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Adsorbents in Nuclear Forensics (Review)

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This paper reviews radiochemical methods for manufacturing radioactive sources produced by the Soviet Union between 1960 and 1990. It is concluded that the ideas of the most interesting developments were borrowed from foreign scientific journals. It is shown that synthetic zeolites have been proposed as carriers for ⁹⁰Sr. Methods for creating ⁹⁰Sr-⁹⁰Y sources on synthetic zeolite carriers have been described. A review of other ⁹⁰Sr-⁹⁰Y sources was also made.

Information about the production method of radioactive sources can be useful in nuclear forensics. One of the key characteristics of a radioactive substance is the "age" - the date of its production. In this paper, the term "age-dating" of radioactive materials or sources is defined, and formulas for calculating the time elapsed since the production of this source are given. For effective dating calculations, it is necessary to separate the parent and daughter radionuclides contained in the source. Therefore, the paper also provides a brief overview of modern adsorbents that can be used for the effective separation of radionuclides. Such adsorbents are commercial Dowex 1x8, TEVA, Sr Resin, DGA Resin, and titanium dioxide prototypes with unique properties. The general conclusion of the work is as follows: adsorbents in nuclear forensics can be both an object of research and a necessary material for the age-dating of unknown radioactive sources.

Keywords: Radionuclides, adsorbents, radioactive sources, adsorption, age dating, nuclear forensics.

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Introduction

Nuclear forensics identifies, examines, and controls radioactive devices or compounds out of Regulatory

Control. In particular, the first task of nuclear forensics is the creation of libraries of radioactive compounds and devices. The second task is the creation of guidance on nuclear security issues relating to the prevention and detection of, criminal or intentionally unauthorized

nuclear material or other radioactive material [1]. Nuclear Forensic Science (often referred to as Nuclear Forensics) has been defined by the International Atomic Energy Agency (IAEA) as “a discipline of forensic science involving the examination of nuclear and other radioactive material, or of other evidence that is contaminated with radionuclides, in the context of legal proceedings. A nuclear forensic examination aims to obtain information on the processing history of the material (including its method and date of production) and its intended use. Moreover, hints can be obtained on the place of production and about the last legal owner.” This is achieved by measuring material properties indicative of the material's origin and processing history [1-4].

The rapid development of nuclear physics and related sciences in the early 1900s led to the use of sources of ionizing radiation in various spheres of life: from the military and defense industries to energy and aircraft construction. Various technical devices were actively developed and implemented, the main component of which was a certain radionuclide in the 50s and 60s of the last century. For example, aircraft icing detectors were based on the ^{90}Sr radiation, which was a component of the detection system. Radioactive materials have been widely used in science, agriculture, and industry, and finally, radionuclides are widely used in medicine at present time.

At the end of their service life, such devices require special disposal. Their chemical composition is not always known, they may have residual activity. Based on the knowledge of the basic methods of creating such devices, it is possible to develop recommendations to simplify their disposal and protect the environment as much as possible from the consequences of their destruction.

Nuclear forensics is "the discipline of forensics involving the examination of nuclear and other radioactive materials or other evidence contaminated with radionuclides in the context of litigation" by the International Atomic Energy Agency (IAEA).

The purpose of nuclear forensics is to obtain information about the processing history of the material (including its method and date of manufacture) and its purpose. Moreover, clues can be obtained if the place of production is established, or information about the last legal owner is obtained.

This is achieved by measuring the properties of the material, which can indicate the origin of the material and the history of its processing [1-4]. The experimental part of this work was carried out in 2020-2021. The events that took place after February 24, 2022, clearly showed that the development of radiochemistry in the aggressor country was devoted to the greatest extent to military goals and was aimed at causing maximum damage. That is, the description of the methods of production of radioactive sources is at the same time a description of the production of weapons and means of terrorist attacks against civilians, and this critically increases the need for research and development of ways to counteract such devices.

The peculiarities of the organization of scientific research in the soviet union were that foreign scientific literature was inaccessible to a wide range of scientists. Only the "chosen ones" could read foreign publications.

Therefore, if you look through the scientific publications on radiochemistry of those years, you will see

works of higher quality compared to others, the authors of which had the opportunity to get acquainted with foreign (Western) publications.

This leads to two conclusions: (a) the overall level of radiochemistry in the soviet union was still low; (c) Although there was no radiochemistry in Ukraine, thanks to the inner craving for free thinking and the active development of chemistry, our country is not inferior in intellectual and scientific capabilities to the aggressor country.

Ukrainian scientists can solve any problem related to nuclear weapons and nuclear terrorism, even without the so-called technologies.

I. Overview of methods of creating radioactive sources from 1960 to 1990

In publications from the 60s, there are descriptions of methods for the manufacture of radioactive sources. For example, publication [5] shows, that there are several methods for obtaining relatively homogeneous radioactive sources: (a) evaporation of solutions; (b) precipitation from an alcohol solution; (c) evaporation in vacuum; (d) cathodic sputtering.

A new method of electrocapillary sputtering was proposed in 1957 to produce thin, homogeneous radioactive sources on metal carriers [5], which were subsequently proposed to be placed on a spinning disk [6]. Publication [6] is devoted to the manufacture of flat β -emitters. They can be obtained by evaporation of aqueous solutions of radioactive salts on the surface of aluminum or organic glass. The main difficulty is to create conditions for uniform crystallization of salts from aqueous solutions. Even in the case of small sources (diameter = 4 cm), there is a contraction of the substance to the edges of the source, due to uneven crystallization. In the case of sources with a large diameter (up to 40 cm), the heterogeneity of the application of the radioactive substance is even greater due to the uneven drying of the solution applied to the substrate. These crystals are tightly packed near the edges of the source. In this case, crystals of radioactive salt are obtained of large sizes and separated by gaps of free space. The authors propose to obtain a fine-crystalline surface that will contain a relatively uniform concentration of radioactive substances over almost the entire area if a small amount of surfactants is added to the radioactive salt solution.

Surfactants— modifiers with dipolar-oriented molecules, which, adsorbed on the faces of the nascent crystal, were used in the work to reduce the linear growth rate of its crystals. This achieves a fine structure of the resulting crystalline surface. Surfactant additives (including isopropyl-naphthalene-sulfonic acid and two unknowns) were applied in the form of a 0.5% solution to the initial aqueous solution of the used salts of radioactive substances. In the case of large surfaces, the action of these substances also leads to a uniform distribution (spreading) of the liquid over the surface of the substrate, since they create a hydrophilic film on the surface of the "substrate"-solution distribution.

Table 1.

Results of using isopropyl-naphthalene-sulfonic acid as a surfactant

Substance	Crystal size without surfactants, mm	Crystal size with surfactants, mm
NaI	0.1	0.02
Y ₂ (CO ₃) ₃	0.1	0.04
Tl(NO ₃) ₃	0.5	0.013
Sr(NO ₃) ₂	0.005	0.002

The authors of the publication [7] arising the following stages of production of ⁵⁹Fe radioactive sources:

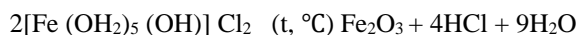
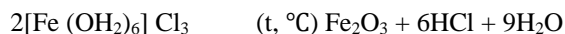
(a) preparation of radiochemically pure FeCl₃ (purification of ⁵⁹Fe isotopes from ⁵⁴Mn, ⁶⁰Co and other isotopes of γ-emitters).

(b) preparation of glass mass with an approximate composition of 3.1% BeO; 7.5% Li₂O₃; 89.4% B₂O₅. By the way, the glass was developed at the Kyiv Institute of Physics and was previously used in X-ray tubes to study the soft characteristic X-ray spectrum.

(c) Applying glass mass and FeCl₃ in the proportion of FeCl₃: glass mass 1:2 on a degreased ceramic substrate.

(d) The last stage is the heating of the mass applied to the ceramics at high temperatures. The mass is heated to temperatures of 680-720°C for 30-50 minutes.

Reactions can occur on the surface of the source:



The oxalate technique for isolating strontium from a mixture of uranium fission products was popular, and still popular in some countries at present time. This fact is evidenced by the publication [8]. The author used stable barium as a carrier for ²²⁶Ra. In this publication, the separation of ²²⁶Ra from a solution containing both radium and strontium by co-precipitation of radium with barium chromate using the salt K₂CrO₄ is described. The separation can be performed due to the difference between the ionic radii of Ba²⁺ and Sr²⁺. Then, yttrium and strontium salts were added to the filtrate, which contained ⁹⁰Sr, and yttrium was precipitated with calcium oxalates (oxalate techniques). ⁹⁰Sr was determined from the daughter ⁹⁰Y in their secular equilibrium state. It should be noted that ⁹⁰Sr was a little fascinated by barium chromate.

