

METHOD FOR THE COEXTRACTION OF ACTINIDES AND TECHNETIUM FROM AQUEOUS SOLUTIONS FOR RADIOLOGICAL MONITORING PURPOSES

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Radionuclide concentrations in natural samples and their monitoring appear to be essential when it comes to the environmental safety assessment and the evaluation of the consequences inflicted by nuclear weapons testing, as well as accidents at nuclear power plants. However, large volumes of natural water samples require some additional concentration. To date, no method has been developed that could provide the coextraction of actinides and technetium from large volumes of natural waters. Model experiments were implemented to study simultaneous coprecipitation of actinides and ⁹⁹Tc with iron (II and III) hydroxides and their subsequent separation using chromatographic resins. A technique providing ⁹⁹Tc concentration and extraction was adjusted: the amount of Fe³⁺ was taken equal to 0.8 g/l, K₂S₂O₅ in a concentration of 4 g/l was selected as a reducing agent. A technique has been developed to coextract Am, Pu, U, and Tc from large-volume natural samples and to specify their concentrations with a yield of 40–70%.

Keywords: actinides, technetium, coprecipitation, natural samples, radioecological monitoring, radioactive waste.

Introduction

On April 13, 2021, ten years after the Fukushima accident, Japanese Government made a decision providing for a discharge of over a million ton of liquid radioactive waste into the World Ocean [1]. By summer 2022, loading of RW containers with waste was planned to be completed and Japan was to start liquid radioactive waste discharges into the Pacific Ocean. The plans called not for a simultaneous LRW discharge, but rather for continuous ones that could take some three decades [2]. According to the monitoring reports of wastewater treatment facilities provided by Tokyo Electric Power Company Holdings, Incorporated (TEPCO) (TEPCO,

2012–2020) and the Japanese Nuclear Regulatory Authority (NRA) (NRA, 2013–2020), radioactive materials mainly contained ³H, ¹⁴C, ¹³⁴Cs, ¹³⁷Cs, ⁶⁰Co, ¹²⁵Sb, ⁹⁰Sr, ¹²⁹I, ⁹⁹Tc, ¹⁰⁶Ru and ²³⁸Pu. Most of Japan's neighboring countries are seriously concerned about the situation at hand, and therefore particularly urgent becomes the challenge associated with rapid concentration of various radionuclides from the sea water.

A number of difficulties has been faced during the analysis of radionuclides found in the World Ocean: it appears quite challenging to measure the actinide levels in the sea water due to the complexity

of its composition and the required low detection limits of the tools applied. Large sample volumes are required to deal with low concentrations of radionuclides in natural waters; therefore, additional preconcentration is required to reduce the analysis time. In addition, radionuclides can be often present in several oxidation states at once in the environment. Most of the methods used provide a chemical yield of only 30–60% [3]. Literature sources present a big number of different sorbents providing radionuclide extraction from aqueous media [4].

Coprecipitation method is used to extract actinides: using $\text{Fe}(\text{OH})_3$ [5–7]; iron hydroxide enhanced with Ti^{2+} reducing agent followed by coprecipitation of lanthanum fluoride [3]; calcium phosphate [8]; as well as manganese dioxide [9, 10]. To identify plutonium isotopes in sea water, precipitation with manganese dioxide from 200–400 l is traditionally used in the field conditions. Subsequently, the resulting precipitate is dissolved in the laboratory using the reducing agent $\text{NH}_2\text{OH}\cdot\text{HCl}$ and reprecipitated with iron (III) hydroxide [11]. Precipitation with $\text{Fe}(\text{OH})_3$ alone can be used as well: a sea water sample (about 1,000 liters) is emplaced into 80-liter drums with 700 mg of iron(III) chloride being added to each of them, the chemical yield of plutonium following further extraction and treatment via several extractions with various organic extractants amounts to 3–68% [12]. Precipitation method with calcium phosphate is suitable for samples of a small volume, although the radiochemical yield of actinides is high: for Am, U – more than 70%, Pu – 50% [8]. Several preconcentration methods are used to extract ^{99}Tc : evaporation [13], sorption on activated carbon [14] and coprecipitation with $\text{Fe}(\text{OH})_2$ [15]. Evaporation is considered a suitable preconcentration method for samples of relatively small volumes with low amounts of dissolved salts, such as precipitate, river and lake waters and some types of groundwater [13]. The co-precipitation method is the most commonly used method based on the co-precipitation of insoluble forms of technetium in the +4 oxidation state with iron hydroxide $\text{Fe}(\text{OH})_2$, FeSO_4 [15], hydrazine [16], sulfite anion, etc. are used to reduce technetium [17]. FeCl_3 can be used as an iron source, which is reduced simultaneously with technetium, or it can act as a reducing agent itself, which in this case is FeSO_4 [17]. After co-precipitation, the precipitate is separated, dissolved, then iron and technetium are moved to the oxidation state +3 and +7, respectively, and iron is separated from technetium precipitating $\text{Fe}(\text{OH})_3$. The chemical yield of technetium amounts to 50–80%. This method is considered

