



Testing a method for ^{90}Sr determination in natural waters in radioecological monitoring

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Abstract

A method of ^{90}Sr determination in natural waters was tested in this study. The method included the steps of strontium preconcentration by a carbonate-containing zirconium hydroxide (Termoxid-3 K), strontium stripping with 1 M HCl and preparation of a counting source, followed by its measurement using a low background alpha/beta radiometer UMF-2000. Using the described method, we have determined activity concentrations of ^{90}Sr in 16 samples of natural water collected at the territories of Sverdlovsk region and Chelyabinsk region (Middle Urals, Russia) as well as 8 samples from observing wells at a radioactive waste storage facility and 3 samples from observing wells at a point of radioactive waste final disposal. The dependence of strontium chemical yield in the method on calcium concentration and water hardness was determined. It was shown that strontium chemical yield was constant ($81 \pm 2\%$) for natural waters with a hardness less than 5.2 mmol/L and calcium concentration less than 76 mg/L; thus, a control of strontium chemical yield is not necessary for such water samples. A decrease of strontium chemical yield to $66.5 \pm 1.5\%$ was observed at higher calcium concentrations up to 178 mg/L. The method provided a minimum detectable activity of ^{90}Sr as low as 0.02 Bq/L.

Keywords Strontium-90 · Carbonate-containing zirconium hydroxide · Termoxid-3 K · Sorption · Natural water · Radioecological monitoring

Introduction

Since the twentieth century, ^{90}Sr has become a component of natural ecosystems presenting in natural water, soil, and biota. Strontium shows a high ability for bioaccumulation due to its affinity for bones of humans and animals resulting in elevated internal irradiation.

The presence of fission products and actinides in the environment is conditioned by the work of enterprises of nuclear fuel cycle and nuclear weapon tests. ^{90}Sr is one of the relatively long-lived fission products with a high yield. At present, the release of anthropogenic radionuclides into the environment by the enterprises of nuclear fuel cycle is controlled strictly; however, the safety problems of radioactive waste storage facilities founded in the 1960s–1990s are still unsolved. It should be noted that these storage facilities

have been under exploitation for 35–55 years, and they do not meet the modern requirements for long-term storage of radioactive waste (RW) [1]. Thus, failure of the seal and release of radionuclides into the environment is possible that may result in the appearance of an additional source of irradiation for the population and ecosystems. In such emergencies, rehabilitation measures will be required in order to provide radiation safety including the prevention of radionuclide migration in the environment. In its turn, realization of the rehabilitation measures will require regular monitoring of radionuclides activity in contaminated landscapes [1]. Regular monitoring of territories contaminated with anthropogenic radionuclides and in-time detection of radionuclides migration from RW storage facilities are necessary for the radiation safety of the population [2].

Radiation control of territories around RW storage facilities and points of radioactive waste final disposal requires very low detection limits of ^{90}Sr in environmental samples. For example, according to the Decree of the Government of the Russian Federation No. 1847 ‘‘On approval of the list of measurements related to the scope of state regulation of ensuring the uniformity of measurements’’, the detection

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limit of beta emitting radionuclides (including strontium isotopes) in samples of seawater and water of surface water bodies is 0.02 Bq/L [3].

The same requirements for minimum detectable activity of ^{90}Sr are applied to the water of control wells at points of radioactive waste final disposal. A high calcium content in groundwater and underground water makes it difficult to achieve a low minimum detectable activity (MDA) of ^{90}Sr .

Figure 1 summarizes some methods for ^{90}Sr determination in natural waters based on selective separation of ^{90}Sr or its daughter ^{90}Y . The methods include the stages of ^{90}Sr or ^{90}Y preconcentration from a water sample, followed by selective separation, counting source preparation, and measurement. Radionuclide preconcentration steps are based on evaporation, co-precipitation, or ion exchange chromatography; whereas, extraction chromatography is commonly used for selective separation of ^{90}Y or ^{90}Sr . Water samples or counting sources should be stored to achieve equilibrium between ^{90}Sr and ^{90}Y . The suggested methods provide minimum detectable activities within 0.001–2.4 Bq/L [4–12]. The methods for providing low MDA are long and labor consuming, include many operations, and require a liquid scintillation spectrometer for measurement. Preconcentration of ^{90}Sr from seawater for further analysis is reported by Bezhin et al. [13].

The publications [14, 15] suggest a method for ^{90}Sr determination in aqueous samples based on selective preconcentration of ^{90}Sr using a carbonate-containing zirconium hydroxide (Termoxid-3 K or T-3 K sorbent produced by JSC “Inorganic Sorbents”, Zarechny city, Russia). The method provides a detection limit for ^{90}Sr in natural waters as low as

0.02 Bq/L. The detailed characteristics of the T-3 K sorbent are described in [16, 17].

The present paper is focused on the results of testing a new method of ^{90}Sr determination in natural waters during radioecological monitoring of natural waters in the territory of Ural Federal District, Russia. The water bodies of Sverdlovsk and Chelyabinsk regions were chosen for testing the analytical method because several enterprises of nuclear fuel cycle, RW storage facilities, and final disposal points, as well as lands contaminated as a result of nuclear weapon tests and major radiation accidents (mainly, accidents at “Mayak” PA, Chernobyl nuclear power plant (NPP) and Fukushima-1 NPP) are located in these regions.

