 | 82 |
| | | 25 mL | 98 | 276 | 4 mg $L^{-1}$ | 88.3 ± 0.5 | 82 |
| | | 25 mL | 101 | 291 | 4 mg $L^{-1}$ | 91.6 ± 0.5 | 82 |
| | | 25 mL | 100 | 315 | 4 mg $L^{-1}$ | 90.9 ± 0.5 | 82 |
| | | 25 mL | 102 | 470 | 4 mg $L^{-1}$ | 85.6 ± 0.6 | 82 |
| | | 5 mL (1 g) | 40 | 50 | 0.1 mg $L^{-1}$ | 95.0 | 83 |
| | | 5 mL (1 g) | 40 | 100 | 0.1 mg $L^{-1}$ | 82.0 | 83 |
| | | 5 mL (1 g) | 40 | 200 | 0.1 mg $L^{-1}$ | 68.0 | 83 |
| | | 5 mL (1 g) | 40 | 50 | 0.4 mg $L^{-1}$ | 85.0 | 83 |
| | | 5 mL (1 g) | 40 | 100 | 0.4 mg $L^{-1}$ | 72.0 | 83 |
| | | 5 mL (1 g) | 40 | 200 | 0.4 mg $L^{-1}$ | 57.0 | 83 |
| | | 5 mL (1 g) | 40 | 50 | 4 mg $L^{-1}$ | 46.0 | 83 |
| | | 5 mL (1 g) | 40 | 100 | 4 mg $L^{-1}$ | 38.0 | 83 |
| | | 5 mL (1 g) | 40 | 200 | 4 mg $L^{-1}$ | 30.0 | 83 |
| Copper ferrocyanide – Amberlite IRA-904 (National Institute of Radiological Sciences, Japan) | Seawater | 3 g | 1.5 | 2 | See [a] | 99.9 | 88 |
| | | 3 g | 1.5 | 8 | See [a] | 99.9 | 88 |
| | | 3 g | 1.5 | 15 | See [a] | 99.8 | 88 |
| | | 3 g | 3 | 15 | See [a] | 99.4 | 88 |
| | | 3 g | 1.5 | 18 | See [a] | 94.4 | 88 |
| | | 3 g | 3 | 18 | See [a] | 90.9 | 88 |
| AMP – $SiO_2$: ammonium molybdophosphase on $SiO_2$ (Kanazawa University, Japan) | Ocean water | 5 g | 40 | 100 | 0 | 99.9 | 89 |
| | | 5 g | 60 | 100 | 0 | 77.0 | 89 |
| | | 5 g | 80 | 100 | 0 | 50.0 | 89 |
| | | 5 g | 100 | 100 | 0 | 89 | 89 |
| KCFC – $SiO_2$: potassium cobalt ferrocyanide on $SiO_2$ (Kanazawa University, Japan) | Ocean water | 5 g | 40 | 100 | 0 | 99.0 | 89 |
| | | 5 g | 60 | 100 | 0 | 97.0 | 89 |
| | | 5 g | 80 | 100 | 0 | 90.0 | 89 |
| | | 5 g | 100 | 100 | 0 | 77.0 | 89 |
| | | 10 g | 40 | 100 | 0 | 99.9 | 89 |
| | | 10 g | 100 | 100 | 0 | 97.5 | 89 |
| ANFEZH: cellulose-supported iron potassium ferrocyanide (LLC Research and Production Enterprise Eksorb, RF) | Seawater | 150 mL | 80 | 150 [b] | See [a] | 86.6 ± 4.2 | 100, 101 |
| | | 150 mL | 80 | 130 [b] | See [a] | 88.2 ± 3.5 | 100, 101 |
| | | 150 mL | 80 | 120 [b] | See [a] | 94.1 ± 2.6 | 100, 101 |
| | | 150 mL | 80 | 150 [b] | See [a] | 88.2 ± 3.3 | 100, 101 |
| | | 150 mL | 150 | 150 [b] | See [a] | 85.8 ± 4.2 | 100, 101 |
| | | 100 mL | 150 | 120 [b] | See [a] | 89.5 ± 1.1 | 100, 101 |
| | Ocean water | 80 g | 200 | 1000 – 2000 | See [a] | 95.0 | 104 |
| | | 0.5 g | 10 | 13 | See [a] | 49.1 | 105 |
| | | 0.5 g | 10 | 16.14 | See [a] | 97.1 | 105 |
| Potassium cobalt ferrocyanide KCFC (1–3 mm) (Texas University A&M, USA) | Ocean water | 0.5 g | 10 | 16.12 | See [a] | 89.3 | 105 |