The paper [9] describes the adsorption of americium, curium, and californium under batch conditions by Dauex 1x4 ion exchange resin (200-400 mesh in Cl-form). The authors of this publication [9] chromatographically purified californium (97.3%) by washing it out of a column with Dowex 1x4 using 15 milliliters of a mixture of 80% and 96.6% ethanol and 2M HCl respectively, at a rate of 6-7 ml per hour. The impurities were washed out in the following order Mg, Al, Ca, Cu, Fe. The yield of purified Cf was 97±3%. Targets (sources) of californium were made by the method of electrolytic deposition from solutions. It was the quantitative deposition of thin layers of Cf on metal plates: at the first stage, the authors precipitated californium on a cathode-platinum petal, and in the next stage transferred the Cf from the cathode-

platinum petal to the metal plate). Purified HNO₃ was used as the electrolyte. The authors determined the optimal conditions for the quantitative isolation of californium on a platinum petal. The electrolyte pH was 3.1±0.1; the current density was 100-150 mA/cm². The duration of electrolysis is 110±10 minutes.

Table 2.

Distribution of ⁹⁰Sr in [²²⁶Ra]BaCrO₄ after precipitation

⁹⁰ Sr in the precipitate of [²²⁶ Ra]BaCrO ₄ , The arithmetic mean of 13 experiments, %	⁹⁰ Sr in solution, %
11.7 ± 2.5	88.3 ± 6.3
Least Value 7.9	92.0
Highest value 15.4	74.6

Metal plates were made from titanium, stainless steel, platinum, and tantalum. The method was also suitable for the manufacture of Bk sources. The authors refer to the worldwide known scientific journal "Talanta" [10, 11]. In the original article, it is stated that:

«The anion-exchange behavior of uranium, thorium, rare earth, and several other elements representing the various groups of the Periodic Table, has been investigated in 12 organic solvents containing hydrochloric acid as the complexing agent. Based on the determination of the distribution coefficients of these elements in such media, possible separation methods are indicated and discussed. The relationship between the dielectric constants of the applied solvents and the adsorption behavior of the elements is also described».

In the early 1970s, research was also carried out on TiO₂, although for some reason it was described as titanium hydroxy-oxide [12]. The authors determined the distribution coefficients under static conditions at pH = 3.5-4 and pH = 7-7.5. ⁹⁰Sr (5·10⁻⁸ Ci) 1.5·10⁻³ M SrCl₂ was studied. ⁴⁵Ca (1,5·10⁻⁷ Ci) 1,5·10⁻³ M CaCl₂. Although the author writes that he has titanium hydroxide he has oxide, this is indicated in the table, which shows the percentages of TiO₂ in each sample. The studied TiO₂ samples are of amorphous, anatase, or rutile modification with a surface area of approximately 25 m²/g.

The authors of the publication [13] mention the well-known method of isolating yttrium from rubidium chloride using the precipitation of yttrium hydroxide, followed by its dissolution and adsorption on a column with anionite in carbonate form.

Another method of yttrium separation is precipitation with iron hydroxide, followed by dissolution and adsorption on an anionic column. At the same time, iron is also adsorbed by an anionic column. The authors propose to carry out leaching with 0.01 M ammonium carbonate. The authors describe the separation of yttrium produced in the strontium target as follows: the strontium target (from which the nickel foil was mechanically removed) was dissolved in 0.1 N HCl. The dissolution process lasted 1-2 hours. The amount of acid was such that the resulting strontium solution was in the range of 0.08-0.2 N. Immediately this solution was fed into a column with anionite. Yttrium was delayed and the authors concluded that yttrium is an anion. Strontium passed

Table 3.

Data on the adsorption of strontium and calcium ions by TiO₂ samples, according to [12].

Number of samples	Features of synthesis	% TiO ₂	Structure	Size of crystallites
1	TiCl ₄ + NH ₄ OH	78	Amorphous	-
2	TiCl ₄ + KOH	71.7	Amorphous	-
2*	TiCl ₄ + KOH (t висушувания=200°C)	80	Amorphous	-
3	TiOSO ₄ + NaOH	69.4	Anatase 100%	4.6
4	TiCl ₄ +HCl+H ₂ O	87.4	Rutile	7.9

Sample	Kd ml/g (pH=3.5-4)		Kd ml/g (pH=7-7.5)	
	Sr	Ca	Sr	Ca
1	-	-	8900	1390
2	120	170	10800	2340
2*	300	230	5300	580
3	90	50	1960	280
4	-	-	400	50

through the column. It should be noted that the chemists of that time made the same mistake in considering yttrium to be an anion, or highly hydrated cation, while yttrium is a hard cation in an aqueous solution at a neutral pH, and even more so in an acidic solution. One of the differences between yttrium and strontium is the higher charge of the cation and greater reactivity with ion exchange resins. There may also be a situation in which the authors exaggerated the resolution coefficients, believing that few people would be able to verify their results.

1.1. Use of zeolites in the production of radioactive sources

At the end of the 60s, there were works on the use of zeolites for the adsorption of radionuclides ¹³⁷Cs, ⁹⁰Sr, and ⁹¹Y. One of the first works of the author [14] has an environmental orientation.

Adsorption of strontium, cesium, and yttrium by NaX zeolite was studied from NaCl solution and humic acid solution. The paper uses a linear approximation of the adsorption isotherm by Langmuir's theory, however, not quite correct. Other adsorption theories or kinetic models were not used by the authors. The results indicate that the adsorption of strontium ions by zeolite does not depend on the presence of humic acids and remains high. The adsorption of cesium is not affected by changes in the acidity of the solution, and the adsorption of yttrium is reduced by humic acids, since ⁹¹Y forms associations with humic acids.

At the beginning of the 1970s, a publication in which the adsorption of strontium ions on NaX, NaA, and CaA zeolites was investigated for the first time, and the prospect of using zeolites as carriers for ⁹⁰Sr was discussed [15-19]. The second paragraph of the publication indicates that zeolites are used as adsorbents, molecular sieves, and catalysts, however, there is no information about the use of zeolites as carriers for radionuclides. The third paragraph of the paper describes the possibility of introducing other alkaline earth elements (in this case, strontium) into zeolite instead of sodium ions, concerning literary sources, the vast majority of which are foreign.

The article concludes that the NaX zeolite turned out to be the best among the studied zeolites. This zeolite adsorbed an amount of ⁹⁰Sr greater than the equivalent

amount of sodium cations that passed into the solution. However, all strontium turned out to be firmly bonded in zeolite's pores.

The use of such an adsorbent as a carrier for ⁹⁰Sr greatly simplifies the production of ⁹⁰Sr radioactive sources, since it does not require strong purification of the original strontium solution.

The use of zeolite as a carrier for ⁹⁰Sr makes the radiation from the source uniform and reduces the accompanying gamma background. The authors refer to the works of [20-23] and several other works by R.M. Barrer. In his works, the ion exchange adsorption of a large number of cations, including Sr, Ba, Mg, and Co by synthetic zeolites, the equilibrium of ion exchange in zeolites, methods of hydrothermal synthesis of synthetic zeolites in lithium, sodium, and calcium or rubidium forms are discussed.

These are fundamental scientific works and their results were used by the authors [16]. Since the works of the author R.M. Barrer are often the first in the list of literary references of soviet authors, the conclusion suggests that the ideas of these works were "borrowed" from foreign scientists.

The possibility of adsorption of yttrium ions (or ⁹⁰Y) by zeolite can be judged from the results presented in the publication [16]. This work describes the possibilities of ion exchange adsorption of lanthanides by zeolites CaA and NaX. It was shown that the degree of substitution of sodium ions for lanthanide ions is 82% and the mobility of REEs in zeolite is lower than the mobility of sodium ions.