as a fast and convenient preconcentration method, moreover, it can be applied under field studies allowing to avoid the challenge associated with the transportation of large sample volumes [18]. Under this study, an important analytical task was to select a combination of co-precipitation methods in such a way as to obtain good yields for both actinides and technetium.

Actinides are alpha emitting radionuclides and therefore can be measured via alpha spectrometry. Mass spectrometry (ICP-MS, AMS, TIMS, RIMS) is widely used at low concentrations providing more accurate measurements [11]. The following methods are also typically used to measure ^{99}Tc contained in natural objects: ICP-MS [15], AMS [19] and TIMS [20]. In case of ICP-MS, the detection limit for ^{99}Tc amounts to 1 Bq/l. The liquid scintillation (LS) spectrometry method has a number of disadvantages rendering it inadequate for natural object evaluations, i. e., the measurement limit amounts to 17 Bq/l [21].

Most of known methods used to identify plutonium, uranium, americium and technetium isotopes are focused only on one of these elements; no method provides simultaneous extraction. In natural water, the concentration of these radionuclides is very low resulting in high sampling, transportation costs and lengthy analytical process. This study is focused on the development of a method that would provide simultaneous extraction of Pu, Am, U, and Tc from large volumes of marine and fresh natural waters to monitor their content, as well as on the study of their speciation and the environmental impact of so-called nuclear legacy of the Soviet Union and the accident at Fukushima-1 in 2011.

Materials and methods

To provide joint preconcentration and extraction of actinides (U, Pu, Am) and ^{99}Tc from sea and fresh water, three precipitation methods with iron hydroxide (II and III) were tested. Testing was followed by radionuclide extraction (Figures 1–3) via extraction chromatography (TrisKem Int). A number of model experiments was implemented: in the first experiment, solid salt $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ was taken as an iron source, which simultaneously acted as a reducing agent; in the second experiment, solid salt $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was chosen as an iron source and solid $\text{K}_2\text{S}_2\text{O}_5$ salt was used as a reducing agent. Technetium co-precipitation experiments involved a mononuclide.

Model solutions of sea and fresh water (Table 1) were produced based on the actual compositions of natural water bodies [22].

Table 1. Compositions of model sea and fresh water solutions

Ion	Sea water model solution, $\times 10^{-3}$ M	Fresh water model solution, $\times 10^{-3}$ M
Na ⁺	507	0.57
K ⁺	8.7	0.03
Mg ²⁺	52.2	0.25
Ca ²⁺	10.1	0.17
Sr ²⁺	0.08	-
Cl ⁻	591	0.27
SO ₄ ²⁻	24.8	0.42
HCO ₃ ⁻	2	0.57
Br ⁻	0.74	-
H ₃ BO ₃	0.37	-
F ⁻	0.07	-