**Table 3** (continued).

| Sorbent (manufacturer) | Solution | Sorbent weight or volume in the column | Processed volume, L | Flow rate, mL $min^{-1}$ | Caesium added | Radio-chemical yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Potassium cobalt ferrocyanide KCFC (88–250 μm) (Texas University A&M, USA) | Ocean water | 0.5 g | 10 | 6.6 | See [a] | 99.8 | 105 |
| FeCN–SAMMS (HCF on self-assembled monolayers on mesoporous supports) (Texas University A&M, USA) | Ocean water | 0.5 g | 10 | 4.5 | See [a] | 87.3 | 105 |
| Copper ferrocyanide-based fibre (Dalat Nuclear Research Institute, Vietnam) | Ocean water | 0.5 g | 4 | 30 | $3 \cdot 10^{-4}$ Bq $L^{-1}$ | 100.0 | 122 |
| | | 0.5 g | 4.5 | 30 | $3 \cdot 10^{-4}$ Bq $L^{-1}$ | 96.3 | 122 |
| | | 0.5 g | 5 | 30 | $3 \cdot 10^{-4}$ Bq $L^{-1}$ | 82.0 | 122 |
| CFS Zn-K: zinc potassium ferrocyanide supported on granulated chitosan (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 23 g | 20 | 400 | 30 Bq $L^{-1}$ | 99.0 | 123 |
| | | 23 g | 100 | 400 | 30 Bq $L^{-1}$ | 82.0 | 123 |
| Resorcinol formaldehyde resins (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 1 mL | 0.7 | 0.125 | 0.3 Bq $L^{-1}$ | 95.0 | 126, 127 |
| Zirconium ferrocyanide (V.G.Khlopin Radium Institute, RF) | Seawater | 30 g | 25 | 200 | See [a] | 81.6 | 132, 133 |
| | | 30 g | 160 | 300 | See [a] | 53.1 | 132, 133 |
| | | 30 g | 90 | 500 | See [a] | 34.6 | 132, 133 |
| | | 30 g | 160 | 900 | See [a] | 29.4 | 132, 133 |
| | | 30 g | 240 | 1000 | See [a] | 27.8 | 132, 133 |
| | | 30 g | 200 | 1400 | See [a] | 27.0 | 132, 133 |
| | | 30 g | 250 | 1400 | See [a] | 29.0 | 132, 133 |
| | | 30 g | 350 | 1500 | See [a] | 29.5 | 132, 133 |
| | | 30 g | 360 | 2000 | See [a] | 22.6 | 132, 133 |
| | | 30 g | 390 | 2100 | See [a] | 19.0 | 132, 133 |
| | | 30 g | 540 | 3000 | See [a] | 16.3 | 132, 133 |
| | | 30 g | 320 | 3000 | See [a] | 20.4 | 132, 133 |
| | | 30 g | 340 | 11400 | See [a] | 16.2 | 132, 133 |
| Ferrocyanide organic ion exchanger on AV-18G (V.G.Khlopin Radium Institute, RF) | Seawater | 15 g | 70 | 700 | See [a] | 3.20 | 132, 133 |
| Ferrocyanide organic ion exchanger on AV-18G pre-saturated with stable $^{133}Cs$ (V.G.Khlopin Radium Institute, RF) | Seawater | 15 g | 60 | 200 | See [a] | 35.5 | 132, 133 |
| | | 15 g | 60 | 500 | See [a] | 25.7 | 132, 133 |
| | | 15 g | 90 | 600 | See [a] | 13.2 | 132, 133 |
| | | 15 g | 40 | 700 | See [a] | 11.0 | 132, 133 |
| | | 15 g | 40 | 900 | See [a] | 7.90 | 132, 133 |

[a] No data are given in the source; [b] the flow rate in the source is indicated in mL $cm^{-2}$ $min^{-1}$; column parameters are not given.

more active. Therefore, mass spectrometry is used for $^{135}Cs$ determination.[134]

The equations that describe the recovery of caesium with sorbents based on transition metal ferrocyanides (*a*),[135] ammonium phosphomolybdate (*b*),[136] resorcinol formaldehyde resins (*c*),[127] zirconium phosphate-based sorbent (Termoxid-3A) (*d*)[137] and sodium silicotitanate (*e*) are depicted in Scheme 1.[130]

## 5.2. Sorption of $^{90}Sr$ from seawater

Direct sorption of $^{90}Sr$ from seawater has been very little studied. This radionuclide was most often recovered from model solutions of NaCl or $CaCl_2$ under static conditions. However, the distribution constants of $Sr^{2+}$ determined in the presence of $Na^+$ and $Ca^{2+}$ ions do not necessarily coincide with the distribution constants of $Sr^{2+}$ characterizing sorption from seawater.

Currently, a number of efficient sorbents have been developed for the recovery of $^{90}Sr$ from seawater and LRW containing seawater: sorption reagents based on barium silicate SRM-Sr,[138–141] composite material based on resorcinol formaldehyde resin and 15.4–28.2 mass % barium silicate,[129,142] barium silicate and aluminosilicate,[143] barium hexafluorosilicate,[144] barium sulfate-modi-

fied Mikoton [145] and sodium titanosilicate (STS) $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$.[130]

Sorbents containing $MnO_2$ as the active component are widely used to recover $^{90}Sr$ from seawater. The highest efficiency was observed for MDM [140, 141, 146] and Modix,[146] which are made of highly dispersed manganese dioxide. However, high hydrodynamic resistances of these sorbents prevent pumping of seawater through these materials at desired rates. The sorbents containing $MnO_2$ supported on some material (manganese-modified wood, DMM, and a fibre impregnated with $MnO_2$) [146] are less efficient because of lower contents of manganese dioxide. Nevertheless, these sorbents, especially the fibre, have low hydrodynamic resistances.

In addition, it was shown that high distribution constants are attained for birnessite ($\delta$-$MnO_2$) based sorbents,[147] which are meant for the recovery of $^{90}Sr$ from LRW containing seawater.

Table 4 [90, 129 – 131, 138 – 141, 143 – 150] presents the $Sr^{2+}$ distribution constants for recovery from seawater or artificial seawater.

Mention should also be made of sorption materials based on crown ethers,[151, 152] which are used to recover radionuclides from complex multicomponent mixtures. However, direct recovery of radionuclides from seawater using these materials is impossible due to low distribution constants.[153] First, radionuclides are collected by co-precipitation, which is followed by extraction chromatographic separation from concomitant impurities.[42] A number of sorbents based on dicyclohexyl-18-crown-6 and its derivatives have been developed for the selective sorption of strontium.[154 – 159] The most well-known among these materials are commercially available Sr Resin [154, 156] and TK100 sorbent.[159]

A number of methods using extraction chromatographic resins based on crown ethers were developed for $^{90}Sr$ sorption recovery and purification.[160, 161] However, these methods are poorly adapted to determination of $^{90}Sr$ in seawater: the procedure described in Ref. 161 is more appropriate for analysis of freshwater, while that reported by Maxwell *et al.*[160] needs to be corrected, because the real concentration of $^{90}Sr$ in most seas is an order of magnitude lower, while an increase in the sample volume is accompanied by an increase in the amount of stable strontium in the sample and necessitates an increase in the amount of the sorbent.

