

New Process for Transuranide Preconcentration in Water Samples from the Yenisei River

L. G. Bondareva^a, A. Ya. Bolsunovskii^a, A. V. Trapeznikov^b,
and Corresponding Member of the RAS A. G. Degermendzhi^a

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In natural surface waters, transuranides occur in various physicochemical species. They can be associated, ranging from simple ions and molecules to hydrolyzed species, colloids, and pseudocolloids and organic and inorganic species [1]. Depending on their species, transuranides can either migrate over considerable distances or be sorbed by components of the ecosystem directly near the discharge locality. The overall concentration of dissolved transuranides in surface water bodies is very low (10^{-10} to 10^{-15} mol/L), that is, within the detection limits of the most sensitive spectral methods, such as mass spectrometry [2]. Therefore, hybrid determination techniques, which combine preconcentration and separation of transuranides with various detection methods, such as alpha- and gamma-ray spectrometry [3, 4], are more frequently used for the adequate determination of transuranides in water systems.

Currently, several types of transuranide preconcentration processes are used. Some processes are based on the sedimentation of insoluble compounds on the surface of colloid particles, such as iron(III) oxide hydroxide and manganese(IV) oxide [5–7]. Other processes are based on the separation of transuranides from a complex solution using their selective complexation with ligands of a certain type dissolved in organic solvents (e.g., tributyl phosphate) [8]. Radionuclide preconcentration processes are also known on the basis of cosedimentation with sparingly soluble finely disperse compounds (oxalates, sulfates, and others) [9] and sorption on sorbents impregnated with complexing agents [10]. To date, the concentration of large volumes (up to 1 m³) of water to a dry residue has been the most

widely used process [11]. All the aforementioned processes have both advantages and disadvantages.

In Yenisei River waters sampled in the region where the Rosatom Mining and Chemical Combine (MCC) discharges its wastewater, the following radionuclide levels were obtained: 0.015 mBq/L for ^{239,240}Pu [12] and 0.016 Bq/L for ²⁴¹Am [13]. These transuranide levels were determined after preconcentration (water samples were concentrated to dry salts) and radiochemical separation on an α -spectrometer. There are also some separate ²³⁹Np determinations in MCC discharge waters: 143 Bq/L [13]. Any other data on transuranide levels in Yenisei River waters have not been reported.

This work uses a new process for preconcentrating transuranides in Yenisei River water samples.

The object used was water sampled from the Yenisei River in the zone of influence of the MCC in the period of September and October 2007 and during March, July, and September 2007. Samples were collected in the region of the village of Atamanovo at distances of 0.3 and 5 km from the radioactive water discharge site. Volumes of water samples were up to 30 L. Each sample was divided into two parts. One part, 1 L in volume, was measured on a Marinelli gamma-ray spectrometer in a standard geometry without sample preparation. The other part was concentrated.

Two versions of transuranide preconcentration were used. One version was the consecutive sedimentation of transuranides and other induced radionuclides from one water sample first on iron(III) oxide hydroxide particulates [7] and then on manganese(IV) oxide particulates [7]. The other version was the direct preparation of a suspension consisting of iron(III) oxide hydroxide and manganese(IV) oxide particulates in a water sample. In this case, solutions containing manganese(VII) and manganese(II) were introduced into the mixture after an iron(III) solution was introduced into a water sample with pH 3 and equilibrium was acquired between the introduced radionuclides and those contained in the sample but before sedimentation.

^a Institute of Biophysics, Siberian Branch, Russian Academy of Sciences, Akademgorodok 50, Krasnoyarsk, 660036 Russia

^b Institute of Plant and Animal Ecology, Uräl Division, Russian Academy of Sciences, ul. Vos'mogo Marta 202, Yekaterinburg, 690144 Russia

Table 1. Determination of ^{239}Np and other induced radionuclides using consecutive and simultaneous sedimentation of iron(III) oxide hydroxide and manganese(IV) oxide particulates

Radionuclide	Radionuclide level		
	Initial water samples, Bq/L	Sedimentation in 30 L, Bq	
		consecutive	simultaneous
^{46}Sc	—	0.11 ± 0.02	0.14 ± 0.02
^{51}Cr	—	2.6 ± 0.2	2.7 ± 0.2
^{58}Co	—	—	0.07 ± 0.02
^{60}Co	—	0.14 ± 0.02	0.08 ± 0.01
^{65}Zn	—	0.10 ± 0.03	0.06 ± 0.02
^{76}As	0.14 ± 0.06	3.1 ± 0.3	3.4 ± 0.3
^{106}Ru	—	0.3 ± 0.1	0.3 ± 0.1
^{131}I	—	0.04 ± 0.01	0.03 ± 0.02
^{137}Cs	0.12 ± 0.06	0.07 ± 0.02	0.04 ± 0.02
^{239}Np	0.31 ± 0.04	8.1 ± 0.2	8.5 ± 0.3