Experimental

Characteristics of the sources of radioactive contamination and sampling points in Ural region

The East Ural Radioactive Trace (EURT) is one of the main locations of radioactive contamination in Ural region. A radiation accident at the “Mayak” PA in 1957 resulted in a release of $^{144}\text{Ce} + ^{144}\text{Pr}$ (66% of total activity), $^{95}\text{Zr} + ^{95}\text{Nb}$ (25%), $^{90}\text{Sr} + ^{90}\text{Y}$ (5.4%), $^{106}\text{Ru} + ^{106}\text{Rh}$ (3.7%) as well as ^{137}Cs (0.35%) and plutonium isotopes (0.0043%) to the atmosphere [18] and the formation of the EURT. Today, ^{90}Sr makes the main contribution to radioactive contamination of soils and biota due to the decay of the relatively short-lived ^{144}Ce , ^{95}Zr , and ^{106}Ru . The second radiation accident at the “Mayak” PA in 1967 resulted in the formation of the “Karachay cesium radioactive trace”, which partially

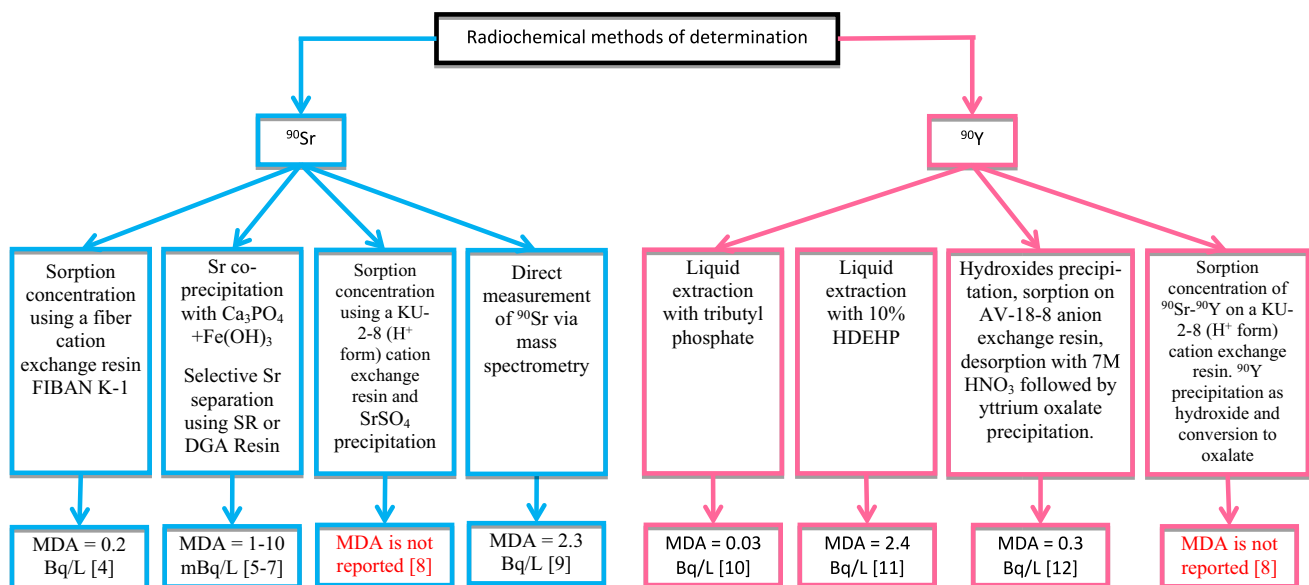


Fig. 1 The methods of ^{90}Sr determination in natural waters

coincides with the territory of EURT [19]. Daily work at the “Mayak” PA resulted in intensive radioactive contamination of the Techa River since the first years of this enterprise. Low-level liquid radioactive waste from plutonium production was released to the Techa River. The period of intensive RW release to the river was in 1949–1952 [20].

The Ural region also suffered from the world’s largest radiation accident at the Chernobyl NPP. The so-called East Chernobyl radioactive trace has passed through the territory of the European part of Russia and covered some territories of Ural region. The density of surface contamination with ^{137}Cs radionuclide in the Sverdlovsk region was 3.7–7.5 GBq/km²; however, some anomalous areas contained more than 18.5 GBq/km² [21].

In 1988–1994, aerial gamma monitoring on a 1:10,000 scale as well as automotive and pedestrian gamma monitoring on a 1:2000 scale were performed in Yekaterinburg city (Fig. 2). Totally, 439 locations of radioactive contamination were found at the territory of Yekaterinburg city. Among them, 219 locations had dose rates above 0.6 $\mu\text{Sv/h}$, 186 locations—from 1 to 10 $\mu\text{Sv/h}$, 33 locations above 10 $\mu\text{Sv/h}$ and one point with a dose rate greater than 10,000 $\mu\text{Sv/h}$ was found.

The contaminated lands remained an open source of secondary dissipation of radionuclides for a long time after the accident. Today, the release of radionuclides into river basins is conditioned by washout from radioactive drainage areas.

Radioisotopes of Kr, Xe, I, Cs, Sr, Ru, Ce etc. were released as a result of Fukushima accident [22–24]. According to the assessment by the Japan Atomic Energy Agency (JAEA) and the Nuclear Safety Commission of Japan, the release of ^{137}Cs and ^{134}Cs to the atmosphere was approximately 1.1×10^{16} Bq resulting in global dispersion

of radiocesium, a part of which is probably deposited in Ural region.