The equations describing the sorption of strontium by $MnO_2$-impregnated sorbents (*a*) [162] and sorbents based on barium salts (*b*),[163] zirconium hydroxide

**Table 4**. Parameters of sorption of $^{90}Sr$ from seawater (according to publications [90, 129 – 131, 138 – 141, 143 – 150]).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| Termoxid-3K: modified hydrated zirconium dioxide containing zirconium carbonate (JSC Scientific Production Company Termoxid, RF) | Artificial seawater | 400 | 110 | 90 |
| | Seawater | 200 | $520 \pm 80$ | 146 |
| NPF – HTD: nickel potassium ferrocyanide based on hydrated titanium dioxide (UrFU, RF) | Artificial seawater | 400 | 110 | 90 |
| MD – HTD: manganese dioxide based on hydrated titanium dioxide (UrFU, RF) | Artificial seawater | 400 | 190 | 90 |
| NPF – CL: nickel potassium ferrocyanide based on clinoptilolite of the Shivertuyskoye deposit, Transbaikal Region, Russia (UrFU, RF) | Artificial seawater | 400 | 64 | 90 |
| PF – GL: nickel potassium ferrocyanide based on quartz glauconite concentrate of the Karinskoye deposit, Chelyabinsk Region, Russia (UrFU, RF) | Artificial seawater | 400 | 87 | 90 |
| Composite material on resorcinol formaldehyde resin with different contents of barium silicate, mass % (Institute of Chemistry, Far Eastern Branch of the RAS): | Ocean water | | | |
| 0 | | 100 | 0 | 129 |
| 4.5 | | 100 | $4.0 \times 10^3$ | 129 |
| 10.9 | | 100 | $2.3 \times 10^4$ | 129 |
| 15.4 | | 100 | $6.0 \times 10^4$ | 129 |
| 28.2 | | 100 | $6.0 \times 10^4$ | 129 |
| 100 | | 100 | $1.8 \times 10^4$ | 129 |
| Sodium titanosilicate (STS) $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ (Texas University A&M, USA) | Artificial seawater | 50 | $2.26 \times 10^4$ | 130 |
| | | 100 | $1.23 \times 10^4$ | 130 |
| | | 140 | $8.2 \times 10^3$ | 130 |
| | | 180 | $4.3 \times 10^3$ | 130 |
| | | 250 | $1.64 \times 10^3$ | 130 |
| | | 400 | 580 | 130 |
| | | 1000 | 210 | 130 |
| Montmorillonite from the Cherkasskoye deposit (A.V.Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences, Ukraine) | Seawater | 500 | 10 | 131 |

**Table 4** (continued).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| Montmorillonite from the Cherkasskoye deposit with $Fe(OH)_3$ (5 mass %) precipitated on the surface (A.V.Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences, Ukraine) | Seawater | 500 | 15 | 131 |
| FMM: fibre-supported hydrated magnesium manganite (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 1000 | 315 | 138 |
| DMT: granulated thermally treated manganese dioxide (Institute of Physical Chemistry and Electrochemistry, RAS) | Ocean water | 1000 | 125 | 138 |
| Silicotitanate IE-911 (UOP LLC, USA) | Ocean water | 1000 | 70 | 138 |
| TiIE-96 (UOP LLC, USA) | Ocean water | 1000 | 11 | 138 |
| Sodium titanate (TiNa) (pilot sample; Allied Signal, USA) | Ocean water | 1000 | 70 | 138 |
| Styrene divinylbenzene resin Duolite C-467 (Rohm&Haas, USA) | Ocean water | 1000 | 7 | 138 |
| SRM-Sr: sorption reagent based on barium silicate (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 1000 | $1.26 \times 10^4$ | 138 |
| | | 100 | $6.0 \times 10^4$ | 139 |
| | | 500 | $6.0 \times 10^3$ | 139 |
| | | 1000 | $3.0 \times 10^3$ | 139 |
| | Artificial seawater | 200 | $(6.4 \pm 0.3) \times 10^3$ | 140, 141 |
| | Seawater | 200 | $(1.1 \pm 0.3) \times 10^4$ | 146 |
| Synthetic ivanyukite $Na_{0.98-1.51}K_{0.92-1.02}Ca_{0.00-0.04}$·$.[(Ti_{4.09-4.58}Fe_{0.00-0.02}Si_{2.92-2.95}Al_{0.05-0.08}O_{15.36-16.18})] \cdot (6-8)\,H_2O$ (Kola Science Center, RAS) | Artificial seawater | 200 | $61 \pm 3$ | 140 |
| SL-3 titanosilicate (Kola Science Center, RAS) | Artificial seawater | 200 | $29 \pm 2$ | 140 |
| MDM: modified manganese dioxide (Institute of Physical Chemistry and Electrochemistry, RAS) | Artificial seawater | 200 | $590 \pm 30$ | 140, 141 |
| | Seawater | 200 | $(3.7 \pm 0.1) \times 10^3$ | 146 |
| Synthetic chabazite IE-95 (UOP LLC, USA) | Artificial seawater | 200 | $70 \pm 5$ | 141 |
| Sodium titanosilicate TiSi-Na (Institute of Sorption and Problems of Endoecology, National Academy of Sciences, Ukraine) | Artificial seawater | 200 | $520 \pm 20$ | 141 |
| Barium silicate $BaSiO_3 \cdot 2.3\,H_2O$ (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 1000 | $8.0 \times 10^4$ | 143 |
| Barium aluminosilicate $BaAl_2Si_2O_8 \cdot 2.6\,H_2O$ (Institute of Chemistry, Far Eastern Branch of the RAS) | Ocean water | 40 | $1.29 \times 10^3$ | 143 |
| | | 400 | $1.95 \times 10^3$ | 143 |
| | | 1000 | $1.33 \times 10^3$ | 143 |
| Barium hexafluorosilicate $BaSiF_6$ (V.G.Khlopin Radium Institute, RF) | Seawater, salinity 35 | 1000 | $9.0 \times 10^3$ | 144 |
| Mikoton biopolymer (LLC Mikoton Aglycon, Ukraine) | Seawater | 1000 | 330 | 145 |
| MSB15: Mikoton modified with 15 mass % $BaSO_4$ (National Research Center Kurchatov Institute, RF) | Seawater | 1000 | $1.15 \times 10^3$ | 145 |
| MDM15: Mikoton modified with 15 mass % $MnO_2$ (National Research Center Kurchatov Institute, RF) | Seawater | 1000 | 580 | 145 |
| Modix: granulated manganese dioxide (LLC Research and Production Enterprise Eksorb) | Seawater | 200 | $(3.2 \pm 0.2) \times 10^3$ | 146 |
| FD: phosphorylated wood (Institute of Physical Chemistry and Electrochemistry, RAS) | Seawater | 200 | $64 \pm 20$ | 146 |
| DMM: manganese-modified wood (Institute of Physical Chemistry and Electrochemistry, RAS) | Seawater | 200 | $240 \pm 30$ | 146 |
| $MnO_2$-impregnated fibre (Marine Hydrophysical Institute, RAS) | Seawater | 200 | $350 \pm 75$ | 146 |
| Birnessite type sorbents (Institute of Chemistry, Far Eastern Branch of the RAS): | Ocean water | | | |
| $MnO_2$(105) | | 1000 | 520 | 147 |
| $MnO_2$(500) | | 1000 | 890 | 147 |
| $MnO_2$(500)HNa | | 1000 | $1.24 \times 10^3$ | 147 |