The adsorption of strontium, calcium, and barium ions by mordenite was described in an article [17] published in 1973. The authors showed that the adsorption values of strontium ions by mordenite are lower than by NaX zeolite. In an acidic environment, mordenite does not adsorb strontium, and in an alkaline environment, it adsorbs 65% of all strontium (in neutral pH were adsorbed 64% percent of all Sr²⁺ amount; at pH = 4 strontium cations were not adsorbed at all according to this publication [17]; however at pH = 1 a half of all Sr²⁺ (49%) was adsorbed). The authors determined the stability of mordenite in an acidic environment, that is, the instability of zeolite NaX in an acidic environment was already

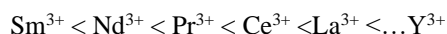
known. The authors also found that isotopes of alkaline earth elements are adsorbed in an equivalent amount to displaced sodium.

And finally, in 1974, was published a work [18], which already said that "... At present, a technology has been developed for the production of zeolites-based radioactive sources of ^{147}Pm , ^{144}Ce , ^{90}Sr , and ^{137}Cs ..." that is, the beginning of the production of ^{90}Sr sources using NaX zeolite as a carrier in the Soviet Union can be attributed to approximately 1970-1972.

Accordingly, the maximum age of such sources is not difficult to calculate.

In addition, the authors point out that a significant disadvantage of the studied zeolites is their low chemical stability in an acidic environment, which requires the use of neutral solutions of radioactive cations designed to saturate zeolite. In the case of making sources from radioactive isotopes of rare earth elements, it is difficult to keep these elements in a neutral solution, since they can change their oxidation state due to autoradiolysis. Especially when you consider that the duration of interaction sometimes reaches several days. The paper shows that in zeolite, NaY replaces 74% of all sodium with lanthanides. 16 of the 61 sodium atoms of the zeolite unit cell placed inside the "sodalite cages" cannot be replaced by lanthanides.

A series of selectivity of lanthanides on NaX zeolite (this is not a mistake, in all works the authors compare all zeolites with NaX)



The authors of publications on zeolites mainly (90%) refer to foreign articles. Probably, this indicates that the union simply did not have its works on zeolites and therefore could not have produced such sources before 1970.

The adsorption of strontium ions labeled with the ^{89}Sr from the CaCl_2 solution was investigated and described in the publication [19]. As adsorbent, there were chosen synthetic zeolites of different types: type A, type X - synthesized from various kaolin X*, X**, type Y, Z, mordenite (M), and erionite (E). It has been shown that X-type zeolites are the most selective for strontium ions.

The adsorption of uranium ions from uranyl nitrate solutions by NaY zeolite was described in an article [24] published in 1979. The initial concentration of uranium ions was in the range of 0.05N-1.0N uranyl nitrate solution. The authors showed that only one uranyl ion can enter the zeolite during ion exchange in a large plane of zeolite (super cage), which is about 100 mg/g. The introduction of more uranium, as far as I understand, leads to the destruction of zeolite.

The process of ion exchange of neodymium on NaY zeolite was investigated in [25]. There was chosen NaY zeolite as an adsorbent because it has more silicon dioxide than NaX and NaA zeolites, which can lead to greater chemical resistance in acidic environments, according to the publication [25]. The relevance of such studies is the same as in the previous works of the same authors, namely, the creation of ionizing radiation sources based on zeolites. The adsorption of neodymium was studied from Nd nitrate solutions in the range of pH = 5-0.15.

There observed an equivalence of the neodymium ion exchange to sodium. However, during decreases of pH to the acidic medium, the equivalence of ion exchange is broken. The neodymium is not introduced in place of sodium exchange cations if all sodium passes from zeolite to the solution. The surface of the adsorbent begins to be protonated. However, after the contact of zeolite NaY with 0.1N HNO_3 , this zeolite is not able to exchange hydrogen protons for neodymium ions, in other words, it is not able to adsorb neodymium.

It should be noted that in the period 1976-1990, strontium sources were also produced in the United States [26-28]. These were usually salts of strontium titanate, or SrH_2 or SrF_2 [26-32], which were the basis of thermoelectric generators.

Strontium titanate, according to [27, 28], has a perovskite structure. Radioactive beta decay does not lead to the formation of classical radiation defects [26]. Detailed studies of the chemical evolution of strontium titanate, carried out by the authors of the paper [26-28], showed that in the $\text{Sr}_{1-x}\text{Zr}_x\text{TiO}_3$ system, the formation of the structure of zirconium perovskite is very disadvantageous compared to the formation of a phase mixture of ZrO_2 , TiO_2 and an excess of metal. However, under the influence of beta decay over a long time, strontium titanate can be transformed into TiO_2 with a separate phase of ZrO_2 isolated. This is an undesirable process, from the point of view of the possibility of age dating such devices, because the separation of metals into a different phase can shift the initial ratio of $^{90}\text{Zr}/^{90}\text{Sr}$.

However, for the SrH_2 compound, phase changes in structure are not observed during the decay of ^{90}Sr in the daughter ^{90}Zr , despite their large difference in ionic charges and the size of the Sr^{2+} and Zr^{4+} cations.

Another difficulty lies in the fact that during the explosion of devices based on strontium titanates, which have a high content of yttrium and zirconium, a separate phase of pure TiO_2 (rutile and anatase modifications) is formed, and yttrium or zirconium ions are released into a separate phase and can be "lost", which also makes it impossible to accurately determine the age of the device used. We could not find scientific papers that would investigate the chemical evolution of NaX-type zeolites under the influence of beta decay. Synthetic zeolites are unstable to acids, although it is quite difficult to completely dissolve them in HNO_3 acid.

Summarizing all of the above, it can be argued that radioactive sources can be in the form of a solution, in the form of a salt, or in the form of ^{90}Sr adsorbed on a carrier.

The objects for the nuclear forensic examination can also be uranium compounds, plutonium, spent nuclear fuel, and radionuclides for medical purposes, for example, ^{60}Co , ^{90}Sr , ^{59}Fe , ^{54}Mn , ^{90}Y , ^{99}Tc , etc. Among them are synthetic radionuclides, and fission radionuclides, such as ^{90}Sr , ^{137}Cs , transuranic elements, and uranium compounds. Also, the properties of the microstructure of nanomaterials may indicate the transformation and "history" of a particular device.

A detailed study of the publications of the journal *Radiochemistry* indicates that the methods of separating radionuclides from the mixture, which were developed and implemented by the Soviet Union and are now fully adopted by the aggressor country of the Russian Federation,

are completely borrowed from foreign technologies. Among them are the use of ion exchange resins, electrochemical deposition of radionuclides on metal substrates, the interaction of radionuclides with synthetic zeolites (creation of synthetic zeolites), etc.

II. Age dating of radioactive sources or radioactive materials

One of the key characteristics of a radioactive substance from the point of view of forensics investigations is the date of manufacture of this substance. To be more precise, the date of separation of the parent radionuclide from a mixture of radionuclides, for example, ^{90}Sr from a mixture of fission radionuclides.

The date of production of the radioactive source is sometimes also referred to as the age of the radioactive device. The publication [1] states that age dating, also known as determining the date of production, is a basic, key characteristic of a "self-explanatory signature" that does not require a comparative dataset for evaluation. Dating techniques are based on the radioactive decay of parent radionuclides into daughter nuclides. For example, $^{230}\text{Th}/^{234}\text{U}$, $^{234}\text{Th}/^{238}\text{U}$ [30-32]. The measured ratios of the parent and daughter elements indicate the date of the specific step when the daughter stage was separated from the parent nuclide (e.g., ion exchange separation step, metal casting stage).

The principle of this procedure is very similar to the principle of archaeological dating and consists of separating the parent and daughter radionuclides and measuring their ratio. This principle is based on the radioactive decay law (1):

$$A = \lambda \cdot N_{\text{Sr}} \quad (1)$$

The time elapsed date production of the radioactive source may be calculated using Bateman equations (formula (2)). The experimentally determined $N_{\text{D}}/N_{\text{P}}$ ratio allows calculating the age of any radioactive source, which consists of some radio chronometer $N_{\text{D}}/N_{\text{P}}$ by the following equation:

$$T = \frac{1}{\lambda} \ln \left(1 + \frac{N_{\text{D}}}{N_{\text{P}}} \right) \quad (2)$$

λ - is the parent radionuclide's decay constant (s^{-1}); T - is the time elapsed since the last chemical separation; N_{D} is the amount of daughter radionuclide; N_{P} is the amount of parent radionuclide.

Small differences in the dating of radioactive devices for nuclear forensics and archaeological dating are the higher radioactivity doses of nuclear forensics objects compared to archaeological dating, as well as the much shorter time to be determined.