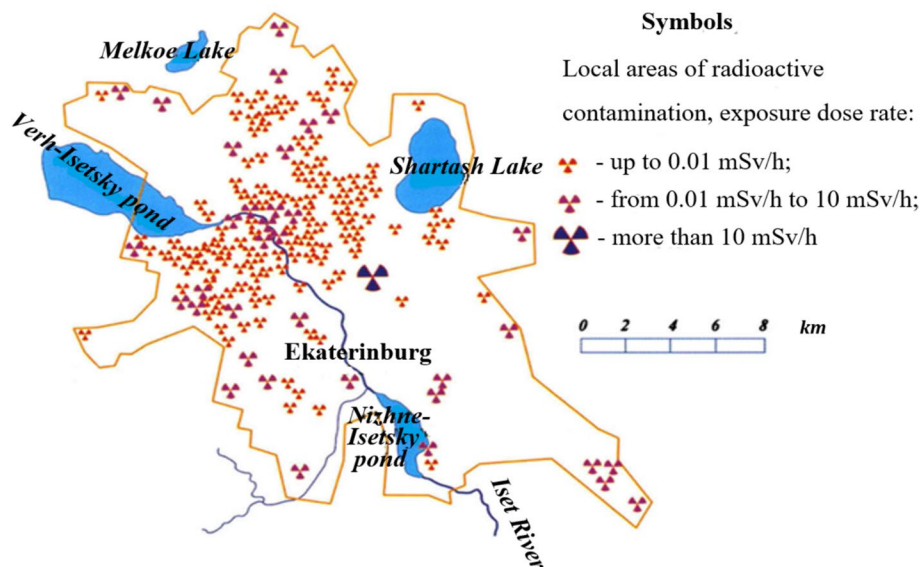
Taking into account the radioactive contamination described above, we have chosen a number of sampling points in the territories of Sverdlovsk region and Chelyabinsk region for testing the method for ^{90}Sr determination in natural waters. Seven samples were taken from natural water bodies in the Sverdlovsk region: Central, Nizhne-Isetsy and Verkh-Isetsy ponds (Yekaterinburg), Iset River in Kamensk-Uralsky, Beloyarsk Reservoir, Volchikhin Pond and Ivdel River. Among them, Volchikhin Pond is used as the main source of tap water in Yekaterinburg city. Four natural water samples were taken in the Chelyabinsk region: Sungul Lake, Kasli Lake as well as two points in Techa River (crossing the M5 road and near Muslumovo village). Additionally, 8 water samples were collected from observing wells at a RW storage facility (Federal Ecology Operator) and 3 water samples from observing wells at a point of RW final disposal (National Ecology Operator for Radioactive Waste Treatment).

Analysis of the chemical composition of the water samples and assessment of the limitations of the method for ^{90}Sr analysis

The element composition of the natural water samples was determined by ICP-MS using a mass spectrometer NexION 350X (Perkin Elmer, USA) with Total Quant software.

The water samples from observing wells at a point of RW final disposal had high calcium and magnesium concentrations. Therefore, we have studied the effect of calcium concentration on $\text{Sr}^{2+}/\text{Ca}^{2+}$ separation factor and assessed the possibility of using this method for the analysis of waters with high hardness. A dependence of $\text{Sr}^{2+}/\text{Ca}^{2+}$

Fig. 2 The map of local areas of radioactive contamination in Yekaterinburg city, Russia [21]



separation factor on calcium concentration (up to 0.6 g/L) was obtained. Certain amounts of CaCl_2 were added to tap water in order to adjust the required calcium concentration. The concentration of strontium was 1 mg/L in all solutions. The time of sorption was one week. Aliquots of solutions were collected before and after sorption and analyzed by ICP-MS.

Characteristics of the method for ^{90}Sr determination in natural waters

Analysis of ^{90}Sr was performed using a method developed by the Department of Radiochemistry and Applied Ecology, Ural Federal University. The method of ^{90}Sr analysis included four main steps: sorption of ^{90}Sr by the T-3 K sorbent, desorption of ^{90}Sr , counting source preparation, and source measurement by beta radiometry or liquid scintillation spectrometry.

The T-3 K sorbent was a carbonate-containing zirconium hydroxide, $\text{Zr}(\text{OH})_{3.5}(\text{NaCO}_3)_{0.5}$ produced commercially by JSC Inorganic Sorbents (Zarechny town, Russia). The sorbent had a grain size of 0.4–1.0 mm, a bulk density of 1.0–1.1 kg/dm^3 , and a humidity of 40.0–50.0%.

The flowsheet of the method for ^{90}Sr determination in natural waters is shown graphically at Fig. 3.

In the case of liquid scintillation spectrometry used for sample measurement, no preparation of the counting source

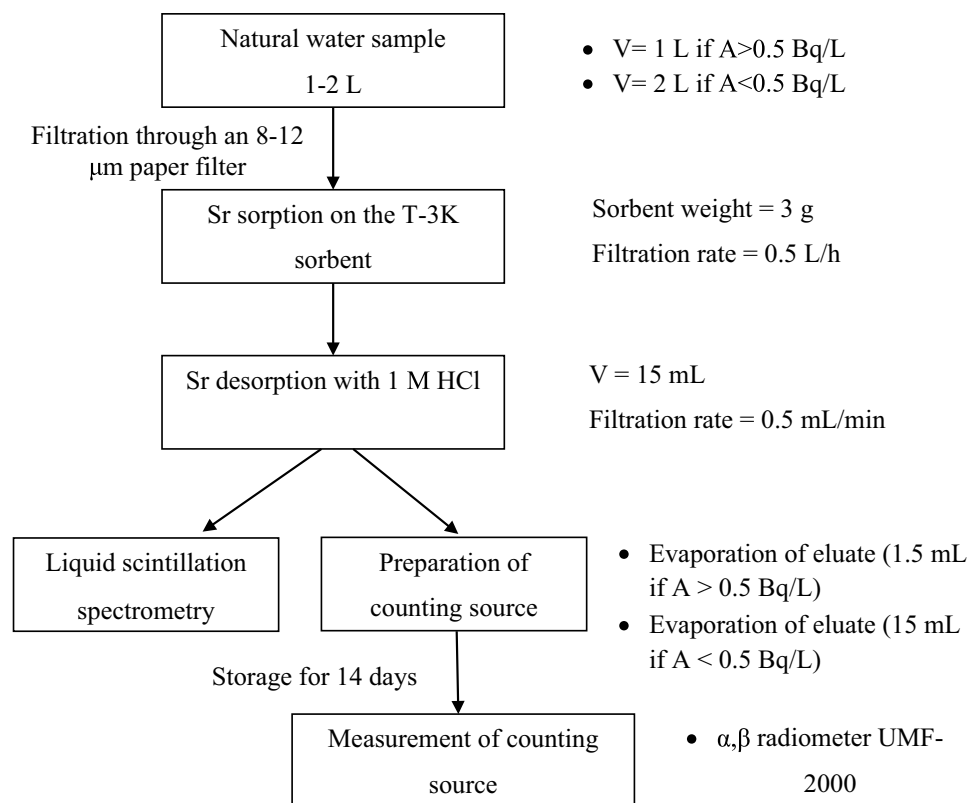
is needed. If liquid scintillation spectrometry is unavailable, the option of eluate evaporation followed by beta radiometry of the counting source is possible for routine measurements of the samples.

