



Original Article

Analysis of ultra-low radionuclide concentrations in water samples with baromembrane method



Maxim Vasyanovich ^{a, *}, Aleksey Ekin ^a, Alexander Trapeznikov ^b, Anatoly Plataev ^b

^a Institute of Industrial Ecology UB RAS, Ekaterinburg, Russia

^b Institute of Plant and Animal Ecology UB RAS, Ekaterinburg, Russia

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ABSTRACT

This work demonstrates the use of baromembrane method based on reverse osmosis (RO) process. The method is realized on mobile complex, which allows to concentrate and determine ultra-low activity of radionuclides in water cooling ponds of Russian nuclear fuel cycle enterprises. The existence level of radionuclide background creates difficult conditions for identification the contribution of liquid discharges enterprise, as standard monitoring methods have a very high detection level for radionuclides. Traditional methods for determining the background radionuclides concentrations require the selection of at least 500 liters (l) of water, followed by their evaporation to form a dry residue. This procedure with RO membranes requires at least 5 days. It is possible to reduce the time and energy spent on evaporation of hundreds of water liters by pre-concentrating radionuclides in a smaller sample volume with baromembrane method. This approach allows preliminary concentration of water samples from 500 l volume till 20 l volume during several hours. This approach is universal for the concentration of dissolved salts of any heavy metals, other organic compounds and allows the preparation of water countable samples in much shorter time compared to the traditional evaporation method.

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1. Introduction

One of the flux pathways of radioactive substances into the environment is liquid discharges during the operation of nuclear facilities. At the same time, the radionuclides are discharged in cooling pond which has already had some technogenic activity background level due to industrial accidents and global fallout. Analysis of available information demonstrates the need to take into account the background level of radionuclides concentration in cooling pond of Nuclear Power Plants (NPPs) for radiological protection purposes [1]. The background levels should be subtracted from the measurement results for determination of population effective dose from NPP operation in according to the International Atomic Energy Agency (IAEA) recommendations [2]. IAEA considered 31 radionuclides are as the most important with a view to environmental impact from NPPs liquid discharges [3]. National requirements of the Russian Federation indicate the need for state regulation 81 radionuclides in liquid discharge [4]. Monitoring 81 radionuclides in liquid discharges is a difficult task and requires

optimization procedures. Existing approaches to monitoring radionuclides in liquid discharges allow optimizing the list of controlled radionuclides under two conditions [5]:

- the radionuclide in question doesn't create annual effective dose more than 10 μ Sv;
- not included in the number of radionuclides forming 99% of the effective dose with all irradiation ways.

Since the dose assessment is carried out taking into account the detection limit of the monitoring method, the correct dose assessment can be performed if the detection limit of the method is comparable with the background activity values in liquid discharges.

Existing radionuclide concentration in liquid discharge in Russian NPPs is presented by low values [6]. In this case measurement methods with high detection limit will not allow to justify the optimal radionuclides list for the radiation control of liquid discharge and will make the monitoring program useless.

The determination of radionuclide background level in cooling ponds requires instruments and methods for measuring ultra-low radionuclide concentrations. Existing highly effective sorption

* Corresponding author.

E-mail address: vme@ecko.uran.ru (M. Vasyanovich).

methods for radionuclides based on sulfides, dioxides and cyanides of various metals are selective and can't be universal [7,8].

The most universal method for the preparation of water samples by the concentration method is the baromembrane method based on RO membranes. This method was developed in the middle 1960s for distilled water. This technology is used for purification and volume contraction of liquid radioactive waste in the nuclear industry and for analysis of chemical composition of natural water [9–12].

Existing methods for monitoring radionuclides in cooling ponds of Russian NPPs have a high detection limit. This fact makes it difficult to assess the annual activity in liquid discharges. There is a necessity to develop an approach to reduce the detection limit of radioactive substances in liquid discharges in the same way as was done in the work [13]. The possibility of using RO membranes to determine the detectable amounts of radioactive substances in the cooling ponds of Russian NPPs is considered in this article.

2. Materials and methods

An approach for concentrating water samples from natural sources for further radiometric and spectrometric analyzes was suggested in this paper. The method allows 30–40 times concentrating of radionuclides in water using RO membranes, while the initial sample volume can be reduced from 1000 to 30liters.

Feed water is supplied to the membrane under the pressure. Water molecules pass through a semi-permeable membrane and collect in a permeate collection layer (Fig. 1a). Suspended particles, heavy metal ions, organic components, etc. can't pass through a semi-permeable membrane and remain a concentrate collection layer (Fig. 1b). Thus, the initial water under the pressure is divided into two fluxes: concentrate and permeate (Fig. 1a).