And, of course, there are differences in the parent-daughter radionuclide pairs. For archaeological dating, natural radionuclides are used, for example, $^{40}\text{Ar}/^{40}\text{K}$, while nuclear forensic objects of investigations are very radioactive, as usual, toxic and dangerous radionuclides. For example, the above-mentioned $^{230}\text{Th}/^{234}\text{U}$, $^{234}\text{Th}/^{238}\text{U}$, in addition, can be $^{244}\text{Cm}/^{246}\text{Cm}$, $^{245}\text{Cm}/^{246}\text{Cm}$, $^{90}\text{Zr}/^{90}\text{Sr}$ [1-3, 30-33]. To accurately determine the amount of these

radionuclides, it is necessary to separate them. The task of separating microquantities of radionuclides is difficult, but for some nanomaterials, it is quite "lifting".

The next section of our work will deal with nanomaterials used for the adsorption and separation of microquantities of radionuclides.

2.1. Adsorption and separation of microquantities of radionuclides using different types of adsorbents during age dating of radioactive materials

Historically, ion exchange resins played a key role in the separation of radionuclides. Ion exchange resins have retained their leading role in radiochemistry to the present day. Usually, ion exchange resins consist of an inert matrix with grafted functional groups, the most famous ion exchange resins include Dowex HCR s/s, Dowex 1x8, Sr resin, PSresin, DGA, TEVA, etc.

The properties of the ion exchange resin were determined by the type of functional groups grafted onto the inert matrix. According to the monograph [33], sulfone groups $-\text{SO}_2\text{OH}$ impart strongly acidic properties to ion exchange resin.

Dowex HCR s/s has such functional groups. Ion exchange on such ion exchangers occurs best in a strongly acidic environment and this material usually strongly adsorbs cations [our work]. Carboxyl groups $-\text{COOH}$ impart slightly acidic properties to the ion exchange resin. Quaternary ammonium groups $-\text{NR}_3^+$ impart force-base properties to ion exchange resin. Such ion exchange resins are capable of adsorbing anions from aqueous solutions.

However, oddly enough, ion exchange resins with surface quaternary ammonium groups sometimes adsorb multi-charged cations as well. Therefore, they are quite widely used for the separation of lanthanides, actinides such as thorium and uranium, and even some alkaline earth radioactive elements.

2.1.1. Dowex 1x8 and TEVA

For example, in the publication [34], an ion exchange resin based on a polystyrene matrix with quaternary amines and quaternary ammonium salt present on the surface was used to analyze plutonium isotopes.

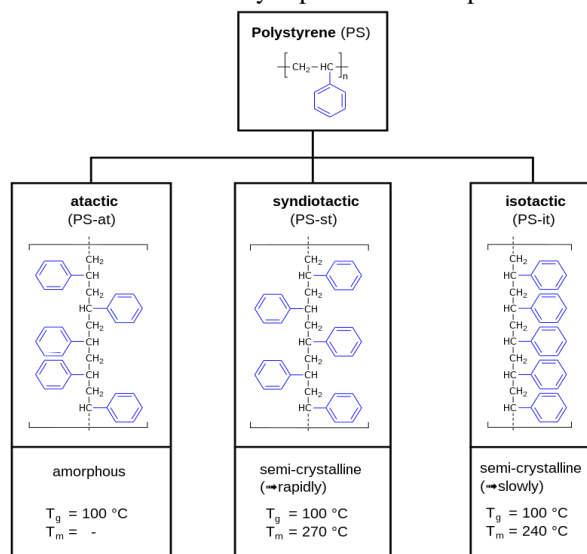


Fig.1. Examples of polystyrene matrix. Adapted from source [36].

Such an ion exchanger in combination with selective precipitation of ^{210}Pb iodates is proposed by the authors for the detection of ^{90}Sr . After all, it is known that ^{210}Pb introduces errors in the determination of ^{90}Sr using the oxalate technique [34].

A scientific publication on the dating of plutonium materials, shows, that the dating of plutonium materials can be carried out using several radio chronometers, for example, $^{241}\text{Am}/^{241}\text{Pu}$, $^{234}\text{U}/^{238}\text{Pu}$, $^{235}\text{U}/^{239}\text{Pu}$, $^{236}\text{U}/^{240}\text{Pu}$ or $^{238}\text{U}/^{242}\text{Pu}$ [35]. In addition, to separate these pairs of radionuclides, the authors use TEVA resin ion exchange resin with quaternary ammonium functional groups on the surface. It should be noted that Dowex 1x8 and TEVA resin ion exchange resins have the same functional groups (b).

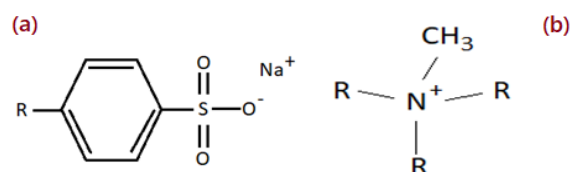


Fig.2. Surface sulfone functional groups (a) and quaternary ammonium groups (b) of ion-exchange resin.

At the same time, quite a few scientists use these materials to separate cations. The name TEVA resin stands for TEtraValent Actinides and technetium. That is, the manufacturers of this adsorbent indicate that it is designed for the adsorption of tetravalent actinides and technetium. The description of this adsorbent indicates the possible mechanism of actinide adsorption:



Fig.3. Scheme of adsorption of tetravalent actinides by anion exchange resin. 2AC^+ is an anion exchange adsorption center (quaternary ammonium salt) according to [37].

A direct comparison of Dowex 1x8 ion exchangers and TEVA resin for adsorption and experimental mass spectrometric determination of ^{99}Tc isotopes, which is also a cation, was performed in the publication [38]. The authors did not observe any significant differences in the operation of the two ion exchangers. This once again proves that the functional surface groups determine the properties of ion exchangers.

It should be noted that at the present stage, for effective adsorption of ^{90}Sr ions (which from a chemical point of view is a divalent alkaline earth cation), many authors recommend using the Sr Resin ion exchanger. It is a resin composed of inert polymer beads loaded with a 4,4'(5')-di-*t*-butylcyclohexano-6 creaser in a 1-octanol solution. In a subsequent publication [39], for a rapid method for the determination of strontium in solution, the authors suggest using Sr Resin as well.

2.1.2. Sr Resin, DGA Resin, and other materials with ion-exchange property

It should be noted that the modern analytical procedure for determining strontium in water samples is based on the use of ion exchange resin - Sr Resin.

The recommendations are as follows: strontium is separated from the rest of the radionuclides using the ion exchange resin Eichrom Sr Resin before measuring the activity using liquid scintillation, or Vavilov-Cherenkov radiation. At the initial stage, however, cation exchange resins or coprecipitation of strontium with calcium phosphate are used to concentrate strontium from water samples [40-43].

The authors of the next publication [42] use Eichrom Sr ResinTM and the isotopic dilution method to determine the strontium/zirconium ratio and age dating of strontium-yttrium sources. Strontium and zirconium are adsorbed on Sr ResinTM resin simultaneously. They are separated at the stage of eluting from the column with an adsorbent: zirconium is washed out with a mixture of acids 3 M

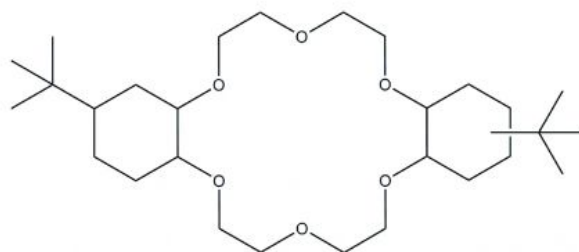


Fig. 4. Functional groups of Sr ResinTM resin are involved in the adsorption of strontium cations. Figure is adapted from source [40-43].

NO_3^- / trace HF, and strontium with a 1% acetic acid solution. The authors also used two mass spectrometry techniques, inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS), and concluded that inductively coupled plasma mass spectrometry is better suited for measuring the ratio of strontium and zirconium isotopes.

The next method of separation of strontium and zirconium, or strontium and yttrium, involves the use of solid-phase extraction using tetra-octyl-diglycolamide TODGA, comprised of inert polymer beads (DGA Normal Resin) loaded with N, N, N', N'-tetra-n-octyldiglycolamide) according to [42-44].