**Table 4** (continued).

| Sorbent (manufacturer) | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|
| Birnessite type sorbents (Institute of Chemistry, Far Eastern Branch of the RAS): | Artificial seawater | | | |
| $MnO_2$(105) | | 1000 | 950 | 147 |
| $MnO_2$(500) | | 1000 | $1.69 \times 10^3$ | 147 |
| $MnO_2$(500)HNa | | 1000 | $1.83 \times 10^3$ | 147 |
| Pure alginate foam (Korea Institute of Bioscience and Mineral Resources, KIGAM, South Korea) | Ocean water | 1000 | 397 | 148 |
| Alginate foam immobilized with 10% zeolite (Korea Institute of Bioscience and Mineral Resources, KIGAM, South Korea) | Ocean water | 1000 | 692 | 148 |
| Ca – Mg phosphate supported on dolomite (Institute of General and Inorganic Chemistry, National Academy of Sciences, Belarus): | Artificial seawater | | | |
| PD-1 ($Ca_2Mg(HPO_4)_3 \cdot 8.7\,H_2O$) | | 500 | 13 | 149 |
| PD-2 ($CaMg_{1.5}(NH_4)(PO_4)_2 \cdot 12.5\,H_2O$) | | 500 | 179 | 149 |
| PD-3 ($Ca_{0.6}Mg_x(PO_4)_y(HPO_4)_{1.6-y}(CaCO_3)_{4.7}(MgO)_{5.1-x} \cdot 7.8\,H_2O$) | | 500 | 40 | 149 |
| SZ-6: anionic layered compound $(NC_4H_{12})(NC_2H_8)_2[In_3(pydc)_6] \cdot 13.1\,H_2O$ (pydc is 2,5-pyridinedicarboxylic acid (Xian Research Institute of High Technology, China) | Seawater | 10 | 8.9 | 150 |
| | | 20 | 3.5 | 150 |

**Scheme 2**

(*a*) $n\,Sr^{2+} + K_{1.33}Mn_8O_{16} \rightarrow 2n\,K^+ + K_{1.33-2n}Sr_nMn_8O_{16}$

(*b*) $n\,Sr^{2+} + BaSiO_3 \rightarrow n\,Ba^{2+} + Ba_{1-n}Sr_nSiO_3$

(*c*) $2n\,Sr^{2+} + (HO)_2Zr\text{-}\bigcirc \rightarrow$
$\rightarrow 2n\,H^+ + (H_{1-n}Sr_nO)_2Zr\text{-}\bigcirc$

(*d*) $2n\,Sr^{2+} + (HO)_2PO-O\text{-}\bullet \rightarrow$
$\rightarrow 2n\,H^+ + (H_{1-n}Sr_nO)_2PO-O\text{-}\bullet$

(*e*) $nSr^{2+} + Na_2Ti_2O_3SiO_4 \cdot 2\,H_2O \rightarrow$
$\rightarrow 2n\,Na^+ + Na_{2-2n}Sr_nTi_2O_3SiO_4 \cdot 2\,H_2O$

$\bigcirc$ carbonate complex Zr(IV); $\bullet$ cellulose support

(Termoxid-3K) (*c*),[164] phosphorylated wood (FD sorbent) (*d*)[146] and silicotitanate (*e*)[130] are summarized in Scheme 2.

### 5.3. Sorption methods in analysis of $^{239,240}$Pu isotopes in seawater

Direct sorption recovery of $^{239,240}$Pu from seawater is not widespread. Plutonium and some other isotopes are concentrated by co-precipitation with $MnO_2$ (Ref. 165) or $Fe(OH)_3$.[166] The separation of plutonium from accompanying elements is based on the reduction of $Pu^{6+}$ and $Pu^{5+}$ to $Pu^{4+}$ by sodium nitrite followed by isolation of $Pu^{4+}$ nitrate complexes using highly basic anion exchange resins. The $^{236}$Pu and $^{242}$Pu isotopes were used as yield tracers.

The $MnO_2$ collector is formed upon co-proportionation of $MnCl_2$ and $KMnO_4$, which are introduced into seawater, while bring pH is brought to a slightly alkaline value.[165] The main disadvantages of precipitation methods are labour intensity and the need for decantation/siphoning of large volumes of seawater, which is accompanied by losses of the radionuclide. In particular, co-precipitation with $Fe(OH)_3$, which is a versatile collector, was used in one of the first methods[166] of recovery of plutonium isotopes from seawater together with some other radionuclides from seawater. After dissolution of the precipitate in concentrated $HNO_3$, the plutonium isotopes were separated from impurities using highly basic anion exchange resin Bio-Rad AG21-K and a concentrated HCl/1 M $NH_4I$ mixture for desorption. Later, this procedure was advanced: chemical methods for purification of the radionuclides were replaced by the use of selective extraction chromatographic resins.[42]

Several fast procedures for determination of actinides in seawater are based on the use of extraction chromatographic resins such as TEVA Resin, UTEVA Resin, TRU Resin and DGA Resin.[167, 168] The application of TEVA + TRU Resin[167] to 2 to 8 litres of seawater provides an average chemical yield of 89.3% (in terms of $^{236}$Pu); the procedure using TEVA + DGA Resin[167] and 16 to 80 litres of seawater gives 86.4% yield (in terms of $^{242}$Pu); the procedure with TEVA Resin[167] and 10 to 20 litres of seawater results in 91.1% yield (in terms of $^{236}$Pu); and the use of TEVA + UTEVA Resin[168] and processing of 10 litres of seawater produces 72.3% yield (in terms of $^{242}$Pu).