Special mobile complex with membranes for sampling radioactive substances was developed, during the survey this complex was transported to four Russian NPPs (Fig. 2).

The analyzed natural water sample is collected into the receiving capacity, after this water is transferred to pre-cleaning module through the integrated flowmeter. All suspended particles and insoluble impurities with size more than 5 μm are removed with the polypropylene filter in the pre-treatment module. After this, the water is pumped into the concentration capacity with module of osmotic membranes. All dissolved salts and suspended particles less than 5 μm are removed from water with RO membranes module. The water is supplied with RO membranes under the pressure up to 10 bar in flow mode. The semi-permeable membrane module separates permeate from water and deletes

from module, but concentrate returns back to concentration capacity. This approach is realized as closed system with step by step volume decreases due to removal of permeate from the system. After concentrating, the membranes must be cleaned with special acid and alkaline solutions to remove settled organic and inorganic impurities.

The efficiency and effectiveness of the osmotic membranes are checked by analyzing various chemical elements of radionuclides. Macro- and microcomponents in natural water samples were determined using atomic sorption and volumetric methods. Other microcomponents were analyzed with Inductively Coupled Plasma (IPC) mass spectrometry with standard error (SD) 20% in each cycle measurements (Table 1).

The results from Table 1 demonstrates that the substances concentrations are increased from cycle by cycle, especially for the macrocomponents. Cesium can detect with concentration above the detection limit after 5 cycles.

During operation of RO membranes is necessary to know the main important parameters: salt impermeability, selectivity, hydraulic efficiency [14,15]. The hydraulic efficiency of baromembrane installation is characterised the coefficient of useful activity and is calculated by formula (1):

$$\eta = \frac{Q_{fil}}{Q_{fd}} \cdot 100\% \quad (1)$$

where η – hydraulic efficiency, %; Q_{fil} and Q_{fd} – filtrate and feed water flows, 1/h.

The average baromembrane complex efficiency in our experiments was about 30%. However, this coefficient may change during the concentration process. Molecules of H_2O are transferred through the membrane, but the concentration of sparingly soluble salts in the concentrate is increased in the boundary layer above the membrane surface. This effect is leads to precipitation crystals of sparingly soluble salts on the membrane and decrease effectiveness of baromembrane installation.

The ability of the baromembrane installation to demineralize initial water is called selectivity and calculated by formula (2):

$$S_y = \frac{q_{fd} - q_{fil}}{q_{fd}} \cdot 100\% \quad (2)$$

where S_y – demineralization coefficient, %; q_{fd} and q_{fil} – amount of dissolved salts in the feed water and filtrate, mg/l. In practice, the specific conductivity of water χ ($\mu\text{S}/\text{sm}$) is measured, which proportional to q . The value of the selectivity parameter for the

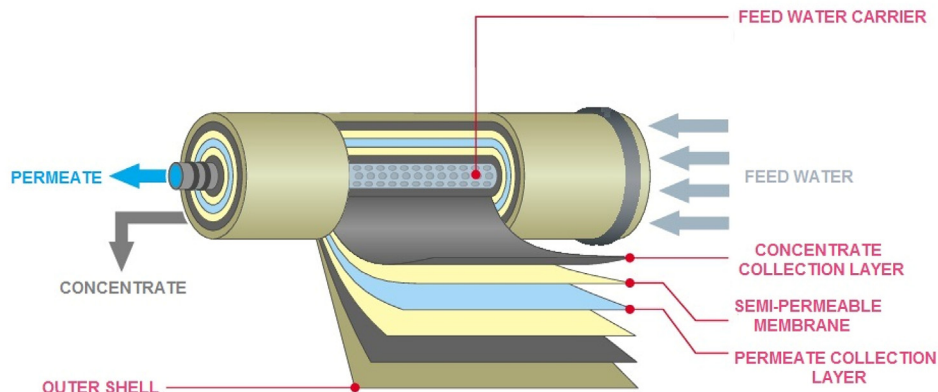


Fig. 1a. The physical configuration of RO membrane and the principle of operation of the RO membrane.