All required radionuclides and technetium were involved in the final experiment. Actinides and technetium with the following activities were added to the produced sea and fresh water solutions: NH₄⁹⁹TcO₄ – 240 Bq·ml⁻¹, 690 ng·ml⁻¹; ²³³UO₂(NO₃)₂ – 1,700 Bq·ml⁻¹, 8,300 ng·ml⁻¹; ²³⁹Pu(NO₃)₄ – 900 Bq·ml⁻¹, 390 ng·ml⁻¹; ²⁴¹Am(NO₃)₃ – 9,500 Bq·ml⁻¹, 133 ng·ml⁻¹. Counting sample preparation involved coprecipitation with CeF₃ on a Resolve filter (Eichrom Tech.). The content of actinides was analyzed based on alpha spectrometry method (multichannel alpha spectrometer with a semiconductor detector Alpha-Ensemble-2).

To detect ⁹⁹Tc and actinides in the experiments with individual radionuclides, a Tri-Carb 2810TR liquid scintillation spectrometer was used; the spectra were processed using the SpectraDec software. To consider the detection efficiency under the technetium activity calculations, a quenching curve was plotted. The first two methods were focused on the concentration of technetium.

During the experiment, the measurement uncertainty includes random errors, namely, dispenser, weighing errors, losses during reloading from beaker to beaker and during filtration, instrumental activity measurement errors, etc. In total, the error did not exceed 8% of the results obtained: the statistical counting error was 0.2–2.0%, detection efficiency – 2.5–4.5%, volume measurement error – 1–3%, random measurement error, i. e., standard deviation and relative statistical uncertainty of the results amounted to 0.03–7.70%.

Experiment № 1 (I). ⁹⁹Tc from model sea and fresh water solutions (sample volume – 500 ml, added activity – 25 Bq) was extracted by co-precipitation

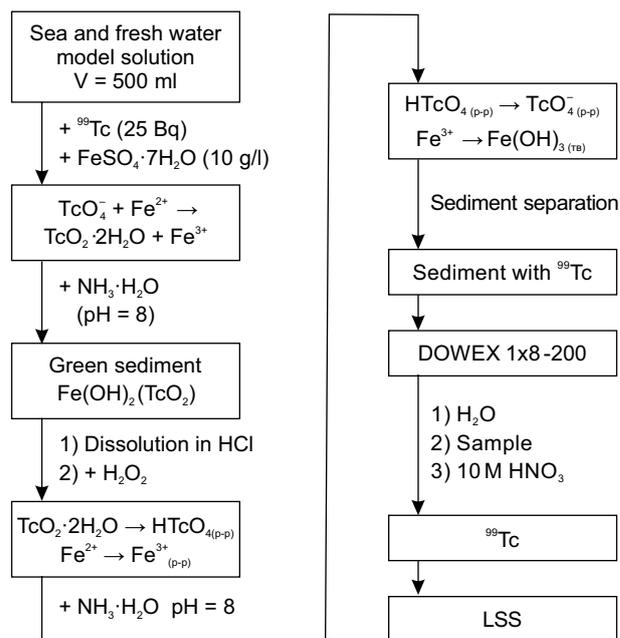


Figure 1. Experimental flowchart I: technetium co-precipitation from a model solution

with iron (II) hydroxide according to an established procedure [23] (Figure 1).

FeSO₄·7H₂O was added to the analyzed solution (given that Fe²⁺ – 10 g/l), while Tc⁺⁷ was reduced to Tc⁺⁴. Concentrated ammonia solution was used to provide alkaline reaction of the medium (pH=8–9) and form iron (II) hydroxide. The precipitate was separated on a paper filter, washed with water and then dissolved in HCl_{conc.}, a 37% H₂O₂ solution was added so that technetium and iron changed to +3 and +7, respectively. Then, excess amount of concentrated ammonia solution was added to precipitate Fe(OH)₃. Afterwards, the precipitate was separated on a paper filter and washed with water.

Technetium was separated from the resulting solution by anion-exchange chromatography on a DOWEX 1x8 200 column involving 20 ml of distilled water passed through the sample, washed with 20 ml of distilled water, washed off with 20 ml of 10 M HNO₃ solution. The eluent was evaporated at 60 °C and its activity was measured.