The main drawback of these methods is high cost of the sorption materials; considering the necessity of large-scale sampling in marine expeditions, wide implementation of these methods can hardly be expected.

## 6. Sorption of natural radionuclides

### 6.1. Sorption methods in analysis of $^{210}$Pb and $^{210}$Po in seawater

Like in the case of plutonium, sorption methods are not widely used for the direct recovery of $^{210}$Pb and $^{210}$Po from seawater. For this purpose, they are co-precipitated with $Fe(OH)_3$. Extraction chromatographic resins, Sr Resin and Pb Resin, based on crown ethers were proposed for the separation of $^{210}$Pb and $^{210}$Po from accompanying radionuclides.[43, 169 – 171] These sorbents consist of the same crown ether, that is, di-*tert*-butyldicyclohexyl-18-crown-6, but different diluents: octan-1-ol in Sr Resin and isodecanol in Pb Resin. Also, crown ether concentrations in the diluent are different: 1 M in Sr Resin and 0.75 M in Pb Resin. Analogues of the sorbents based on an organofluorine diluent were obtained.[172, 173]

The Sr Resin sorbent and its analogues can be used to determine $^{90}$Sr, $^{210}$Pb and $^{210}$Po. Isotopes are separated by varying the desorption conditions. When $^{90}$Sr and $^{210}$Pb are analyzed using Sr Resin, they are separated from impurities

by passing a solution of the radionuclide in 8 M nitric acid through the sorbent. The desorption of $^{90}Sr$ is performed by treatment of the sorbent with 0.05 M $HNO_3$; $^{210}Pb$ is desorbed with 6 M HCl or a 0.05 M solution of ammonium citrate.

In the case of $^{210}Pb$ and $^{210}Po$, sorption is carried out using 2 M hydrochloric acid solutions. Sorption of $^{90}Sr$ does not take place under these conditions. The $^{210}Po$ radionuclide is desorbed by treatment with 0.1–1 M $HNO_3$, while $^{210}Pb$ is desorbed with a 0.05 M solution of ammonium citrate. Due to the lower concentration of the crown ether, Pb Resin is used only for the sorption of $^{210}Pb$ and $^{210}Po$; the yield of $^{210}Po$ can be 15–25% lower than that in the case of Sr Resin.[170]

In a number of papers,[111,174,175] sorbents based on manganese compounds were proposed for the recovery of $^{210}Pb$ from seawater. Athon[111] carried out the recovery with chemisorbents based on $MnO_2$. Towler *et al.*[174] and Colley and Thomson[175] used magnetite impregnated with 14% $MnO_2$ and cartridges impregnated with manganese oxyhydroxide, respectively.

### 6.2. Sorption of radium and thorium isotopes from seawater

The recovery of radium and thorium isotopes from seawater is, most often, accomplished by sorbents based on mixed manganese oxides. The chemical composition of these sorbents is described by the simplified formula $MnO_2$; however, it was shown[51,162] that the materials comprise $K_{1.33}Mn_8O_{16}$ and $K_{1.39}Mn_3O_6$. Particularly these compounds are responsible for chemisorption of some radionuclides that occur in water as ionic species, *e.g.*, radium isotopes. As a possible mechanism of radium sorption, we proposed ion exchange (Scheme 3).[51]

**Scheme 3**

$$n\,Ra^{2+} + K_{1.33}Mn_8O_{16} \rightarrow 2n\,K^{+} + K_{1.33-2n}Ra_nMn_8O_{16}$$

Sorbents based on $MnO_2$ can be used to recover thorium isotopes and $^{7}Be$; soluble species of these radionuclides are concentrated by physical adsorption mechanism for neutral hydrolyzed forms or by ion exchange mechanism in the case of positively charged forms.

Materials used as $MnO_2$ supports include membrane filters,[176] polypropylene cartridges,[177] acrylate fibre[178,179] and cellulose fibre;[179] unsupported granulated $MnO_2$ is also used.[180] The application of $MnO_2$-impregnated membrane filters (nuclear filters) for seawater is problematic, since the concentration of radium isotopes in seawater is an order of magnitude lower[181] than that in freshwater.

A sorbent based on acrylic fibre and $MnO_2$ is used most widely for the recovery of radium isotopes. This sorbent, developed by Moore[182] in the 1970s, is practically used all over the world and is currently manufactured and supplied together with the RaDeCC counters for determination of short-lived $^{223}Ra$ and $^{224}Ra$ isotopes. For counting the indicated radionuclides, the fibre with a residual humidity of ~10% is placed into a system in which helium is circulated. The decay of the daughter radon isotopes $^{219}Rn$ and $^{220}Rn$ is registered by the detector. The long-lived $^{226}Ra$ and $^{228}Ra$ isotopes can be measured after the radiochemical sample preparation.[183] It was found[51,52] that a 20–25 g sample (~150 mL) of the sorbent based on acrylic fibre and $MnO_2$ provides a quantitative recovery of $^{226}Ra$ and $^{228}Ra$ from seawater (0.5–2 $m^3$) at a flow rate of 1–2 L $min^{-1}$.

Sorption is not widely used for the recovery of of $^{234}Th$ because of the need to perform detailed profiling of POC fluxes and to analyze the concentration of the short-lived radionuclide directly during marine expeditions. The main method used to recover $^{234}Th$ is co-precipitation with $MnO_2$. Cartridges impregnated with $MnO_2$ were proposed for the recovery of $^{234}Th$;[177] however, the validity of determination of the sorption efficiency remains an open question, since it is fairly difficult to obtain cartridges with identical efficiency. The concentration of $^{234}Th$ can be measured, together with $^{226}Ra$ and $^{228}Ra$ concentrations, by γ-spectrometry[51] after collection on a $MnO_2$-impregnated fibre.