In the case of beta radiometry, any beta emitting radionuclides forming sparingly soluble carbonates or any beta emitting daughter decay products of radionuclides forming sparingly soluble carbonates may interfere. However, the list of potential interferences is quite limited for the analysis of natural waters or waters from observing wells at RW storage or disposal sites.

^{137}Cs is the main anthropogenic beta emitter. Cesium forms soluble carbonates and hydrocarbonates. It was shown experimentally that the T-3 K sorbent does not adsorb cesium.

^{60}Co with a half-life of 5.27 years emits low energy beta particles with a maximum energy of 0.310 MeV. The counting efficiency of ^{60}Co measurement by the UMF-2000 radiometer was 0.0457 counts per decay. A dependence of the counting efficiency of ^{60}Co on the thickness of the counting source was obtained. Considering the counting efficiency and chemical yield of cobalt in the method, we have calculated that ^{60}Co will contribute a significant count rate to a sample containing 0.02 Bq/L of ^{90}Sr (MDA for ^{90}Sr) if its activity in the water sample will be more than 1.23 Bq/L (a thin counting source) or 28.2 Bq/L (a thick counting source). Being a relatively short-lived neutron

Fig. 3 The flowsheet of the method for ^{90}Sr determination in natural waters



activation product ^{60}Co , is not a common pollutant of natural water. However, in the case of the potential presence of ^{60}Co (e.g., observing wells and waste streams at RW disposal sites), control measurement of the counting source by a gamma spectrometer is recommended.

Natural radionuclides may also interfere with the determination of ^{90}Sr . The uranium chemical yield in the method was 7.2%. After 14 days of sample storage, the decay of ^{238}U will result in the appearance of 33.1% of activity of the daughter ^{234}Th . Therefore, the activity of ^{238}U should not exceed 2 Bq/L for determination of 0.02 Bq/L of ^{90}Sr . This is an abnormally high concentration for natural waters. Uranium presence in the counting source may be controlled via the alpha activity count rate. If the alpha count rate is significantly higher than the background count rate, gamma spectrometry measurements of the counting source will be required.

The T-3 K sorbent can uptake also ^{226}Ra and ^{228}Ra from natural waters if they are present there. Radium desorption from the T-3 K sorbent is rather complicated than that of strontium. This provides a lower chemical yield of radium. ^{226}Ra is an alpha emitter, which decays to alpha emitting ^{222}Rn and several short-lived beta emitting daughter products. Since ^{222}Rn is an inert gas, it will emanate from the counting source during storage; thus, beta-emitting ^{214}Pb and ^{214}Bi should not contaminate the counting source. ^{228}Ra is a beta emitter that has a short-lived ($T_{1/2}=6\text{ h}$) beta emitting daughter ^{228}Ac . Nevertheless, the typical activities of ^{226}Ra and ^{228}Ra in natural waters do not exceed several mBq/L, so low interference is expected, taking into account a lower chemical yield of radium.

Finally, a long-lived natural beta emitter ^{210}Pb may present in natural waters and waste streams. The T-3 K sorbent adsorbs lead well with a chemical yield of 83%. However, we expect a low interference from ^{210}Pb due to its low beta energy and low activities in natural waters.

The analysis of the natural water samples was performed according to the suggested method with measurements by a beta radiometer. The 2 L water samples were filtered through an 8–12 μm paper filter prior to analysis. Then the samples were loaded through a T-3 K sorbent column using a Masterflex L/S peristaltic pump, followed by elution of ^{90}Sr with 1 M HCl solution. The eluate was evaporated on a 4-cm planchet. The counting source was stored for 14 days in order to achieve radioactive equilibrium between ^{90}Sr and ^{90}Y , followed by measurements using a low background alpha/beta radiometer UMF-2000 (Doza Company, Moscow, Russia). The volume of the eluate and measurement time were chosen, taking into account the suggested activity concentration of the sample and the relative error required.

Water samples with a natural content of stable strontium (0.03–0.66 mg/L) were analyzed. The dependence of strontium chemical yield on calcium concentration and water hardness was plotted using the results of ^{90}Sr determination in the water samples.

Results and discussion

Characterization of sampling points and chemical composition of the natural water samples

We have collected and analyzed 16 samples of natural water from water bodies in Sverdlovsk and Chelyabinsk regions from October 2021 to May 2023. The sampling points are shown on the respective map (Fig. 4). Table 1 shows the data on pH and concentrations of alkaline earth elements in the samples of natural water collected.

The pH values of the water samples was within 7.3–8.4 that corresponded to the maximum strontium sorption at the pH dependence curve for the T-3 K sorbent (Fig. 5). Therefore, preconcentration of strontium was conducted at the optimal pH range for the T-3 K sorbent, and the effect of pH of the samples was insignificant.