Experiment № 2 (II). The experiment was implemented according to the procedure described in [21] (Figure 2). The sample solution (volume – 500 ml, added activity – 25 Bq) was acidified with concentrated HCl (up to pH=2–3), Fe³⁺ was added in the form of a FeCl₃ solution (8 mg/l), K₂S₂O₅ was introduced as a reducing agent (0.5 g/l). After the process was completed (color changed from brown to almost colorless), a 6 M NaOH solution was added to the solution until pH level of 8–9. The precipitated dark green Fe(OH)₂ precipitate was separated by filtration, washed with water, then dissolved

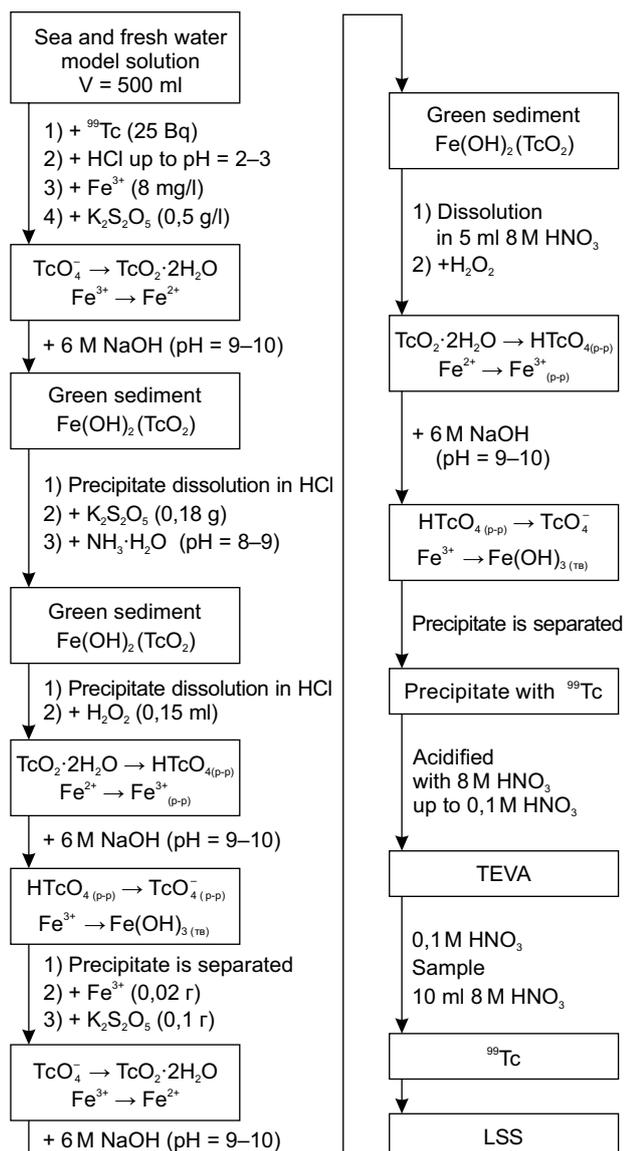


Figure 2. Flowchart for experiment II: coprecipitation of technetium from a model solution

with HCl_{conc} . $\text{K}_2\text{S}_2\text{O}_5$ reducing agent (1 g/l) was added to the resulting solution; after the process was completed, added was the $\text{NH}_{3\text{conc}}$ (pH=8–9). The resulting $\text{Fe}(\text{OH})_2$ precipitate was treated on a paper filter, then dissolved using concentrated HCl . Subsequently, technetium and iron were converted to +3 and +7, respectively, by adding a 30% H_2O_2 solution until the color stopped changing. A 6 M NaOH solution (pH=9–10) was added to form $\text{Fe}(\text{OH})_3$ precipitate and subsequently remove the iron. Then precipitation with iron was repeated: at post-filtration stage, the solution was acidified to pH=2–3, Fe^{3+} (0.2 g/l) and $\text{K}_2\text{S}_2\text{O}_5$ reducing agent (5 g/l) was added. When the process was completed, a 6 M NaOH solution was added to pH=9–10. The precipitate was separated on a paper filter, washed with water. Then it was dissolved in an 8 M HNO_3 solution, 30% H_2O_2 solution was added to convert