The use of this method makes it possible to separate strontium from yttrium with high accuracy, which greatly simplifies the oxalate technique (in fact, it makes the reaction of yttrium oxalate precipitation unnecessary). The DGA Resin can selectively collect ^{90}Y and remove naturally occurring radionuclides such as ^{40}K , ^{210}Pb , ^{214}Bi , ^{238}U , and ^{232}Th and anthropogenic radionuclides such as ^{140}Ba , and ^{140}La .

In this case, an organic extractant is also applied to a solid matrix, such as silica gel, which is inert to radionuclides. Then, under dynamic conditions, strontium and yttrium (in fact, non-radioactive ^{90}Zr – the granddaughter of ^{90}Sr) are washed out in turn using different eluents. In this way, the separation of ^{90}Sr and ^{90}Y is achieved, which greatly simplifies their

determination. According to [43], the high degree of separation of ^{90}Sr and ^{90}Y is ensured by selective adsorption of yttrium using DGA Normal Resin.

A direct comparison of Sr Resin and DGA Resin ion exchangers for age dating of strontium-yttrium radioactive sources was carried out in the publication [44]. The procedure for separating radionuclides at both ion exchangers is similar: the authors concentrate all three elements strontium, yttrium, and zirconium on an ion exchange resin under dynamic conditions. The separation of elements takes place at the stage of eluting (washing out) from the column with the adsorbent by various eluents. The difference between these two materials is that DGA Resin firmly holds yttrium in an adsorbed state (this was also pointed out by Horwitz in his works [43]), and only strontium and zirconium are eluted. In that case, their ratio is easy to measure. In the case of Sr Resin, all three elements are washed out of the ion exchanger. Therefore, when using this material for age dating of strontium-yttrium sources, it is necessary to consider the presence of

the accuracy of mass spectrometry. For example, the authors of the publication [52] used TiO_2 nanofibers to separate and concentrate thallium ions before ICP-MS. Trivalent and monovalent thallium ions are adsorbed by TiO_2 nanofibers. For mass spectrometry analysis, these cations are washed out with dilute HNO_3 .

In the next publication [53], the authors use TiO_2 nanotubes to concentrate heavy metal cations to improve their detection using ICP-MS. Adsorption of heavy metal cations by TiO_2 nanotubes took place under dynamic conditions. The authors call the adsorption process the "process of solid-phase extraction", probably by analogy with the separation of heavy metal ions by anion-exchange resin. However, the observed process is still adsorption, in our opinion. Cations (Mn^{2+} , Co^{2+} , Cr^{3+} , Zn^{2+} , and Pb^{2+}) are adsorbed on a microcolumn filled with titanium dioxide nanotubes (TDNTs) and then washed out by eluents and analyzed by ICP-MS.

The uniqueness and variety of methods for the synthesis of titanium dioxide determines the diversity of

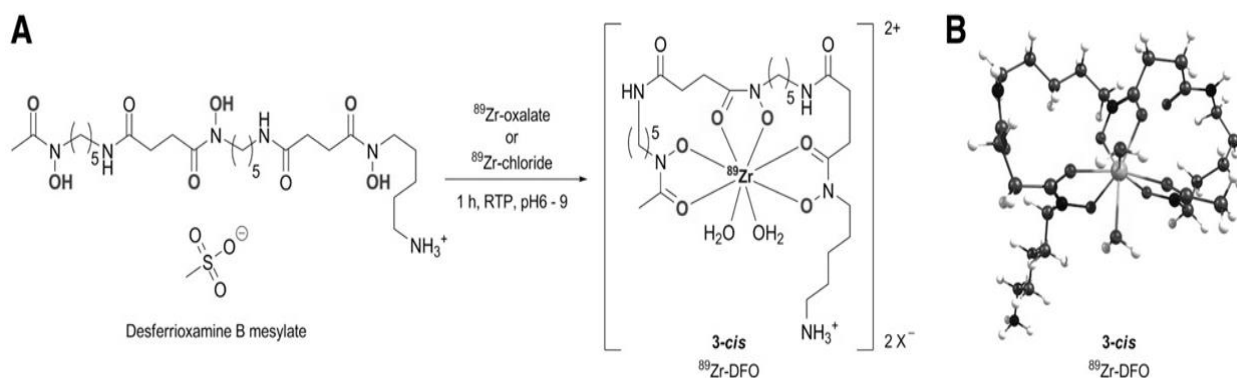


Fig.5. Scheme of the interaction of an ion exchanger based on hydroxamic acid with zirconium cations, which causes selective separation of zirconium $^{88}\text{Zr}(\text{IV})$ from a mixture with yttrium $^{89}\text{Y}(\text{III})$ and Ferrum $^{59}\text{Fe}(\text{III})$. According to works [46-49].

yttrium with strontium and zirconium in eluent solutions.

In general, for the adsorption of zirconium ions, most scientists propose an ion exchanger with weak-based properties, namely hydroxamic acid, or its salts. The use of this material for adsorption and separation of zirconium ions from yttrium ions (irradiated target) dominates in almost all modern works on the production of zirconium isotopes for medical purposes. We can cite the works [45-49] which describe, that since the scientific group Meijs et al. reported the use of hydroxamic resin to separate ^{89}Zr from atoms of a dissolved yttrium target in 1994 [45], the separation of ^{89}Zr medical zirconium PET has been carried out exclusively by this method. This is schematically shown in the figure 5, adapted from the works [46-49].

Taking into account the information provided above, the fact of selective adsorption of zirconium cations in a strongly acidic environment by an adsorbent based on TiO_2 , described in the works [50, 51], turned out to be interesting. The next section is devoted to the consideration of the results of these works.

2.1.3. Adsorbents based on titanium dioxide

First of all, it should be noted that titanium dioxide and TiO_2 -based adsorbents, such as TiO_2 nanotubes or TiO_2 nanofibers, have begun to be widely used to improve

its properties [51-59]. For example, TiO_2 nanotubes and TiO_2 nanofibers are used for adsorption of copper ions and even for high-precision detection of copper ions in environmental objects, as well as for adsorption of strontium ions.

At the same time, the authors of the paper [50] obtained high coefficients of separation of strontium cations, which increases even more in an alkaline environment. It should be noted that in the case of adsorption of strontium ions by titanium dioxide or adsorbents based on it, this is a natural pattern of pH dependence. The adsorption of strontium ions by such materials always increases when the pH passes to the alkaline region [57-60]. This is one of the differences in the adsorption of strontium ions by TiO_2 compared to organic ion exchangers, such as Dowex HCR s/s.

The next publications are devoted to the use of TiO_2 and TiO_2 -based adsorbents for the separation of strontium and zirconium to age dating of ^{90}Sr - ^{90}Y sources. The difference between these works and other methods of age dating of ^{90}Sr - ^{90}Y sources is that the authors used a batch adsorption process to separate these cations. This method of separation is somewhat unusual compared to the classical method of concentrating radionuclides on a column with an adsorbent under dynamic conditions and

subsequently washed out with the help of various eluents. The possibility of separation of cations under batch conditions is due, on the one hand, to the significant differences in the chemical properties of strontium and zirconium, and on the other hand, to the uniqueness of the properties of the used adsorbents based on TiO₂. The authors successfully used this method of separating strontium and zirconium isotopes and performed the age dating of two unknown ⁹⁰Sr-⁹⁰Y sources [61, 62].

It should be noted, that the sources, that were analyzed, were in the form of nitric acid solutions. This made the task much easier. One source contained a large amount of stable isotopes of yttrium, suggesting an oxalate technique for its production. The other source contained only a large amount of stable strontium, radioactive strontium, and trace amounts of its decay products. It was a relatively "young" source (13 years old), therefore, the method of its production has remained a mystery. The ICP-MS spectrum of this source is shown in Fig.6.

Ion exchange resins Dowex HCR s/s, Dowex 1x8, and several TiO₂-based adsorbents were compared for the separation of ⁹⁰Sr, ⁹⁰Y, and ⁹⁰Zr in batch conditions (which were identical for all adsorbents used) and were described in the publications [61-63]. The main results are shown in Table 4.