Table 1 shows significant variations of calcium and magnesium concentrations in natural waters—from 12.74 to 106.6 mg/L and from 3.05 to 54.5 mg/L respectively. The lowest hardness was in the water of the Ivdel' River, whereas the Techa River and Yekaterinburg City Pond had the highest hardness. Also, the water of the Techa River contained the highest concentration of natural strontium. Concentrations of barium did not exceed 0.07 mg/L in all samples; therefore, its effect on strontium chemical yield is assumed to be insignificant.

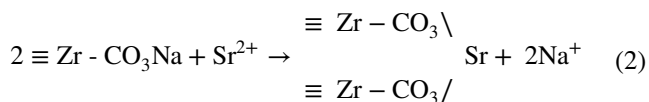
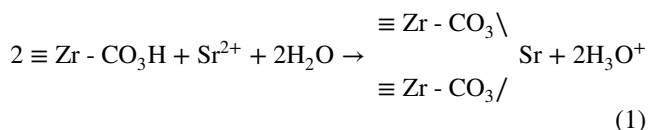
The water samples from the observing wells at the RW disposal site contained up to 177.8 mg/L of calcium and up to 43.2 mg/L of magnesium. Such a high content of alkaline earth ions in the samples motivated us to study the effect of Ca on strontium sorption by the T-3 K sorbent and thus to assess the limitations of the suggested method.

The study of the sorption properties of the T-3 K sorbent for strontium in the presence of calcium up to 600 mg/L

Alkaline earth ions may show a competitive effect on strontium sorption by the T-3 K sorbent. The Eqs. 1 and 2 describe the mechanism of strontium sorption by the T-3 K sorbent:



Fig. 4 Sampling points in Sverdlovsk and Chelyabinsk regions



Distribution coefficient of strontium sorption by the T-3 K sorbent is $(1.3 \pm 0.6) \cdot 10^4$ mL/g [17]. Sorption occurs due to the formation of a sparingly soluble strontium carbonate, which is characterized by a low solubility product $K_{\text{sp}}(\text{SrCO}_3) = 5.3 \times 10^{-10}$. The affinity of the sorbent for the alkaline earths follows in the series $\text{Sr} > \text{Ba} > \text{Ca} > \text{Mg}$, which is determined by a decrease of solubility of their

carbonates. The solubility products of alkaline earth carbonates are $\text{MgCO}_3 = 7.9 \times 10^{-6}$, $\text{CaCO}_3 = 4.4 \times 10^{-9}$, $\text{SrCO}_3 = 5.3 \times 10^{-10}$, $\text{BaCO}_3 = 4.9 \times 10^{-9}$ [25].

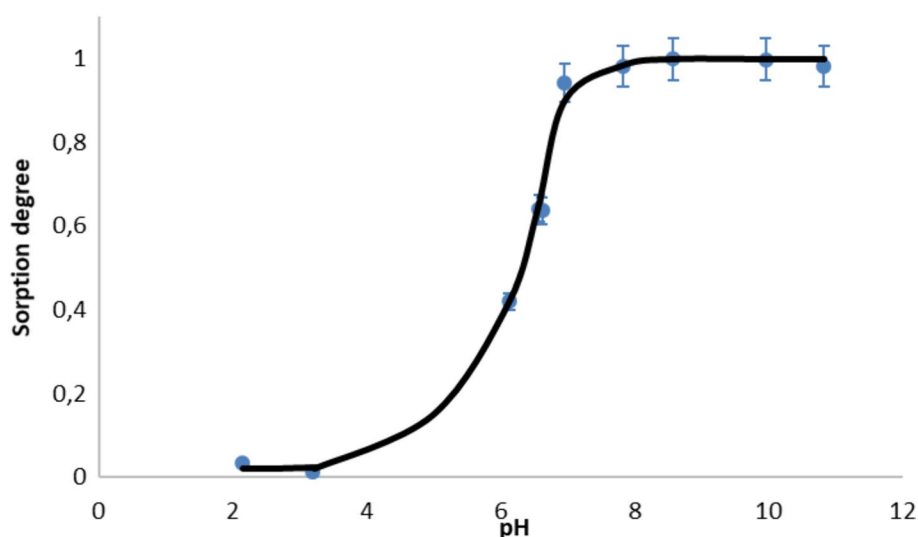
Figure 6 demonstrates a dependence of $\text{Sr}^{2+}/\text{Ca}^{2+}$ separation factor on calcium concentration (up to 600 mg/L).

Separation factor R ($\text{Sr}^{2+}/\text{Ca}^{2+}$) decreased with the increase in calcium concentration but remained almost constant (2–2.2) within the calcium concentration range of 50–600 mg/L.

The maximum separation factors for Sr/Ca and Sr/Mg on the T-3 K sorbent were achieved in case of strontium preconcentration from a spring water containing 13.96 mg/L of Ca and 16.37 mg/L of Mg; the respective values were $R(\text{Sr}^{2+}/\text{Mg}^{2+}) = 74.0$ and $R(\text{Sr}^{2+}/\text{Ca}^{2+}) = 51.2$ [26]. High separation factors were also obtained for low mineralized water