technetium and iron into TcO_4^- and Fe^{3+} , respectively, alkali was added to pH=9–10 and $\text{Fe}(\text{OH})_3$ precipitate was separated by filtration. The resulting solution was acidified with 8 M HNO_3 to 0.1 M HNO_3 , ^{99}Tc was extracted using TEVA resin. The column involved 20 ml of 0.1 M HNO_3 , the sample was passed through, washed with 40 ml of 1 M HNO_3 , washed off with 10 ml of 8 M HNO_3 . The eluent was evaporated and the activity was measured using LS spectrometry.

Experiment №3 (III). Considering the unsatisfactory amount of sediment obtained in the first two experiments, enhanced was the method used in the second experiment: the amount of added iron was 800 mg/l, the amount of reducing agent $\text{K}_2\text{S}_2\text{O}_5$ was 4 g/l. Precipitation with iron was done once. Additionally, an experiment was carried out to isolate technetium using TEVA resin from weakly alkaline solutions. The column was filled with 20 ml of a 0.1 M HNO_3 solution, the sample was passed through a medium with pH=10, washed with 40 ml of 1 M HNO_3 , washed off with 10 ml of 8 M HNO_3 . The eluent was evaporated and the activity was measured.

Experiment №4 (IV). The method of model experiment III was adapted to separate a mixture of radionuclides from model sea and fresh water solutions with a volume of 4 l. At the $\text{Fe}(\text{OH})_3$ precipitation stage, the precipitate contained most of the added actinides [24–26]; therefore, it was not discarded but dissolved in HCl_{conc} and the actinides were further separated and extracted according to a standard method (Eichrom Technologies, Inc. ACW17VBS) using TEVA and TRU resins.

Results and discussion

Table 2 presents the results of model experiments focused on the separation of technetium from sea and fresh water solutions.

Table 2. Results of ^{99}Tc extraction from model sea and fresh water solutions (500 ml)

Experiment	Model solution	Amount of resulting precipitate, ml	Yield, %
I	Sea water	250	96 ± 8
	Fresh water	250	90 ± 7
II	Sea water	30	12 ± 5
	Fresh water	23	< 5
III	Sea water	40	46 ± 4
	Fresh water	40	48 ± 4

High yields were observed under experiment I – 96 and 90% for model sea and fresh water solutions,

respectively. However, given large amounts of the obtained $\text{Fe}(\text{OH})_2$ precipitate with coprecipitated technetium this method cannot be used to analyze natural samples due to its low concentration rate. This also indicates that an excessive amount of FeSO_4 was added.

In experiment II, technetium yields accounted for 12% and less than 5% for sea and fresh water solutions, respectively; therefore, this technique cannot be applied to measure the content of technetium in natural objects; nevertheless, the amount of sediment seems optimal to deal with large sample volumes. Perhaps the problem is due to a small amount of the model solution — 500 ml (compared to natural samples — 50–200 l), since the amount of sediment based on Fe^{3+} of 8 mg/l turned to be too small for a quantitative assessment. Moreover, such an amount of iron provided no visual evidence that could demonstrate the completeness of the reactions.

If ^{99}Tc is measured using mass spectrometry method, for example, based on ICP-MS, ^{99}Ru isobar interference and $^{98}\text{Mo}^1\text{H}$ ion interference should be considered, since their chemical properties are similar to technetium and their large quantities are available in the environment. Molybdenum and ruthenium co-precipitate with technetium at the concentration stage and are enriched jointly at the purification stage. For large volume seawater samples, it has been shown that quantitative removal of molybdenum and ruthenium cannot be done using only one small TEVA column (1.5 ml). Nevertheless, two columns would provide the removal of almost all ruthenium and most of molybdenum [21]. A vacuum system with an extraction chromatographic resin was also used, which significantly reduced the process time.