## 7. Sorption of cosmogenic radionuclides

### 7.1. Sorption of $^{7}Be$ from seawater

The first method of the sorption of $^{7}Be$ from seawater using granulated aluminium oxide was proposed by Silker *et al.*[12] This method has a number of benefits. Aluminium oxide is a cheap and readily available material, which is used to purify gases at industrial plants and for other purposes. Direct counting of the sorbent in Marinelli vessels by γ-spectrometry is possible. The degrees of recovery of $^{7}Be$ at high sample filtration rates [~10 column volumes (CVs) per minute] are moderate: less than 60%; however, this allows reliable determination of the activity in the second adsorber and the sorption efficiency. In 2–8 $m^3$ samples, the activity can be measured even using scintillation γ-spectrometers. Currently, this method is still successfully employed. The results obtained by this method were utilized to design a mathematical model of $^{7}Be$ distribution in the surface layer of the Black Sea.[184,185]

The recovery of $^{7}Be$ from seawater is often accomplished using sorbents based on $Fe(OH)_3$ and acrylate fibre[58] or polypropylene cartridges.[76] In some cases,[81] a stable isotope is added to 0.5–1 $m^3$ seawater samples as tracers of sorption efficiency. Then the fibre is incinerated, the ash is pressed in a mould of a definite geometry for γ-spectrometry measurement. The counting samples with subsequent radiochemical preparation can be used to determine the activity of $^{32}P$ and $^{33}P$ isotopes.[76] The method proposed by Kadko and Olson[58] is most efficient for the concentration of $^{7}Be$, because the sorption efficiency of the radionuclide is determined more accurately relative to a stable isotope and because there is no need to count the radionuclide in the second adsorber, which is often associated with a higher error. The sorption efficiency can be derived from analysis of seawater samples by inductively coupled plasma mass spectrometry. However, for samples of a small volume, low-background γ-spectrometers are required. As drawbacks of this method, note large amount of the fibre used (200 g per sample) and leaching of $Fe(OH)_3$ from the support. The presence of colloidal $Fe(OH)_3$ in the solution after sorption may induce sorption of the introduced stable beryllium and non-uniform distribution of beryllium in the aliquot taken for determination of the sorption efficiency, and, as a consequence, may lead to errors.

### 7.2. Sorption of $^{32}P$ and $^{33}P$ from seawater

The lack of nutrients in seawater is a consequence of their consumption by marine microorganisms. Therefore, the biological productivity of an ecosystem is determined by the most deficient element. Most often, phosphorus is the element determining the rate of primary production.[186] The short-lived cosmogenic phosphorus isotopes can serve for

**Table 5**. Sorption parameters of natural and cosmogenic radionuclides from seawater (according to publications [111, 174]).

| Sorbent (manufacturer) | Recovered radionuclide | Solution | $V/m$, mL g$^{-1}$ | $K_d$, mL g$^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Anion exchange resin Biorad AG 1-X4 Cl impregnated with $MnO_2$ (Texas University A&M, USA) | $^{7}$Be | Artificial seawater | 1000 | $3.89 \times 10^3$ | 111 |
| | $^{210}$Pb | | 1000 | $2.88 \times 10^4$ | 111 |
| | $^{234}$Th | | 1000 | $1.07 \times 10^6$ | 111 |
| Nanostructured mesoporous $MnO_2$ (Texas University A&M, USA) | $^{7}$Be | Artificial seawater | 1000 | $4.90 \times 10^5$ | 111 |
| | $^{210}$Pb | | 1000 | $9.55 \times 10^4$ | 111 |
| | $^{234}$Th | | 1000 | $1.23 \times 10^8$ | 111 |
| Biogenic $MnO_2$ (Texas University A&M, USA) | $^{7}$Be | Artificial seawater | 1000 | $5.75 \times 10^3$ | 111 |
| | $^{210}$Pb | Artificial seawater | 1000 | $2.63 \times 10^3$ | 111 |
| | $^{234}$Th | | 1000 | $5.50 \times 10^4$ | 111 |
| Magnetic adsorbent obtained by impregnation of 14% $MnO_2$ into magnetite (University of Melbourne, Australia) | $^{210}$Pb | Seawater | 20 000 | $(5.7 – 13.3) \times 10^4$ | 174 |
| | $^{226}$Ra | | 20 000 | $(7.4 – 13.3) \times 10^3$ | 174 |

**Table 6**. Sorption parameters of natural and cosmogenic radionuclides from seawater under dynamic conditions (according to publications [65, 76, 175, 177, 179, 180, 182, 189]).

| Sorbent (manufacturer) | Recovered radionuclide | Seawater | Sorbent weight or volume in the column | Processed volume, L | Flow rate, mL min$^{-1}$ | Radiochemical yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Cartridges impregnated with $Fe(OH)_3$ (Woods Hole Oceanographic Institution, USA) | $^{32}$P, $^{33}$P | Ocean water | 1.4 L | 1000 | 4000 – 6000 | 100.0 | 65 |
| | | | 1.4 L | 1500 | 4000 – 6000 | 99.0 | 65 |
| | | | 1.4 L | 3300 | 4000 – 6000 | 90.0 | 65 |
| | | | 1.4 L | 3900 | 4000 – 6000 | 82.0 | 65 |
| | | | 1.4 L | 4000 | 4000 – 6000 | 70.0 | 65 |
| Acrylate fibre impregnated with $Fe(OH)_3$ (Woods Hole Oceanographic Institution, USA) | $^{32}$P, $^{33}$P | Ocean water | 1.4 L | 250 | 4000 – 6000 | 97.0 | 65 |
| | | | 1.4 L | 400 | 4000 – 6000 | 95.0 | 65 |
| | | | 1.4 L | 550 | 4000 – 6000 | 92.0 | 65 |
| | | | 1.4 L | 650 | 4000 – 6000 | 89.0 | 65 |
| | | | 1.4 L | 750 | 4000 – 6000 | 86.0 | 65 |
| | | | 1.4 L | 1000 | 4000 – 6000 | 81.0 | 65 |
| | | | 1.4 L | 1200 | 4000 – 6000 | 77.0 | 65 |
| Large-volume filtration and concentration system (LV-FiCS) based on cartridges impregnated with $Fe(OH)_3$ (National Institute of Radiological Sciences, Japan) | $^{7}$Be | Ocean water | See [a] | 5100 | 29400 | 85.0 ± 4.6 | 76 |
| | | | See [a] | 5500 | 22800 | 86.4 ± 3.9 | 76 |
| | | | See [a] | 4400 | 18300 | 91.0 ± 3.8 | 76 |
| | | | See [a] | 5000 | 20900 | 90.6 ± 3.2 | 76 |
| | | | See [a] | 5100 | 21200 | 87.2 ± 5.5 | 76 |
| | | | See [a] | 5500 | 22800 | 84.2 ± 3.5 | 76 |
| | | | See [a] | 4700 | 19500 | 87.3 ± 3.9 | 76 |
| | $^{32}$P | Ocean water | See [a] | 5100 | 29400 | 65.9 ± 1.2 | 76 |
| | | | See [a] | 5500 | 22800 | 66.5 ± 0.5 | 76 |
| | | | See [a] | 4400 | 18300 | 77.9 ± 1.0 | 76 |
| | | | See [a] | 5000 | 20900 | 76.5 ± 0.8 | 76 |
| | | | See [a] | 5100 | 21200 | 72.8 ± 0.9 | 76 |
| | | | See [a] | 5500 | 22800 | 66.7 ± 0.6 | 76 |
| | | | See [a] | 4700 | 19500 | 78.9 ± 0.8 | 76 |
| Cartridges impregnated with manganese oxyhydroxide (Institute of Oceanographic Sciences, UK) | $^{210}$Pb | Ocean water | See [a] | 950 – 2000 | See [a] | 96.5 ± 2.5 | 175 |
| | $^{230}$Th | | See [a] | 950 – 2000 | See [a] | 91.0 ± 6.0 | 175 |
| | $^{226}$Ra | | See [a] | 950 – 2000 | See [a] | 55.0 ± 24.0 | 175 |
| Cartridge Hytrex II impregnated with $MnO_2$ (Osmonics Inc., USA) | $^{234}$Th | Seawater | See [a] | 800 | 8000 | 86.0 | 177 |
| | | | See [a] | 800 | 10000 | 39.0 | 177 |
| | | | See [a] | 800 | 15000 | 40.0 | 177 |