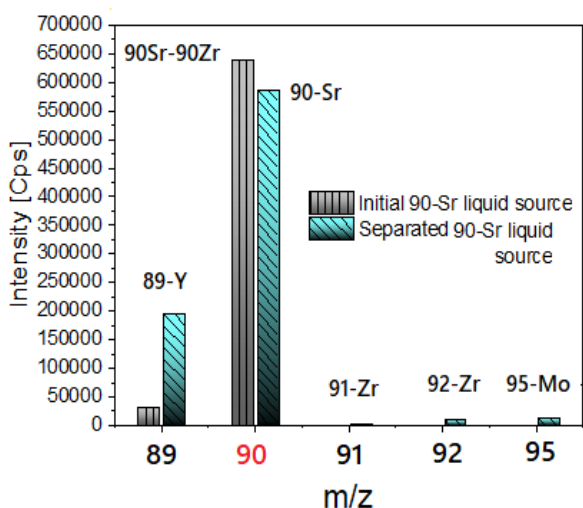


Fig. 6. ICP-MS spectrum of ⁹⁰Zr separation from ⁹⁰Sr by titanium dioxide (4C-TiO₂) in real liquid β source with the presence of an excess of stable ⁸⁸Sr (2 465 198 323 [Cps]) adapted from ref. [62].

Table 4 illustrates the selective adsorption of zirconium ions by all the studied adsorbents. The highest percentage of zirconium removal is obtained for adsorbent 4C-TiO₂. At the same time, the percentage of zirconium ions adsorption from the mixture with strontium and yttrium increases in the species of H-TiO₂, Na-TiO₂, 4As-TiO₂, and 4C-TiO₂ [62, 63].

This result is in good accordance with the quantity of acidic Brønsted sites ($\equiv\text{TiOH}^{\delta+}$) on the adsorbent surface. As can be seen from Table 4, samples of titanium dioxide are promising, since at pH=0-1 they do not adsorb nanogram amounts of strontium and yttrium at all. Therefore, the most promising adsorbents for selective adsorption of zirconium ions were 4As-TiO₂ and 4C-TiO₂.

The results shown in Table 4 show that Dowex 1x8 anion exchange resin removes 90% of all zirconium as well as 45.4% of yttrium from the strontium mixture. However, this ion exchange resin unexpectedly adsorbed rhodium, which was used as an internal standard in ICP-MS analysis [61, 62], which made this analysis difficult. The results of this table show that most of the studied TiO₂-based adsorbents selectively adsorb zirconium cations in the presence of strontium and yttrium. The separation procedure is simple, time-consuming, and does not require expensive equipment. At the same time, the used adsorbents based on titanium dioxide turned out to be inert toward rhodium and very powerful in selective adsorption of zirconium.

Finally, we would like to add a few general points that can indicate the direction of the search in nuclear forensic examination. The presence of a large amount of a stable yttrium carrier indicates an oxalate technique for separating ⁹⁰Sr from a mixture of fission radionuclides in the production of a ⁹⁰Sr-⁹⁰Y source. At the same time, the source may contain short radio chronometers of lanthanides-fission products of ²³⁵U, which decay over time. The presence or absence of these radio chronometers can confirm the general conclusions drawn from the measurement of the zirconium/strontium ratio. The presence of ⁸⁹Sr in the source may also indicate that the source is recent.

Conclusions

Radioactive sources can be in the form of a solution, in the form of a salt, or the form of ⁹⁰Sr adsorbed on a carrier. Uranium, plutonium compounds, spent nuclear

Table 4.

Results of separation of Sr²⁺, Y³⁺, and Zr⁴⁺ from a mixture of super-pure standards with initial concentrations of elements in a mixture of 10 – 100 ppb/g according to our work [62, 63].

Adsorbent	Ppb/g { ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr}	Percentage of ⁸⁸ Sr	Percentage of ⁸⁹ Y	Percentage of ⁹⁰ Zr, %
Dowex HCR s/s	10	5.87	53.64	82.16
Dowex 1x8	10	0	45.4	90.25
TiO ₂ (H-TiO ₂)	10	0	0	85.18
Na-TiO ₂	10	0	0	90.42
4As-TiO ₂	10	0	0	94.7
4As-TiO ₂	100	0	0	98.44
4C-TiO ₂	10	0	0	99.5
4C-TiO ₂	100	trace	0	99.5-100

fuel, and medical radionuclides, such as ^{60}Co , ^{90}Sr , ^{59}Fe , ^{54}Mn , ^{90}Y , and ^{99}Tc can also be material for nuclear forensic examination. Among them are synthetic radionuclides, and fission radionuclides, such as ^{90}Sr , ^{137}Cs , transuranium elements, and uranium compounds. Nanomaterials can be the basis of radioactive sources or carriers of radionuclides. Also, the properties of the microstructure of nanomaterials may indicate the transformation and "history" of a particular device. The production of radioactive strontium-yttrium sources on synthetic zeolite carriers began in 1970-1972 in the soviet union.

One of the key characteristics of a radioactive substance, from the point of view of nuclear forensics, is the date of production of this substance, in other words, age-dating. Age dating is a basic, key characteristic of a "self-explanatory signature" that does not require a comparative dataset to evaluate. Age-dating techniques are based on the radioactive decay of parent radionuclides into daughter nuclides. Materials such as Dowex, TEVA, SrResin, DGA resin, TiO_2 -based adsorbents, etc., are used for the separation of radionuclides. The possibility of separation of Sr, Y, and Zr cations under batch conditions

using TiO_2 -based adsorbent is due, to the selective zirconium ions adsorption. In this context, we may conclude the uniqueness of the properties of the titanium dioxide. The general conclusion of the work is as follows: adsorbents in nuclear forensics can be both an object of research and a necessary material for the age-dating of unknown radioactive sources. Nuclear forensics is a fairly young branch of forensics, so the separation methods and methods of analysis are still developing.

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- [1] Z. Varga, M. Wallenius, M. Krachler, N. Rauff-Nisthar, L. Fongaro, A. Knott, A. Nicholl, K. Mayer. *Trends and perspectives in Nuclear Forensic Science*, TrAC Trends in Analytical Chemistry, 146, 116503 (2022); <https://doi.org/10.1016/j.trac.2021.116503>.
- [2] *Development of a national nuclear forensics library: a system for the identification of nuclear or other radioactive material out of regulatory control IAEA*, Vienna (2018).
- [3] P. Andrew Karam. *Radiological Terrorism*, Human and Ecological Risk Assessment, 11, 501 (2005); <http://www.doi.org/10.1080/10807030590949618>.
- [4] A. Okubo, N. Shinohara, M. Magara. *Uranium age-dating using in-situ isotope ratios by thermal ionization mass spectrometry for nuclear forensics*, J. Radioanal. Nucl. Chem., 314, 231 (2017); <http://www.doi.org/10.1007/s10967-017-5379-7>.
- [5] L.Z. Malkin and others. *A facility for obtaining thin, homogeneous large-area radioactive sources*, Radiochemistry, 6(3), 258 (1964).
- [6] M.P. Kochina and others. *Method of preparation of large β -emitters*, Radiochemistry, 6(2) 120 (1964).
- [7] L.D. Danilov et al. *Method of manufacturing radioactive sources of soft X-rays*, Radiochemistry, 9(6), 742 (1967).
- [8] F.B. Himmelforb. *Determination of ^{226}Ra and ^{90}Sr in bioassays enriched with calcium phosphates*, Radiochemistry, 11(6) (1969).
- [9] V.M. Vdovenko et al. *Some Issues of Chromatographic Purification and Fabrication of Transplutonium Element Sources*, Radiochemistry. 15 (4) 534 (1973).
- [10] J. Korkisch, I. Hazan. *Anion-exchange behavior of uranium, thorium, the rare earth and various other elements in hydrochloric acid-organic solvent media*, Talanta 11, (8) 1157 (1964); [https://doi.org/10.1016/0039-9140\(64\)80166-1](https://doi.org/10.1016/0039-9140(64)80166-1).
- [11] Johann. Korkisch, Gustaf. *Arrhenius Separation of Uranium, Thorium, and the Rare Earth Elements by Anion Exchange*. Anal. Chem., 36(4), 850(1964); <https://doi.org/10.1021/ac60210a044>.
- [12] O. D. Dolmatov et al. *Sorption of ^{90}Sr and ^{45}Ca from Titanium (IV) Hydroxide Solutions*, Radiochemistry, 13 (5), (1971).
- [13] V. I. Levin et al., *Production of yttrium-87 and preparation of strontium 87 generator (isomer)*, Radiochemistry, 14(1), 110 (1972).
- [14] V.N. Shchebetkovsky. *Investigation of sorption from aqueous solutions of ^{137}Cs , ^{90}Sr , and ^{91}Y by synthetic zeolite X in sodium form*. Radiochemistry, 10(2), (1968).
- [15] N.E. Brezhneva et al. *Sorption of strontium ions on NaX, NaA, and CaA zeolites*, Radiochemistry, 12(4) (1970).
- [16] N.E. Brezhneva et al. *Study of ion exchange properties of zeolites toward radioactive rare earth elements*, Radiochemistry, 13(3), 411 (1971).
- [17] N.B. Chernyavskaya, N.R. Andreeva. *Sorption of calcium, strontium, and barium ions by mordenite*, Radiochemistry, 15(1), 111 (1973).
- [18] N.E. Brezhneva et al. *Study of ion-exchange properties of NaY zeolite to radioactive rare earth elements*, Radiochemistry, 16(5), 596 (1974).