After the salt solutions were added to the water sample, its pH was brought to 9–10 and the mixture was allowed to stand for ripening of the precipitate, which consisted of iron(III) oxide hydroxide and manganese(IV) oxide colloid particulates. In both cases, ^{241}Am and ^{242}Pu were added in order to determine the completion of transuranide sedimentation. As-collected water samples and concentrates were measured on a Canberra gamma-ray spectrometer (United States) equipped with an ultrapure germanium detector (HPGe). The Canberra GENIE PC software was used for data processing. The ^{241}Am chemical yield reached 95%. In some concentrates, plutonium isotopes were determined. Plutonium isotope determinations were carried out at the Continental Radioecology Department of the Institute of Plant and Animal Ecology, Russian Academy of Sciences, Yekaterinburg. Plutonium isotopes were separated from the water concentrates radiochemically and measured by alpha-ray spectrometry. The ^{242}Pu chemical yield reached 67%. Table 1 lists the levels of ^{239}Np and other induced radionuclides in the Yenisei River water samples prepared by the two versions of preconcentration.

Both versions lead to determination of high levels of induced radionuclides in comparison to the initial sample. The radionuclide levels determined in the concentrates in the two versions are almost identical.

Analyzing our data on the concentrations of induced radionuclides in Yenisei water samples, we conventionally classified these radionuclides into two groups. One group included radioisotopes that changed their oxidation states (such as ^{76}As). The other included radioisotopes with invariable oxidation states. The latter can also be conventionally divided into three subgroups: (1) radionuclides forming insoluble hydroxides on the

surface of particulates (such as ^{56}Fe , ^{51}Cr , and ^{46}Sc), (2) radionuclides that are concentrated by cosedimentation in particulates (exemplified by ^{137}Cs), and (3) radionuclides whose sedimentation in the concentrate is due to the occlusion of some of the solution by particulates (exemplified by ^{24}Na).

This division of radionuclides can be used for choosing sorbents providing a high efficiency of radioisotope separation from solutions for further study.

Analyzing the relevant literature and our results, we assumed the following. Transuranides can be preconcentrated both by changing their oxidation state with a transition to a less soluble physicochemical species (for example, plutonium(V) reduction to plutonium(IV) on the surface of MnO_2 with subsequent slow oxidation to plutonium(VI) [5]) and by generating poorly soluble compounds without changing their oxidation state (for example, the generation of hydrolyzed neptunium(V) species on the surface of iron(III) oxide hydroxide [5]). Then, the use of a process that combines the two types of transuranide cosedimentation (with changing oxidation states and generating sparingly soluble compounds) offers a means for efficient separation of the target trace radionuclides contained in solute species.

For ^{239}Np , we found a linear correlation between the radionuclide level and the water sample size. For example, when a 1-L water sample was analyzed, the ^{239}Np level was 0.31 ± 0.04 Bq/L; preconcentration from a 20-L sample resulted in 5.4 ± 0.4 Bq of ^{239}Np , which corresponded to a level of 0.27 ± 0.03 Bq/L. From a 30-L water sample, preconcentration gave 8.1 ± 0.2 Bq, which also corresponds to 0.27 ± 0.03 Bq/L. It follows from our data that the new process for preconcentrating transuranides, in particular, ^{239}Np , in Yenisei River water samples gives adequate results satisfying the requirements for radioecological investigations.

Further, we used the simultaneous sedimentation of iron(III) oxide hydroxide and manganese(IV) oxide colloid particulates to determine transuranides.

Table 2 lists the levels of ^{239}Np and plutonium isotopes in Yenisei River water samples. These levels show that the transuranide preconcentration process enables reliable determination of plutonium isotopes in water samples 10–30 L in size. Earlier measurements of $^{239}, ^{240}\text{Pu}$ levels in Yenisei River waters sampled at 0.3 and 5 km from the MCC discharge site were 0.015 and 0.012 mBq/L, respectively [12]. We obtained higher $^{239}, ^{240}\text{Pu}$ levels for these sampling stations: 2.34 and 0.26 mBq/L, respectively. On the other hand, our value of the maximal ^{239}Np level in water (~ 12.5 Bq/L) is considerably lower than the value of 143 Bq/L reported in [13]. This discrepancy arises from the fact that the water samples studied in [13] were collected from the discharge channel, whereas, in our work, water was sampled from the Yenisei River itself.