Table 1 Characteristics of natural water samples

Sampling point	Coordinates	Sampling date	Concentration, mg/L				pH
			Ca	Mg	Sr	Ba	
Beloyarsk reservoir	56.8265, 61.3194	01.10.2021	33.67	17.38	0.23	0.03	7.9
Central city pond (Yekaterinburg)	56.8455, 60.5926	03.10.2021	53.54	19.38	0.28	0.03	8.0
Nizhne-Isetsy pond (Yekaterinburg)	56.7481, 60.8953	21.11.2021	27.29	17.69	0.25	0.03	8.1
		28.03.2022	19.43	9.47	0.17	0.02	7.6
		27.06.2022	30.15	9.79	0.18	0.06	8.1
		18.09.2022	41.42	17.13	0.27	0.07	8.4
Iset river (Kamensk-Uralsky)	56.3972, 61.9481	11.12.2021	28.46	18.00	0.22	<0.01	7.7
Verkh-Isetsy pond (Yekaterinburg)	56.8376, 60.5279	12.05.2022	24.71	8.05	0.41	0.04	7.8
Ivdel river	60.6994, 60.3971	10.05.2022	12.74	3.05	0.03	<0.01	7.3
Volchikhin pond	56.8005, 60.0199	14.05.2022	26.47	9.58	0.09	<0.01	7.7
Sungul lake	55.9825, 60.7062	10.10.2021	34.04	18.61	0.34	0.03	8.6
Kasli lake	55.9356, 60.7781	10.10.2021	21.75	16.55	0.27	0.02	8.4
Techa river crossing M5 road (Yekaterinburg-Chelyabinsk)	55.6069, 61.3133	10.10.2021	106.57	51.11	0.66	0.07	8.4
Techa river near Muslumovo village	55.6144, 61.6246	10.10.2021	20.36	54.47	0.27	<0.01	7.8
Rezh river	57.6012, 61.7401	13.05.2023	39.02	17.9	0.20	0.02	8.1
Spring at Deevo village	57.5678, 61.6560	13.05.2023	85.87	11.21	0.30	0.03	7.9

Fig. 5 The pH dependence of the degree of strontium sorption by the T-3 K sorbent

containing 14.3 mg/L of calcium; $R(\text{Sr}^{2+}/\text{Mg}^{2+}) = 12.8$ and $R(\text{Sr}^{2+}/\text{Ca}^{2+}) = 8.9$ [14].

Thus, the suggested method can be applied for the analysis of water samples with high hardness due to good Sr/Ca separation factors even at high calcium concentrations and the high static exchange capacity of the T-3 K sorbent (44 ± 6 mg/g [17]). This was approved by a series of experiments on strontium preconcentration from waters with a wide hardness range.

Assessment of the effect of calcium concentration and water hardness on strontium chemical yield in the method

Figure 7 demonstrates the dependence of strontium chemical yield on calcium concentration in the sample.

In the case of 16 water samples with a volume of 2 L, the average strontium chemical yield was $81 \pm 2\%$ decreasing only at the calcium concentration of more than 76 mg/L or

Fig. 6 The dependence of $\text{Sr}^{2+}/\text{Ca}^{2+}$ separation factor on calcium concentration

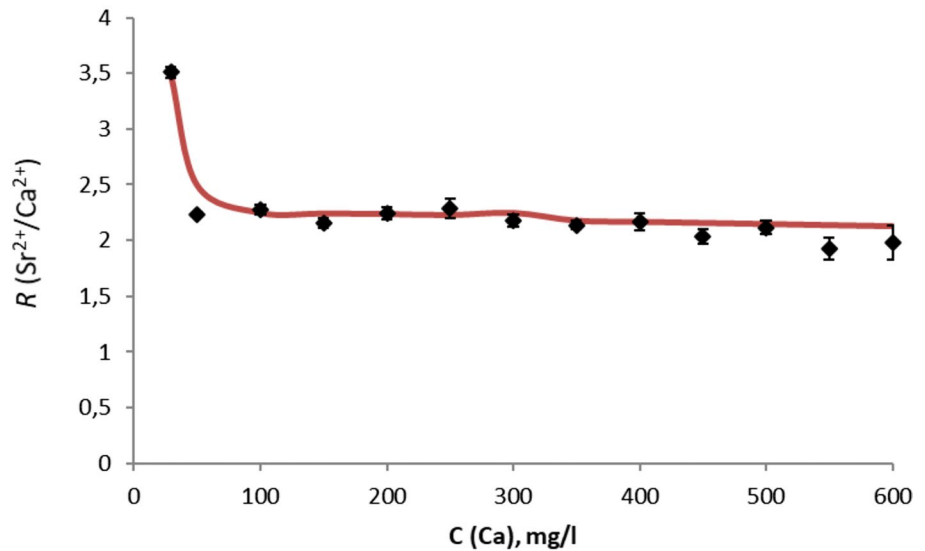
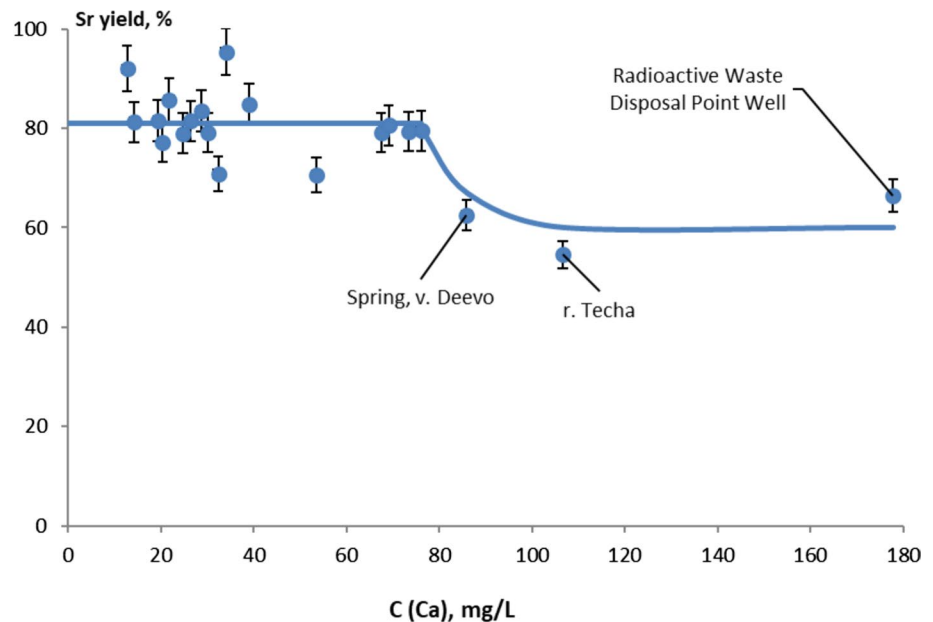


Fig. 7 The dependence of strontium chemical yield on calcium concentration in the sample



total water hardness of more than 5.2 mmol/L. Only two of the 16 tested natural water samples had higher concentrations of alkaline earth elements—the water in the Techa River near Muslumovo village and the spring in Deevo village. An increased salt content in the Techa River was associated with the shallowing of the river due to drought and evaporation of water. In the case of water from the Techa River, the strontium chemical yield was 54.6%. The samples from the RW disposal site demonstrated a much higher hardness. Nevertheless, strontium yield remained as high as $66.5 \pm 1.5\%$ even at calcium concentrations up to 177.8 mg/L.