- [19] V.A. Nikashina et al. *Study of selective sorption of strontium on various types of artificial zeolites*, Radiochemistry, 17(3), 345 (1975).
- [20] R.M. Barrer W.M. Meier *Structural and Ion sieve properties of a synthetic crystalline exchanger*, J.Cem.Soc, 1074 (1955); <https://pubs.rsc.org/en/journals/journal/jr?type=archive&issnprint=0368-1769>.
- [21] R.M. Barrer, D.C.Sammon. *Exchange Equilibria in Crystals of Chabazite*, J.Cem.Soc, 2838 (1955). <https://pubs.rsc.org/en/journals/journal/jr?type=archive&issnprint=0368-1769>, <https://doi.org/10.1039/JR9590000195>.
- [22] Contributions of R. M. Barrer to zeolite synthesis, Editor(s): Ruren Xu, Zi Gao, Jiesheng Chen, Wenfu Yan, *Studies in Surface Science and Catalysis*, Elsevier, 170, 87 (2007); [https://doi.org/10.1016/S0167-2991\(07\)80827-5](https://doi.org/10.1016/S0167-2991(07)80827-5).
- [23] R. M. Barrer, J. W. Baynham, F. W. Bultitude, W. M. Meier. *Hydrothermal chemistry of the silicates. Part VIII. Low-temperature crystal growth of aluminosilicates, and some gallium and germanium analogs* J. Chem. Soc., 195 (1959).
- [24] N.E. Brezhneva et al. *Investigation of ion-exchange properties of NaY zeolite concerning uranium*, Radiochemistry, 21(4), 524 (1979).
- [25] N.E. Brezhneva et al. *Regularities of Ion Exchange of Neodymium on NaY Zeolite from Acidic Solutions*, Radiochemistry, 22(3), 327 (1980).
- [26] Marks, N. A., Carter, D. J., Sassi, M, et al. *Chemical evolution via beta decay: a case study in strontium-90*. J. Phys.Condens. Matter, 25, 065504 (2013).
- [27] B.P. Uberuaga, C. Jiang, C.R. Stanek, K.E. Sickafus, N.A. Marks, D.J. Carter, A.L. Rohl, *Implications of transmutation on the defect chemistry in crystalline waste forms*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 268(19), 3261 (2010); <https://doi.org/10.1016/j.nimb.2010.06.001>.
- [28] V. R. van Maris, M. Naji, F. G. Di Lemma, J.-Y. Colle, D. Bykova and R. J. M. Koningsa. *The behavior of parent and daughter nuclides in aerosols released in radiological dispersion events: a study of a SrTiO₃ source*, J. of Raman Spectroscopy, 48(4), 549 (2017); <https://www.Doi.org.10.1002/jrs.5076>.
- [29] Z. Varga, M. Wallenius, K. Mayer. *Origin assessment of uranium ore concentrates based on their rare-earth elemental impurity pattern*, Radiochimica Acta, 98 (12), 771 (2010); <https://doi.org/10.1524/ract.2010.1777>.
- [30] M. Christl, N. Guérin, M. Totland, A. Gagné, Z. Kazi, S. Burrell, H.-A. Synal *A novel chronometry technique for dating irradiated uranium fuels using Cm isotopic ratios*, J. Radioanal. Nucl. Chem., 322, 1611 (2019); <https://doi.org/10.1007/s10967-019-06767-4>.
- [31] J.M. Rolison, K.C. Treinen, K.C. McHugh, A.M. Gaffney, R.W. Williams. *Application of the 226Ra–230Th–234U and 227Ac–231Pa–235U radio chronometers to uranium-certified reference materials*, J. Radioanal. Nucl. Chem., 314, 2459 (2017); <https://doi.org/10.1007/s10967-017-5619-x>.
- [32] J. M. Rolison, M. Druce, Q. R. Shollenberger, T. M. Kayzar-Boggs, R. E. Lindvall, J. Wimpenny. *Molybdenum isotope compositions of uranium ore concentrate by double spike MC-ICP-MS*, Applied Geochemistry, 103, 97 (2019); <https://doi.org/10.1016/j.apgeochem.2019.03.001>.
- [33] K.M. Mackay, R.A. Mackay, W. Henderson, *Introduction to modern inorganic chemistry* (5th ed., Blackie Academic and professional, and imprint of Chapman and Hall, 2-6 Boundary Row, London, UK (1996).
- [34] Giménez, J. Rotger, E. Apellániz, H. Bagán, J. Tent, A. Rigol, A. Tarancón. *A new method based on selective fluorescent polymers (PSresin) for the analysis of ⁹⁰Sr in the presence of ²¹⁰Pb in environmental samples*, Applied Radiation and Isotopes. 199, 110879 (2023); <https://doi.org/10.1016/j.apradiso.2023.110879>.
- [35] A. Torres, I. Giménez, H. Bagán, A. Tarancón. *Analysis of isotopes of plutonium in water samples with a PSresin based on aliquat-336*, Applied Radiation and Isotopes, 187 110333 (2022); <https://doi.org/10.1016/j.apradiso.2022.110333>.
- [36] Web data. By Minihaa - Own work, CC0, <https://commons.wikimedia.org/w/index.php?curid=82878980>.
- [37] Z. Varga, A. Nicholl, M. Wallenius, K. Mayer. *Plutonium age dating (production date measurement) by inductively coupled plasma mass spectrometry*, J Radioanal Nucl Chem., 307, 1919 (2016); <https://www.doi.org/10.1007/s10967-015-4418-5>.
- [38] K. Kołacińska, Z. Samczyński, J. Dudek, A. Bojanowska-Czajka, M. Trojanowicz. *A comparison study on the use of Dowex 1 and TEVA-resin in the determination of ⁹⁹Tc in environmental and nuclear coolant samples in a SIA system with ICP-MS detection*, Talanta, 184, 527 (2018); <https://doi.org/10.1016/j.talanta.2018.03.034>.
- [39] J. Tormos, A. Jouve, D. Revy, R. Millan-Gomez, R. Zanon, M.J. Erario, *A rapid method for determining strontium-90 in contaminated samples of soil and plant*, Journal of Environmental Radioactivity, 27(3), 193 (1995); [https://doi.org/10.1016/0265-931X\(95\)00005-U](https://doi.org/10.1016/0265-931X(95)00005-U).
- [40] *Strontium-89/90 in Water*. Analytical Procedure, (2014); available at: https://www.eichrom.com/wp-content/uploads/2018/02/srw01-15_sr-water-vbs.pdf
- [41] Web-source: <https://www.triskem-international.com/scripts/files/5f461fcf498f45.09101611/sr-resin-0.jpg>.
- [42] J. L. Steeb, D. G. Graczyk, Y. Tsai, et al., *Application of mass spectrometric isotope dilution methodology for ⁹⁰Sr age-dating with measurements by thermal-ionization and inductively coupled plasma mass spectrometry* J. Anal. At. Spectrom., 28, 1493 (2013); <https://pubs.rsc.org/en/journals/journal/ja>.