**Table 6** (continued).

| Sorbent (manufacturer) | Recovered radionuclide | Seawater | Sorbent weight or volume in the column | Processed volume, L | Flow rate, mL min$^{-1}$ | Radio-chemical yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Cartridge Beta Pure impregnated with $MnO_2$ (CUNO Inc., USA) | $^{234}$Th | Seawater | See [a] | 800 | 8000 | 70.0 | 177 |
| Acrylate fibre impregnated with $MnO_2$ (Woods Hole Oceanographic Institution, USA) | $^{223}$Ra, $^{224}$Ra, $^{226}$Ra | Seawater | See [a] | 250 | 2000 | 91.0 | 179 |
| | | | See [a] | 250 | 4000 | 95.0 | 179 |
| | | | See [a] | 250 | 4500 | 80.0 | 179 |
| Acrylate fibre impregnated with $MnO_2$ (CUNO Inc., USA) | $^{223}$Ra, $^{224}$Ra, $^{226}$Ra | Seawater | See [a] | 250 | 2000 | 97.0 | 179 |
| | | | See [a] | 250 | 4000 | 90.0 | 179 |
| | | | See [a] | 250 | 8000 | 100.0 | 179 |
| | | | See [a] | 250 | 10 000 | 20.0 | 179 |
| Cellulose fibre impregnated with $MnO_2$ (CUNO Inc., USA) | $^{223}$Ra, $^{224}$Ra, $^{226}$Ra | Seawater | See [a] | 250 | 2000 | 91.0 | 179 |
| | | | See [a] | 250 | 4000 | 91.0 | 179 |
| | | | See [a] | 250 | 8000 | 100.0 | 179 |
| Hytrex impregnated with $MnO_2$ (Omonics Inc., USA) | $^{223}$Ra, $^{224}$Ra, $^{226}$Ra | Seawater | See [a] | 250 | 2000 | 75.0 | 179 |
| | | | See [a] | 250 | 4000 | 70.0 | 179 |
| | | | See [a] | 250 | 7500 | 45.0 | 179 |
| $MnO_2$ Resin (Triskem Int., France) | $^{228}$Ra | Artificial seawater | 1 g | 1 | 0.4 [b] | 91.4 | 180 |
| Acrylate fibre impregnated with $MnO_2$ (Woods Hole Oceanographic Institution, USA) | $^{226}$Ra | Seawater | See [a] | See [a] | 1000 | 87.0 | 182 |
| | $^{228}$Ra | Seawater | See [a] | See [a] | 1000 | 89.0 | 182 |
| Acrylate fibre impregnated with $Fe(OH)_3$ (University of California, USA) | $^{32}$P, $^{33}$P | Seawater | 1 L | 10 000 | 1600 | 90.0 | 189 |
| | | | 1 L | 10 000 | 3300 | 88.0 | 189 |
| | | | 1 L | 10 000 | 8300 | 90.0 | 189 |
| | | | 1 L | 10 000 | 16500 | 85.0 | 189 |
| $Fe(OH)_3$ form of Dowex 20 – 50 mesh (University of California, USA) | $^{32}$P, $^{33}$P | Seawater | 1 L | 10 000 | 2500 | 30.0 | 189 |
| | | | 1 L | 10 000 | 4100 | 28.0 | 189 |
| | | | 1 L | 10000 | 7500 | 20.0 | 189 |
| | | | 1 L | 10 000 | 14100 | 3.00 | 189 |
| | | | 1 L | 10 000 | 28300 | 2.00 | 189 |
| $Fe(OH)_3$ form of Dowex 50 – 100 mesh (University of California, USA) | $^{32}$P, $^{33}$P | Seawater | 1 L | 10 000 | 800 | 50.0 | 189 |
| | | | 1 L | 10 000 | 1600 | 35.0 | 189 |
| | | | 1 L | 10 000 | 3300 | 30.0 | 189 |
| | | | 1 L | 10 000 | 5800 | 28.0 | 189 |
| | | | 1 L | 10 000 | 9100 | 28.0 | 189 |

[a] No data are given in the source; [b] the flow rate is indicated in the source in mL cm$^{-2}$ min$^{-1}$; column parameters are not given.

determining the parameters of phosphorus biodynamics in the marine environment.[63]

There are two approaches to solving this task. The first is based on the standard method used to study metabolism in biology:[187] samples of seawater containing microorganisms are taken, and a radiotracer (most often, $^{32}$P) is added; then, after a certain period of time, water is filtered to remove the microorganisms that absorb $^{32}$P, and the residual activity of this isotope is measured. A benefit of this method is the possibility of processing numerous samples, since such activities can be easily counted by most known β-radiometers. In addition, no labour-consuming radiochemical preparation of samples is required. The main disadvantage is the difficulty of handling (production, purchase, delivery) of short-lived isotopes (5% of activity is lost every day). This method was further developed with success by Yu.I.Sorokin, a well-known oceanographer.[188] However, the commercial production of $^{32}$P was terminated for a long time.