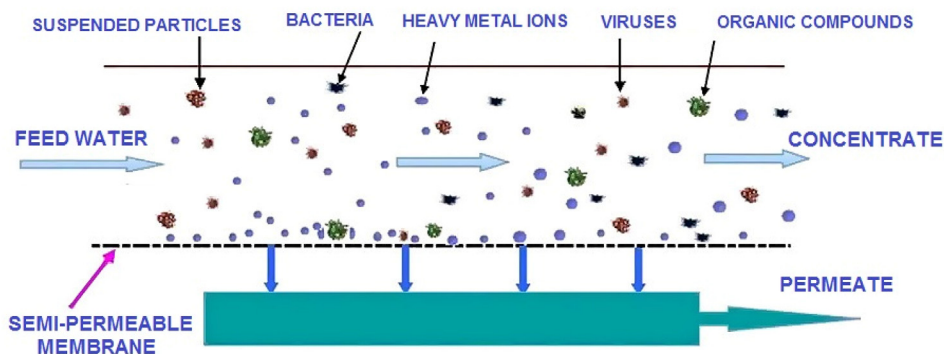


Fig. 1b. The physical configuration of RO membrane and the principle of operation of the RO membrane.

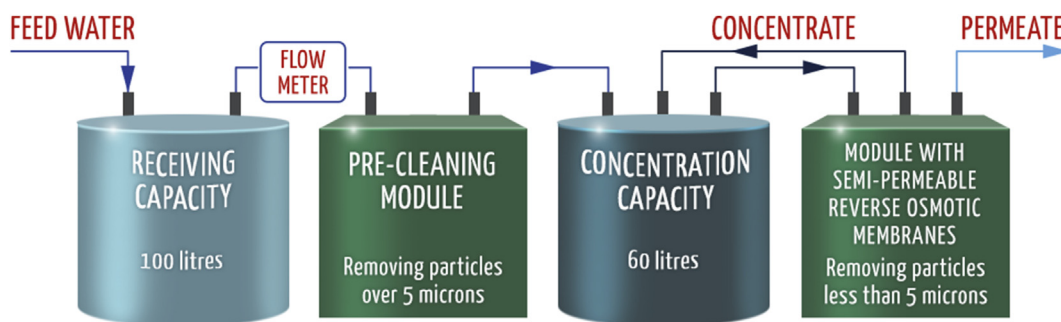


Fig. 2. Functional diagram of installation for concentrating water samples.

Table 1

The concentration process results of various chemical elements during the operation of osmotic membranes.

Element	Initial water, mg/l	Concentrate 1 cycle, mg/l	Concentrate 3 cycle, mg/l	Concentrate 5 cycle, mg/l	Concentrate 10 cycle, mg/l
Na	84.9 ± 12.7	118 ± 18.0	278 ± 42.0	431 ± 65.0	2853 ± 285
K	4.8 ± 0.72	6.3 ± 0.95	13.1 ± 1.97	18.1 ± 2.80	123 ± 18.0
Ca	75.5 ± 10.6	81.0 ± 11.3	189 ± 26.0	224 ± 31.0	335 ± 47.0
Sr	0.67 ± 0.13	0.98 ± 0.20	2.36 ± 0.47	3.19 ± 0.64	10.3 ± 1.40
Element	Initial water, µg/l	Concentrate 1 cycle, µg/l	Concentrate 3 cycle, µg/l	Concentrate 5 cycle, µg/l	Concentrate 10 cycle, µg/l
Mn	1.80 ± 0.33	2.77 ± 0.51	3.94 ± 0.87	6.63 ± 0.99	185 ± 19.2
Co	<0.1	0.14 ± 0.05	0.22 ± 0.06	0.62 ± 0.14	3.57 ± 0.67
Ni	<2.0	4.51 ± 0.82	9.91 ± 1.68	12.7 ± 2.1	63.8 ± 9.0
Cs	<0.05	<0.05	<0.05	0.078 ± 0.039	0.094 ± 0.042

installation in our experiments is presented with range from 37 to 94% and average value of 70%.

Another important parameter for membranes is salt impermeability, which characterizes the amount of salts passing through the membrane and is calculated by formula (3):

$$SP = \frac{C_{fil}}{C_{fd}} \cdot 100\% \tag{3}$$

where SP – coefficient of salt impermeability, %; C_{fil} and C_{fd} – salt concentration in the filtrate and the source water, mg/l. The value of the salt resistance parameter for the installation in our experiments is presented with range from 6 to 63% and average value of 30%.

The amount of permeate obtained from a unit surface of the membrane per unit time at constant pressure is called specific productivity and is calculated by formula (4):

$$J = \frac{Q_{fil}}{S_{mem}} \tag{4}$$

where J – specific productivity, l/(m²·h); Q_{fil} – permeate consumption, l/h; S_{mem} – membrane filtration area, 1/m². The membranes with area of 1.1 m² is used in the baromembrane installation with a filtration made it possible to achieve values of specific productivity in the range from 48 to 70 l/(m²·h) under the pressure up to 10 bar.