- [43] E. Philip Horwitz, Daniel R. McAlister, Anil H. Thakkar. *Synergistic enhancement of the extraction of trivalent lanthanides and actinides by tetra-(n-octyl) diglycolamide from chloride media*, Solvent extraction and ion exchange, 26(1), (2008) <https://doi.org/10.1080/07366290701779423>.
- [44] R. McLain, Y. Tsai, D. G. Graczyk, J. L. Canaday, J. L. Steeb. *An Alternative Separation Procedure for Sr-90 Age Dating Using DGA Resin*, Journal of Radioanalytical and Nuclear Chemistry, 317, 1439 (2018).
- [45] M. J. O'Hara, N. J. Murray, J. C. Carter, C. M. Kellogg, J. M. Link. *Tandem column isolation of zirconium-89 from cyclotron-bombarded yttrium targets using an automated fluidic platform: Anion exchange to hydroxamate resin columns*, Journal of Chromatography A, 1567, 37 (2018); <https://doi.org/10.1016/j.chroma.2018.06.035>.
- [46] W. E. Meijjs, J. D.M. Herscheid, H. J. Haisma, R. Wijbrandts, F. van Langevelde, P. J. Van Leuffen, R. Mooy, H. M. Pinedo. *Production of highly pure no-carrier added ⁸⁹Zr for the labeling of antibodies with a positron emitter*, Applied Radiation and Isotopes, 45(12), 1143 (1994); [https://doi.org/10.1016/0969-8043\(94\)90029-9](https://doi.org/10.1016/0969-8043(94)90029-9).
- [47] G.W. Severin, J.W.Engle, T.E. Barnhart, R.J. Nickles. *⁸⁹Zr radiochemistry for positron emission tomography*, Med Chem., 389 (2011); <https://www.doi.org/10.2174/157340611796799186>.
- [48] J. M. Link, K. A. Krohn, M. J. O'Hara. *A simple thick target for the production of ⁸⁹Zr using an 11MeV cyclotron*, Applied Radiation and Isotopes, 122, 211 (2017); <https://doi.org/10.1016/j.apradiso.2017.01.037>.
- [49] J.P. Holland, V. Divilov, N.H. Bander, P.M. Smith-Jones, S.M. Larson, J.S. Lewis. *⁸⁹Zr-DFO-J591 for ImmunoPET of Prostate-Specific Membrane Antigen Expression In Vivo*, The Journal of Nuclear Medicine, 51 1293 (2010).
- [50] H. Vasylyeva, I. Mironyuk, I. Mykytyn, M. Strilchuk., et al. *A new way to ensure selective zirconium ion adsorption*, Radiochimica Acta, 109(12), 000010151520211083 (2021); <https://doi.org/10.1515/ract-2021-1083>.
- [51] H. Vasylyeva, I. Mironyuk, I. Mykytyn, M. Strilchuk., et al. *Application of Titanium Dioxide for Zirconium Ions Adsorption and Separation from a Multicomponent Mixture*, Physics and Chemistry of Solid State, 3, 460 (2021); <https://doi.org/10.15330/pcss.22.3.460-469>.
- [52] Sh. Chen, J. Yan, J. Li, Y. Zhang, D. Lu. *Solid phase extraction with titanium dioxide nanofibers combined with dispersive liquid-liquid microextraction for speciation of thallium before electrothermal vaporization ICP-MS*. Microchim Acta, 184, 2797 (2017); <https://www.doi.org/10.1007/s00604-017-2309-x>.
- [53] Y. Zhang, S. Chen, X. Guo, D. Lu. *Solid Phase Extraction of Mn, Co, Cr, Zn, and Pb on Titanium Dioxide Nanotubes for Their Determination by Inductively Coupled Plasma MassSpectrometry*, Atomic Spectroscopy, 35(6), (2014) <https://www.doi.org/10.46770/AS.2014.06.001>.
- [54] H. Hu, Y. Lin, Y. Hang Hu, *Synthesis, structures and applications of single component core-shell structured TiO₂: A review*, Chemical Engineering Journal, 375, 122029 (2019); <https://doi.org/10.1016/j.cej.2019.122029>.
- [55] J. Paajanen, L. Pettilä, S. Lönnrot, M. Heikkilä, T. Hatanpää, M. Ritala, R. Koivula. *Electroblown titanium dioxide and titanium dioxide/silicon dioxide submicron fibers with and without titania nanorod layer for strontium(II) uptake*, Chemical Engineering Journal Advances, 13, 100434 (2023); <https://doi.org/10.1016/j.cej.2022.100434>.
- [56] B. Bejaoui Kefi, I. Bouchmila, P. Martin, N. M'Hamdi. *Titanium Dioxide Nanotubes as Solid-Phase Extraction Adsorbent for the Determination of Copper in Natural Water Samples* Materials, 15(3), 822 (2022); <https://doi.org/10.3390/ma15030822>.
- [57] I. Mironyuk, T. Tatarchuk, Mu. Naushad, H. Vasylyeva, I. Mykytyn. *Highly efficient adsorption of strontium ions by carbonated mesoporous TiO₂*, Journal of Molecular Liquids, 285, 742 (2019); <https://doi.org/10.1016/j.molliq.2019.04.111>.
- [58] I. Mironyuk, T. Tatarchuk, V. Gun'ko, H. Vasylyeva, I. Mykytyn. *Effects of chemisorbed arsenate groups on the mesoporous titania morphology and enhanced adsorption properties towards Sr (II) cations*, Journal of Molecular Liquids, 282, 587 (2019); <https://doi.org/10.1016/j.molliq.2019.03.026>.
- [59] I. Mironyuk, T. Tatarchuk, Mu. Naushad, H. Vasylyeva, I. Mykytyn. *Adsorption of Sr (II) cations onto phosphate mesoporous titanium dioxide: Mechanism, isotherm and kinetics studies*, Journal of Environmental Chemical Engineering, 7(6), 103430 (2019); <https://doi.org/10.1016/j.jece.2019.103430>.
- [60] I. Mironyuk, H. Vasylyeva, I. Mykytyn, Kh. Savka. *Sodium-modified mesoporous TiO₂: Sol-gel synthesis, characterization and adsorption activity toward heavy metal cations*, Journal of Molecular Liquids, 316, 113840 (2020); <https://doi.org/10.1016/j.molliq.2020.113840>.
- [61] H. Vasylyeva, I. Mironyuk, M. Strilchuk, K. Mayer, L. Dallas, M. Grygorenko, V. Tryshyn, et al. *Age dating of liquid ⁹⁰Sr-⁹⁰Y sources*, Applied Radiation and Isotopes, 200, 110906 (2023), <https://doi.org/10.1016/j.apradiso.2023.110906>.
- [62] H. Vasylyeva, I. Mironyuk, M. Strilchuk, *Age Dating of ⁹⁰Sr-⁹⁰Y β⁻-Source* (May 25, 2023), Available at SSRN: <https://ssrn.com/abstract=4458721> or <http://dx.doi.org/10.2139/ssrn.4458721>.
- [63] H. Vasylyeva, I. Mironyuk, M. Strilchuk, et al. *Adsorption and possibility of separation of heavy metal cations by strong cation exchange resin*, Chemical Physics Impact, 100056. <https://doi.org/10.1016/j.chphi.2021.100056>.
- [64] Ulrike Diebold. *The surface science of titanium dioxide*, Surface Science Reports, 48(5–8), 53 (2003); [https://doi.org/10.1016/S0167-5729\(02\)00100-0](https://doi.org/10.1016/S0167-5729(02)00100-0).

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У даній роботі зроблено огляд радіохімічних способів виготовлення радіоактивних джерел, які продукувались радянським союзом у період між 1960 та 1990 роками. Зроблено висновок про те, що ідеї найбільш цікавих розробок були запозичені із іноземних наукових журналів. Показано, що синтетичні цеоліти були запропоновані як носії для ^{90}Sr і описані способи виготовлення стронцій-ітрієвих джерел на носіях синтетичних цеолітів. Також зроблено огляд інших стронцій-ітрієвих джерел. Інформація про спосіб виготовлення радіоактивних джерел може бути корисною у ядерно криміналістичній експертизі. Однією із ключових характеристик радіоактивної речовини є дата її виготовлення. У даній роботі дано визначення терміну «дата виготовлення» або «датування» радіоактивних матеріалів чи джерел, наведені формули для розрахунку часу, що пройшов з моменту виробництва даного джерела. Для ефективних розрахунків датування необхідно розділити материнські і дочірні радіонукліди, що містяться у джерелі. Тому у роботі також здійснений короткий огляд сучасних адсорбентів, які можуть бути використані для ефективного розділення радіонуклідів. Серед таких адсорбентів комерційні Dowex 1x8, TEVA, Sr Resin, DGA Resin та дослідні зразки діоксиду титану з унікальними властивостями. Загальний висновок роботи наступний: адсорбенти у ядерній криміналістиці можуть бути як об'єктом досліджень, так і необхідним матеріалом для проведення датування невідомих радіоактивних джерел.

Ключові слова: Радіонукліди, адсорбенти, радіоактивні джерела, адсорбція, датування, ядерна криміналістика.