The minimum detectable activity (MDA) was calculated by two methods, taking into account the worst conditions: the

strontium yield = 54.6% and the counting efficiency = 0.143 counts per decay. According to an approach described in [14], we have calculated the MDA value taking into account the strontium yield, counting time, counting efficiency, and sample volume; the MDA value was 0.02 Bq/L. Alternatively, we have calculated the MDA value in accordance with ASTM Standard [27] by Eq. 3:

$$\text{MDA} = \frac{2.71 + 4.66\sqrt{I_b}}{t \times Y \times \varepsilon} \quad (3)$$

where I_b is the blank count rate, ε is the counting efficiency, t is the counting time, and Y is the chemical yield. The respective MDA value was 0.003 Bq/L.

The results of determination of ^{90}Sr activity concentrations in natural waters from Sverdlovsk and Chelyabinsk regions

Activity of the samples were calculated according to the Eq. 4 taking into account the counting efficiency for equilibrium ^{90}Sr – ^{90}Y by the UMF-2000 beta radiometer:

$$A = I/\varepsilon \quad (4)$$

where A is activity of the counting source, Bq; I is the count rate, cps; ε is the counting efficiency, counts per decay. Figure 8 shows the dependence of the counting efficiency on the thickness of the counting source.

Fig. 8 The dependence of the counting efficiency on the thickness of the counting source

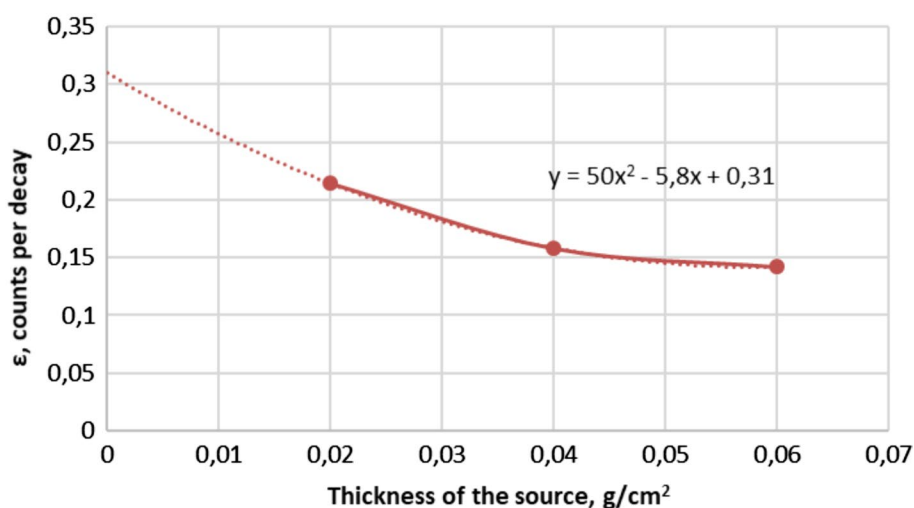


Table 2 Activity concentrations of ^{90}Sr in natural waters collected at Sverdlovsk and Chelyabinsk regions

Sample	Activity of ^{90}Sr (in equilibrium with ^{90}Y), Bq/L	$^{90}\text{Sr}/^{137}\text{Cs}$ activity ratio
Beloyarsk reservoir	0.08 ± 0.02	0.64
Central city pond (Yekaterinburg)	0.04 ± 0.01	0.5
Nizhne-Issetsky pond (Yekaterinburg)	0.16 ± 0.02 (21.11.2021)	0.12
	0.02 ± 0.01 (28.03.2022)	0.18
	0.02 ± 0.01 (27.06.2022)	
	0.03 ± 0.01 (18.09.2022)	
Iset river (Kamensk-Uralsky)	0.04 ± 0.01	2.86
Verkh-Issetsky pond (Yekaterinburg)	0.05 ± 0.01	0.46
Ivdel river	0.03 ± 0.01	0.21
Volchikhin pond	0.02 ± 0.01	0.17
Sungul lake	0.03 ± 0.01	0.06
Kasli lake	0.04 ± 0.01	0.48
Techa river crossing M5 road (Yekaterinburg-Chelyabinsk)	51 ± 1	106
Techa river near Muslumovo village	56 ± 3	394
Rezh river	< 0.02	n/a
Spring at Deevo village	< 0.02	n/a

Table 2 shows the results of the determination of ^{90}Sr activity concentrations in the water samples as well as $^{90}\text{Sr}/^{137}\text{Cs}$ ratios in them.

The water samples collected from Techa River contained the highest activities of ^{90}Sr (~50 Bq/L) that is conditioned by the release of low-level liquid radioactive wastes into the river from Mayak PA in 1950s. All other water samples have shown activities of ^{90}Sr ranging from 0.02 to 0.16 Bq/L, which is much less than the allowed limit of ^{90}Sr in drinking water in Russia (4.9 Bq/L according to the Russian National Norms of Radiation Safety-99/2009 [28]).