From the ^{239}Np levels in Table 2 and previous ^{239}Np determinations in samples of aquatic plants from the

Table 2. ^{239}Np and plutonium isotopes in Yenisei River water samples collected from the river at various distances from the MCC discharge site

Sampling date	^{239}Np , Bq/L		^{238}Pu , mBq/L		$^{239}, ^{240}\text{Pu}$, mBq/L	
	distance from the radioactive water discharge site, km					
	0.3	5	0.3	5	0.3	5
September 2006	—	0.27 ± 0.04	0.17	0.13	2.34	0.26
October 2006	—	0.28 ± 0.08	—	—	—	—
March 2007	3.25 ± 0.07	—	—	—	—	—
July 2007	12.4 ± 0.6	0.29 ± 0.09	—	—	—	—
September 2007	3.3 ± 0.1	0.28 ± 0.08	—	—	—	—

Yenisei River [14] collected at various distances downstream from the discharge site, we infer that ^{239}Np has a high migration ability. The ^{239}Np concentration can decrease downstream both due to dilution by Yenisei waters without changing physicochemical speciation in the environment and due to sedimentation in poorly soluble compounds on the surface of plants. Although the plutonium isotope levels in water near the discharge site are lower than the ^{239}Np level, plutonium isotopes were also detected in plants at distances up to 200 km downstream from the discharge site [14]. This signifies that plutonium isotopes can travel considerable distances from the discharge site either in the particulate form or in the dissolved form with subsequent sedimentation on plants.

In summary, the new process for the preconcentration of transuranides from Yenisei waters based on the simultaneous formation of iron(III) oxide hydroxide and manganese(IV) oxide colloid particulates directly in assay samples efficiently separates a number of trace transuranides (^{239}Np , ^{238}Pu , ^{239}Pu , and ^{240}Pu) that occur as solute species.

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REFERENCES

- Salbu, B., *J. Radioanal. Nucl. Chem.*, 1987, vol. 1127, no. 1, pp. 169–174.
- Solatie, I.D., Carbol, P., Betti, M., et al., *Fresenius J. Anal. Chem.*, 2000, vol. 368, pp. 88–94.
- Crespo, M.T., Gascon, J.L., and Acena, M.L., *Sci. Total Environ.*, 1993, vol. 131/132, pp. 383–391.
- Livingston, H.D. and Cochran, J.K., *Radioanal. Nucl. Chem.*, 1987, vol. 115, pp. 299–308.
- Khasanova, A.B., Shcherbina, N.S., Kalmykov, S.N., et al., *Radiokhimiya*, 2007, vol. 49, no. 4, pp. 367–372.
- Methods of Seawater Analysis*, Ch. 13: *The Analysis of Natural Radionuclides in Seawater*, Grasshoff, K., Ehrhardt, M.G., Kremling, K., Eds., Weinheim: Verlag Chemie, 1999.
- Livingston, H.D., Mann, D.R., and Bowen, V.T., in *Reference Methods for Marine Radioactivity Studies II*, Vienna: IAEA, 1975, pp. 69–76.
- Babaev, N.S., Demin, V.F., Il'in, L.A., et al., *Yadernaya energetika, chelovek i okruzhayushchaya sreda* (Nuclear Energetics, Humans, and the Environment), Moscow: Energoatomizdat, 1984.
- Harvey, B.R., Ibbett, R.D., Lovett, M.B., and Williams, K.J., *Analytical Procedures for the Determination of Strontium Radionuclides in Environmental Materials*, Lowestoft: Ministry of Agriculture, Fisheries and Food Directorate of Fisheries Research; Aquatic Environment Protection; CEFAS Lowestoft Laboratory, 1989.
- Eikenberg, J., Bajo, S., Beer, H., et al., *Appl. Radiat. Isotopes*, 2004, vol. 61, pp. 101–106.
- Metodologicheskoe rukovodstvo po opredeleniyu radioaktivnogo zagryazneniya v vode* (Methodological Guide for Determination of Radioactive Water Pollution), Vakulovskii, S.M., Ed., Moscow: Gidrometeoizdat, 1986.
- Kuznetsov, Yu.V., Revenko, Yu.A., and Legin, M.K., *Radiokhimiya*, 1994, vol. 36, pp. 546–559.
- Vakulovskii, S.M., Tertyshnik, E.G., Borodina, T.S., and Iskra, A.A., in *Materialy mezhdunarodnoi konferentsii "Radioaktivnost' posle yadernykh vzryvov i avarii," Moskva, 2005* (Proceedings of International Conference "Radioactivity after Nuclear Explosions and Accidents," Moscow, 2005), Moscow, 2005, pp. 294–299.
- Bolsunovsky, A., *Aquat. Ecol.*, 2004, vol. 38, pp. 57–62.