To enhance the model experiment II, the above method was the one selected due to the ease of its application when TEVA resin was involved, as opposed to the DOWEX packed column, and since it was possible to determine whether the reactions were completed visually by the color change. Based on the results obtained in the first two experiments, a modified technetium separation flowchart was implemented by adjusting the iron carrier and reducing the amount of agent (Figure 3). In the experiment, a sufficient amount of sediment was obtained (10–15-fold concentration of the initial volume), color change was observed in all reduction and oxidation reactions. In experiment III, the yield of technetium increased to $(38 \pm 3)\%$ for sea water and to $(33 \pm 4)\%$ for fresh water. Technetium treatment from alkaline solutions using TEVA resin has yielded in a satisfactory result, which is consistent with the curves showing the dependence between

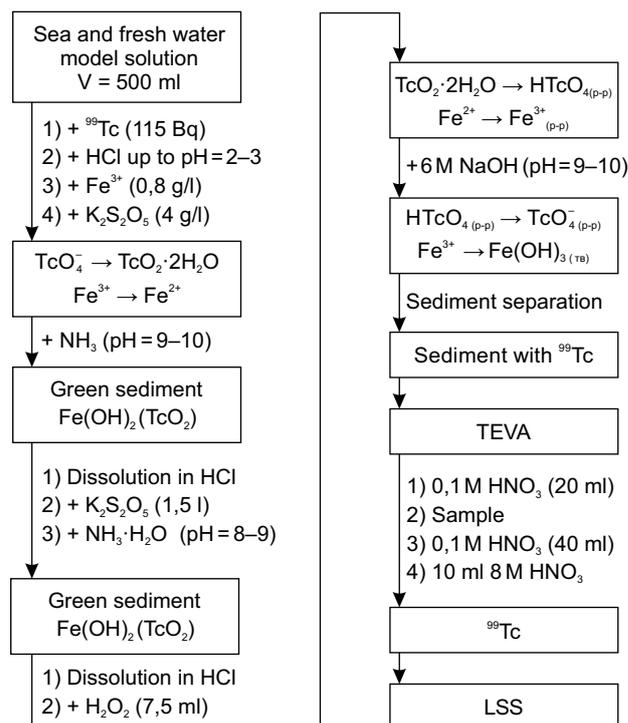


Figure 3. Flowchart of an adapted technique designed for technetium extraction. Experiment III

the capacity factor (k') for TEVA resin and the acid concentration. In technetium measurements, two key separation stages can be distinguished — co-precipitation and chromatographic separation. The main losses occur in the first stage; therefore, it is important to precipitate as much of the radionuclide as possible with a small amount of iron.

If 6 M NaOH is replaced by ammonia to precipitate iron hydroxide, the first stage of the process would eliminate magnesium and calcium precipitates with their high concentrations found in the seawater. Under the original method, due to $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitation by sodium hydroxide in natural seawater samples, the amount of iron ($8 \text{ mg}\cdot\text{l}^{-1}$) was sufficient for high yield of technetium precipitation. If ammonia is used for precipitation purposes and given pH control, only iron hydroxide is precipitated, which clearly reduces the amount of precipitate produced and does not require further reprecipitation to eliminate magnesium and calcium cations. Since the study aims to develop a universal method providing technetium separation from both sea and fresh water, low content of magnesium and calcium in fresh water should be accounted for. Qualitative reaction helps to understand to which degree the process was completed, which is essential when large volumes of water are involved.

The results obtained show that the adapted technique can be used in case of low technetium

concentrations found within large volumes of natural samples. A separate experiment on technetium extraction from weakly alkaline solutions using TEVA resin showed that the sample solution passed through the column could have an alkaline environment with a pH of 10, while the yield of technetium would amount to over 95 %. The identified coprecipitation conditions considered suitable for technetium were tested based on a model solution involving a radionuclide mixture (^{241}Am , ^{239}Pu , ^{233}U and ^{99}Tc). The adapted technique developed to extract actinides from model sea and fresh water solutions resulted in good Pu and U yields (Table 3). Therefore, it can be used to measure the radionuclide content in natural samples.