After each concentration procedure the RO membranes are cleaned with special acid and alkaline solutions for repeated further use. These special cleaning solutions are transferred to the radiation laboratory. The subsequent laboratory evaporation process allows to get counting samples (CS) from dry residue of the concentrate and cleaning membrane solutions. The radionuclides such as Cs-137, Co-60, Mn-54, etc. in CS were determined with HPGe gamma-spectrometry. The radionuclide Sr-90 in CS was isolated and determined with radiochemistry method.

The comparison between approaches for simultaneous preparing water CS was performed. The results of concentration with baromembrane method was compared with classical approach of preparing water CS with evaporation. For this purpose, water from the Beloyarsk cooling pond (500 l) was taken for each type of sample preparation.

The dry residues from each preparation approach was determined for absolute activity, which is calculated by formula (5):

$$A = \frac{(I_{cs} - I_{bg}) \cdot m_{dr}}{\eta \cdot \varepsilon \cdot m_{cs}} \quad (5)$$

where I_{cs} the count rate from total absorption peak of the studied radionuclide, 1/s;

I_{bg} background count rate in the channel range of the studied radionuclide, 1/s;

m_{dr} mass of ash obtained by evaporation of the liquid, g;

m_{cs} the mass of the counting sample, which was analyzed with HPGe gamma spectrometer, g;

η the intensity of the energy line of the studied radionuclide, %;

ε the registration efficiency for the analyzed energy line, d/q.

The estimation of the activity uncertainty was calculated by formula (6):

$$U(A) = \sqrt{\left(\frac{\partial A}{\partial I_{cs}}\right)^2 \cdot \Delta I_{cs}^2 + \left(\frac{\partial A}{\partial I_{bg}}\right)^2 \cdot \Delta I_{bg}^2 + \left(\frac{\partial A}{\partial m_{dr}}\right)^2 \cdot \Delta m_{dr}^2 + \left(\frac{\partial A}{\partial m_{cs}}\right)^2 \cdot \Delta m_{cs}^2 + \left(\frac{\partial A}{\partial \eta}\right)^2 \cdot \Delta \eta^2 + \left(\frac{\partial A}{\partial \varepsilon}\right)^2 \cdot \Delta \varepsilon^2} \quad (6)$$

where ΔI_{cs} the count rate uncertainty at the total absorption peak of the studied radionuclide, 1/s;

ΔI_{bg} uncertainty of background count rate in the channel range of the studied radionuclide, 1/s;

Δm_{dr} uncertainty of the mass of ash obtained by evaporation, g;

Δm_{cs} uncertainty of the counting sample mass, which was analyzed with HPGe gamma spectrometer, g;

$\Delta \eta$ uncertainty of the intensity of energy line of the studied radionuclide, %;

$\Delta \varepsilon$ uncertainty of registration efficiency for the analyzed energy line, d/q.

Extended measurement uncertainty is calculated by formula (7):

$$U = 2 \cdot U(A) \quad (7)$$

The analysis of dry residues of water CS prepared using both approaches were performed in radiation laboratories in two different institutes: Institute of Industrial Ecology UB RAS (IIE) and Institute of Plant and Animal Ecology UB RAS (IPAE).

3. Results and discussion

During the concentration process with baromembrane method a concentration coefficient for Beloyarsk cooling pond water was achieved about 23. In this case, the salinity of the initial water equal to 193 mg/l was increased in the concentrate to 4.5 g/l during 12 h. The time consumption for the counting sample with baromembrane method was 5 days, while the classical method of evaporation for 500l of source water needed to prepare the CS during 2 weeks. The results of interlaboratory comparisons for the determination of gamma-emitting radionuclides are presented in Table 2.

Table 2

Results of interlaboratory comparisons of gamma-emitting radionuclides in solid samples.

Sample number	Cs-137, 10 ⁻³ , Bq/l		K-40, 10 ⁻¹ , Bq/l	
	IIE	IPAE	IIE	IPAE
1*	3.1 ± 0.9	1.6 ± 0.4	3.2 ± 0.7	2.5 ± 0.1
2*	2.6 ± 0.8	1.8 ± 0.4	2.8 ± 0.6	2.4 ± 0.1
3**	1.9 ± 0.7	2.8 ± 0.8	1.9 ± 0.5	3.6 ± 0.2
4**	1.4 ± 0.7	1.9 ± 0.8	1.6 ± 0.4	3.3 ± 0.1

Note: ± extended measurement uncertainty.

1,2 - samples prepared by evaporation.

3,4 - samples prepared using RO membranes installation.