The second approach was proposed by Lal and coworkers,[189, 190] pioneers in the studies of cosmogenic radionuclides. This method is based on the collection of $^{32}$P and $^{33}$P from seawater using a $Fe(OH)_3$-impregnated fibre. Previously $Fe(OH)_3$ was efficiently used as a collector for co-precipitation of radionuclides from rainwater.[191] Among drawbacks of this method, note the necessity of processing samples of large volume (up to 10 m$^3$), the limited time of radiochemical sample preparation, and the use of ultralow-background instruments. As a consequence, there are few studies in this field. The methods initiated by Lal were

further developed by Benitez-Nelson and Buesseler,[192] who were the first to propose polypropylene cartridges impregnated with $Fe(OH)_3$ for the recovery of $^{32}P$ and $^{33}P$ from seawater.[65] The same procedure was used by Nakanishi *et al.*[76] The impregnated cartridges recover phosphorus from seawater more efficiently than the fibre, but they have a high hydrodynamic resistance. When two adsorbers are used, costly pumping equipment is required to gain data on the sorption efficiency. Furthermore, this value would include a methodical error related to leaching of $Fe(OH)_3$ from the support. Meanwhile, when one adsorber with addition of the natural isotope is used, determination of the sorption efficiency requires the presence of tanks with a large total volume on board the ship in order to construct a detailed profile. Dovhyi *et al.*[77] used tanks with a total volume of 8 $m^3$ to recover $^{32}P$ and $^{33}P$ from seawater by single-column method with addition of stable phosphorus as the yield tracer. The sample with the highest activity (2 $m^3$) was taken from the surface and two samples (3 $m^3$ each) were taken from bottom horizons.

A promising trend is the use of sorbents made of $Fe(OH)_3$ chemically grafted to the support, *e.g.*, acrylonitrile.[193] For this purpose, acrylic fibre is oxidized with $Na_2FeO_4$, which is obtained by electrolysis. It was shown that a fibre in which hydrated iron oxides are chemically bound to a support is more efficient than the fibre impregnated with $Fe(OH)_3$.

The results of sorption of natural and cosmogenic radionuclides from seawater under static and dynamic conditions are summarized in Tables 5 and 6, respectively.

## 8. Conclusion

Today, quite a few materials for the sorption of radionuclides from seawater have been developed and studied. Some of these materials are commercially available, which makes the research and full-scale data collection during marine expeditions much easier. The distribution of radionuclides determined with a high spatial resolution makes it possible to perform numerical modelling, which provides better understanding of the processes taking place in the ocean.

Inorganic sorbents are widely used to recover radionuclides from seawater. The most efficient materials for the recovery of $^{137}Cs$ are sorbents based on TM-HCFs, which have been used for quite a long time to recover $^{137}Cs$ from radioactive waste. The experience of using these sorbents was successfully extended to the recovery of radionuclides from seawater. Sorbents based on $MnO_2$ proved to be most efficient for the recovery of $^{90}Sr$ and radium and plutonium isotopes, while $^{7}Be$ and $^{32}P$, $^{33}P$ are concentrated using $Fe(OH)_3$ supported on various materials. Fibrous sorbents have gained popularity for the recovery of radium isotopes ($MnO_2$ – PAN), $^{7}Be$ and $^{32}P$, $^{33}P$ [$Fe(OH)_3$ – PAN]. These sorbents are able to recover quite a number of radionuclides from large samples (up to several cubic metres) at a high rate (up to 10 CVs per minute); one more benefit is the possibility to further decrease the sample volume by incineration.

Undoubtedly, considerable progress has been attained in marine radiochemistry. As examples, consider modelling of the evolution of $^{137}Cs$ distributions in the Black and Barernts seas and in the Pacific Ocean;[16] study of the contribution of submarine groundwater discharge to the balance of nutrients in the Mediterranean Sea based on the data on $^{228}Ra$ balance;[194] high-resolution study of the fluxes of particulate organic matter carried out using $^{234}Th$ (Ref. 195) and $^{210}Po/^{210}Pb$;[196] study of the upwelling rate based on $^{7}Be$;[58] study of phosphorus biodynamics in relation to $^{32}P$ and $^{33}P$ (Ref. 192); and finally the recent virtually detective investigation that determined an unknown source of radioactive contamination in the Barents Sea on the basis of several radionuclides.[197]

Due to the abundance of nuclear legacy, it is important to monitor artificial radionuclides in the marine environment at the places of submersion of such facilities. In this respect, there are yet numerous methodological (improvement of methods) and practical (the application of methods to study the marine environment) aspects. Currently, mass spectrometric methods are becoming more and more important,[134, 197, 198] The manufacture and use of counters mounted on a floating bouy[199] and probing complexes[200] is being developed. Study of fundamental processes in the ocean using radiotracer methods is also highly important, taking account of the artificial impact on the marine environment, changing climate and the existence of poorly studied regions.

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## 9. List of acronyms and designations

DMM — manganese-modified wood,
FSS — ferrocyanide silicate sorbent,
HCF — hexacyanoferrate,
IAEA — International Atomic Energy Agency,
LRW — liquid radioactive waste,
MDM — modified manganese dioxide,
PAN — polyacrylonitrile,
POC — particulate organic carbon,
RaDeCC — radium delayed coincidence counter,
SCOR — Scientific Committee on Ocean Research,
STS — sodium titanosilicate,
TM-HCF — transition metal hexacyanoferrates,
WOMARS — worldwide marine radioactivity studies.

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