Table 3. Results of model experiments focused on radionuclide concentration and separation

Experiment	Model solution	Yield, %			
		^{241}Am	^{239}Pu	^{233}U	^{99}Tc
IV	Sea water	–	62 ± 3	43 ± 2	38 ± 3
	Fresh water	50 ± 5	67 ± 3	41 ± 3	33 ± 5

Coprecipitation of actinides with iron hydroxide for their further separation is frequently used as a water-concentration method [7]. High sorption capacity of iron hydroxides facilitates the precipitation of actinides with both $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ providing a yield of 97–99 % [27]. Therefore, Tc and actinides can be coprecipitated from large-volume samples of water. For better ^{99}Tc extraction, the degree of Tc^{4+} oxidation should be identified as early as at the stage of precipitation with $\text{Fe}(\text{OH})_2$, which is possible by using H_2O_2 in an acidic environment.

Since hydrogen peroxide is not stable at a room temperature, at this stage, it is important to use it carefully: Pu is converted to Pu^{4+} , while uranium and americium remain in UO_2^+ and Am^{3+} forms respectively. These actinides can be well precipitated together with $\text{Fe}(\text{OH})_3$, while TcO_4^- remains in the solution. At the same time, iron content does not interfere with further americium, uranium and plutonium separation. In contrast to technetium precipitation, the main losses in this process are associated with the separation stage assuming the use of chromatographic resins.

The study showed that the method developed provides simultaneous extraction of Am, Pu, U and Tc from large volumes of natural water (50–200 l) and a yield of 40–70 %. All actinides co-precipitated with iron (III) hydroxide were then separated and treated by means of extraction chromatography (TEVA, TRU). Technetium remaining in the solution was separated using a TEVA column at the

second precipitation stage with $\text{Fe}(\text{OH})_3$. For sea water samples, the yield of technetium amounted to 38 %, plutonium – 62 % and uranium – 43 %; for fresh water, the radiochemical yield amounted to 33, 67 and 41 %, respectively. Technetium was treated and separated using TEVA resin from caustic solution according to a standard flowchart with a yield achieved of over 95 %. The developed technique appears to be quite effective: precipitation of iron (II) hydroxide with ammonia enables the elimination of calcium and magnesium hydroxide with alkaline solution being directly passed through the TEVA column. Technetium can be separated providing no solution acidification, thus, reducing the length of the entire procedure. Complete reduction of technetium in Tc^{4+} can be easily recognized due to the color change of Fe^{3+} and Fe^{2+} . The developed method is applicable for simultaneous measurements of actinides and ^{99}Tc both in sea and fresh water. Co-precipitation with iron(II) hydroxide was adapted as a method providing ^{99}Tc concentration and separation: the amount of Fe^{3+} was taken equal to 0.8 g/l, while the amount of reducing agent $\text{K}_2\text{S}_2\text{O}_5$ was set to 4 g/l. The process resulted in the yields of (33 ± 4) % and (38 ± 3) % for fresh and sea water, respectively.

Conclusion

The paper presents a method developed to provide joint staged uranium, plutonium, americium and technetium separation from sea and fresh water and relevant measurements. By adjusting the amount of iron and reducing agent, actinides and technetium may be extracted at an adequate level. Moreover, sample handling time was reduced significantly since several steps were eliminated, namely, the stages providing for the acidification of the final solution containing technetium and reprecipitation with iron hydroxide. Complete separation of actinides and technetium from a water sample with a volume of at least 100 liters took 8 hours, which greatly simplifies the monitoring tasks in emergency situations.

The developed method for the joint separation of actinides and technetium will be applied to study fresh water from the Khanka Lake and the sea water from the Sea of Japan.