The results of interlaboratory comparisons demonstrate good convergence of radionuclide concentrations. The absence of a significant difference in the results between the two preparation of water CS allows to conclude that the baromembrane method is applicable for studying ultra-low radionuclide concentrations. The absence of activity loss on the elements of the RO membranes was demonstrated. The analysis of dry residue from evaporated concentrate with coaxial HPGe detector allowed to achieve the low detection limit for Cs-137 equal to 5.0 · 10⁻⁴ Bq/l.

This experience of water concentration allowed to obtain the results of radionuclide concentrations in liquid discharges at other Russian NPPs. The results of concentration process of water with baromembrane installation for Russian NPPs are presented in Table 3. These results are presented as salinity in initial and concentrated water with SD not more than 5%.

The difference in the salinity of concentrated water and the concentration coefficient for each liquid discharge of Russian NPPs may be due to various factors. The difference in salinity of the source water is due to location of NPP. Also, it depends on the type of liquid discharge place. Projects of Russian NPPs have discharges both closed cooling ponds and into rivers. The concentration coefficient may be affected by the structural features of the RO membranes, the salinity of the initial water, and the presence of organic compounds (humic and fulvic acids). The results of the radionuclide analysis of dry residues in water samples of Russian NPPs are presented in Table 4.

The analysis of water in liquid discharges of Russian NPPs are represented by Cs-137 and the more mobile radionuclide Sr-90 [16].

The highest values of the radionuclide concentrations were noted in liquid discharges of domestic sewerage. The technological process for radionuclide removal from NPP controlled access area can create liquid discharges of extra radionuclides, therefore, Mn-54 and Co-60.

4. Conclusion

The possibility of using the baromembrane method to determine ultra-low radionuclide concentrations was demonstrated in this investigation. A special mobile installation for concentration of large-volume water samples was developed. This approach can significantly reduce the detection limit of radionuclides in liquid

Table 3

The results of water concentration process with baromembrane installation for Russian NPPs.

NPP	Liquid discharge source	Concentration results		
		Salinity of initial water, mg/l	The salinity of concentrated, water, g/l	Concentration coefficient by sample volume, d/q
Balakovo	Inlet channel	980	13.8	36.8
Kursk	Inlet channel	568	5.9	34.9
	Outlet channel	659	5.5	33.9
	Seim river	345	4.2	43.1
	Domestic sewerage	212	3.1	20.8
Rostov	Domestic sewerage	690	13.5	34.9
	Outlet channel 1,2 units	277	8.2	43.8
	Outlet channel 3,4 units	900	12.0	31.1
Novovoronezh	Outlet channel 1,2 units	246	3.1	27.7
	Another outlet channel	253	3.8	37.6
	Outlet channel 3,4 units	253	3.9	38.6
	Outlet channel 5 unit	362	4.1	23.7
	Field filters	300	4.1	19.1

Table 4

The results of the CS analysis of radionuclides from aqueous samples of Russian NPPs.

NPP	Liquid discharge source	Radionuclide concentration in water, 10^{-3} Bq/l			
		Cs-137	Sr-90	Mn-54	Co-60
Balakovo	Inlet channel	1.5 ± 0.7	3.3 ± 1.3	<0.9	< 0.6
Kursk	Domestic sewerage	11.8 ± 1.3	–	1.6 ± 0.5	13.9 ± 0.9
Rostov	Domestic sewerage	<0.5	15.4 ± 7.1	<0.7	<0.4
Novovoronezh	Field filters	15.1 ± 6.2	37.7 ± 22.0	2.5 ± 1.0	11.5 ± 4.8

discharges and justify the list of monitoring dose-forming radionuclides.

The verification of baromembrane method was performed using the classical approach with water evaporation with the same water volume. The results were demonstrated sufficient convergence for Cs-137 concentration in samples obtained with baromembrane method and evaporation.

The average value of concentration coefficient of initial water volume was established equals 33.0 ± 8.0 during in experimental work. This value is comparable with the theoretical calculations that were obtained during the design of baromembrane installation in the proposed technical design.

The use of a baromembrane method based on RO membranes for preliminary concentration and analysis of CS with HPGe detector made it possible to obtain a detection limit for Cs-137 equal to $5.0 \cdot 10^{-4}$ Bq/l.

The developed method allows to reliably determine the concentration of main radionuclides in the ranges for Cs-137 ($1.48\text{--}15.1$) $\cdot 10^{-3}$ Bq/l and for Sr-90 ($3.3\text{--}37.7$) $\cdot 10^{-3}$ Bq/l. Also, Mn-54 and Co-60 in liquid discharges of Russian NPPs can be occasionally observed in water samples.

Declaration of competing 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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