An elevated content of ^{90}Sr (excluding water from the Techa River) was found in the water from Nizhne-Issetsky

Pond (Yekaterinburg). Monitoring of seasonal variations of ^{90}Sr in this pond has shown a ^{90}Sr activity concentration (in equilibrium with ^{90}Y) of 0.16 ± 0.02 Bq/L in November 2021. Then activity decreased to 0.02–0.03 Bq/L in spring, summer, and autumn. Probably, contamination of Nizhne-Isetsy Pond with ^{90}Sr was conditioned by the transfer of this radionuclide from the bottom sediments of this pond as well as runoff from contaminated soils. In winter, the pond freezes, and the flow rate decreases, resulting in an increase of the radionuclide concentration in the water.

$^{90}\text{Sr}/^{137}\text{Cs}$ activity ratios were determined in the water samples in order to determine the potential source contamination. Analysis of ^{137}Cs activity concentration was performed in the same water samples; the results were reported in [29]. It can be supposed that atmospheric fallouts after the Chernobyl disaster in 1986 were the most probable source of contamination of the soils and bottom sediments affecting the radioactivity of Nizhne-Isetsy Pond since the typical $^{90}\text{Sr}/^{137}\text{Cs}$ ratio in the Chernobyl radioactive trace is 0.1–0.2 [21]. The $^{90}\text{Sr}/^{137}\text{Cs}$ ratio in the Ivdel River was found to be 0.21, indicating Chernobyl fallouts as the source of radioactive contamination too. The Ivdel River also flows through the northern zone of the Chernobyl radioactive trace.

Contamination of water in Verkh-Isetsy Pond and Central City Pond (Yekaterinburg) showed the values of $^{90}\text{Sr}/^{137}\text{Cs}$ activity ratios within 0.4–0.6 that is typical for global fallouts after nuclear weapon tests. The values of the $^{90}\text{Sr}/^{137}\text{Cs}$ activity ratio in the water from the Techa River, the Iset River near Kamensk-Uralsky city, and Beloyarsk Reservoir significantly differed from those values typical for Chernobyl fallouts and global fallouts. This can be explained by the fact that these water bodies are located in the influence zones of nuclear fuel cycle enterprises, or EURT.

The results of monitoring were compared with the literature data (see Table 3). There is no open data on the systematic monitoring of ^{90}Sr in the natural waters of Ural region; the available data are fragmentary and refer to different years. Also, there is no literature data on monitoring

of ^{90}Sr in the water of the Iset River in Yekaterinburg, the Ivdel River and the Volchikhin Pond.

In case of large water bodies such as the Sungul Lake, the Kasli Lake, and the Beloyarsk Reservoir, our determined activities of ^{90}Sr were quite similar to the literature data. However, the experimental data may differ significantly from the literature data in the case of small water bodies, where water levels may vary depending on precipitation. So, our data for the Techa River near Muslumovo village exceeds the reported data in 2010 by 35%. This difference may be due to the dry summer of 2021 resulting in the evaporation of water in the river and concentration of radionuclides.

The results of the study have shown also that the activities of ^{90}Sr in water samples from observing wells did not exceed the control levels.

Conclusions

Testing a new method for determination of ^{90}Sr in natural waters based on selective preconcentration of strontium by a T-3 K carbonate-containing zirconium was performed during the radioecological monitoring of natural waters in the territories of Sverdlovsk region and Chelyabinsk region (Middle Urals, Russia).

The dependence of strontium chemical yield on calcium concentration in the sample was obtained. It was shown that strontium chemical yield of $81 \pm 2\%$ was constant for the samples containing up to 76 mg/L of calcium or ≤ 5.2 mmol/L of total hardness salts. The strontium yield decreased to $66.5 \pm 1.5\%$ at higher calcium concentrations up to 177.8 mg/L. The minimum detectable activity of ^{90}Sr in 2 L water samples was calculated to be 0.02 Bq/L.

Activity concentrations of ^{90}Sr were determined in 16 samples of natural waters from water bodies in the influence zones of nuclear weapon tests at the Novaya Zemlya testing venue, Chernobyl radioactive trace, East Ural radioactive trace, as well as the daily activity of nuclear fuel cycle enterprises. The monitoring of ^{90}Sr activity was performed for the

Table 3 Activity concentrations of ^{90}Sr in some natural surface waters of Ural region

Sample	Year of analysis	Activity concentration of ^{90}Sr , Bq/L	References
Beloyarsk reservoir	2019	0.14	[30]
Techa river near Muslumovo village	2010	18.5	[31]
Techa river, Asanovskoye swamp (near M5 Yekaterinburg–Chelyabinsk road)	2013	26.1–27.2	[32]
Sungul lake		< 0.03	
Kasli lake		< 0.03	
Iset river (Kamensk-Uralsky)		0.4	

first time for some of the natural water bodies. In addition, the method was tested using 8 samples from observing wells at a radioactive waste storage facility and 3 samples from observing wells at a point of radioactive waste final disposal.

It was shown that the water samples collected from the Techa River near Muslumovo village contained the highest activity of ^{90}Sr (56 ± 3 Bq/L in equilibrium with ^{90}Y). The activities of ^{90}Sr in all other water samples were much less than the allowed limit of ^{90}Sr in drinking water in Russia (4.9 Bq/L). The activities of ^{90}Sr in water samples from observing wells did not exceed the control levels.

It was established that contamination of the water of Nizhne-Isetsy Pond (Yekaterinburg) by ^{90}Sr occurred because of runoff from contaminated coastal soils. Seasonal variations of ^{90}Sr activity concentration in this pond were studied. The maximal ^{90}Sr activity in the pond (0.16 Bq/L) was found in winter. Chernobyl fallouts were suggested as the most probable source of contamination in the pond.

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Data availability All raw data are available by request via the corresponding author's e-mail: av.voronina@mail.ru or a.v.voronina@urfu.ru.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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