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References

1. The Japan Times. Fukushima water release to prolong seafood safety woes. — URL: <https://www.japantimes.co.jp/news/2021/04/13/national/fukushima-water-seafood/> (accessed 13 April 2021).
2. Lu Y., Yuan J., Du D., Sun B., Yi X. Monitoring long-term ecological impacts from release of Fukushima radiation water into ocean. *Geography and Sustainability*, 2021, vol. 2, pp. 95–98.
3. Maxwell S., Culligan B., Hutchison J., Utsey R., McAlister D. Rapid determination of actinides in seawater samples. *Journal of Radioanalytical and Nuclear Chemistry*, 2014, vol. 300, no. 3, pp. 1175–1189. DOI: 10.1007/s10967-014-3079-0.
4. Myasoyedova G. V., Nikashina V. A. Sorbtsionnyye materialy dlya izvlecheniya radionuklidov iz vodnykh sred [Sorption Materials for Radionuclide Extraction from Waters]. *Rossiyskiy khimicheskiy zhurnal — Russian Chemical Journal*, 2006, vol. 50, no. 5, pp. 55–63.
5. Zheng J., Yamada M. Determination of plutonium isotopes in seawater reference materials using isotope-dilution ICP-MS. *Applied Radiation and Isotopes*, 2012, vol. 70, no. 9, pp. 1944–1948. DOI: 10.1016/j.apradiso.2012.02.049.
6. Wong K. Radiochemical determination of plutonium in sea water, sediments and marine organisms. *Analytica Chimica Acta*, 1971, vol. 6, no. 3, pp. 355–364. DOI: 10.1016/S0003-2670(01)80923-5.
7. Quinto F., Golser R., Lagos M., Plaschke M., Schäfer T., Steier P., Geckeis H. Accelerator mass spectrometry of actinides in ground- and seawater: an innovative method allowing for the simultaneous analysis of U, Np, Pu, Am, and Cm isotopes below ppq levels. *Analytical Chemistry*, 2015, vol. 87, no. 11, pp. 5766–5773. DOI: 10.1021/acs.analchem.5b00980.
8. Harrison J., Zawadzki A., Chisari R., Wong H. Separation and measurement of thorium, plutonium, americium, uranium and strontium in environmental matrices. *Journal of Environmental Radioactivity*, 2011, vol. 102, no. 10, pp. 896–900. DOI: 10.1016/j.jenvrad.2010.05.010.
9. Wong K., Brown G., Noshkin V. A rapid procedure for plutonium separation in large volumes of fresh and saline water by manganese dioxide coprecipitation. *Journal of Radioanalytical and Nuclear Chemistry*, 1978, vol. 42, pp. 7–15.
10. La Rosa J., Gastaud J., Lagan L., Lee S., Levy-Palomo I., Povinec P., Wyse E. Recent developments in the analysis of transuranics (Np, Pu, Am) in seawater. *Journal of Radioanalytical and Nuclear Chemistry*, 2005, vol. 263, no. 2, pp. 427–436. DOI: 10.1007/s10967-005-0604-1.
11. Lee S., Gastaud J., La Rosa J., Kwong L., Povinec P. Analysis of plutonium isotopes in marine samples by radiometric, ICP-MS and AMS techniques. *Journal of Radioanalytical and Nuclear Chemistry*, 2001, vol. 248, no. 3, pp. 757–764. DOI: 10.1023/A:1010609215926.
12. Imai T., Sakanoue M. Content of plutonium, thorium and protactinium in sea water and recent coral in the North Pacific. *Journal of the Oceanographical Society of Japan*, 1973, vol. 29, no. 2, pp. 76–82.
13. Tagami K., Uchida S. Fundamental studies using ICP-MS for the measurement of technetium-99 in a dried-up deposition sample. *Journal of Radioanalytical and Nuclear Chemistry*, 1995, vol. 190, no. 1, pp. 31–36.
14. Holm E., Gafvert T., Lindahl P., Roos P. In situ sorption of technetium using activated carbon. *Applied Radiation and Isotopes*, 2000, vol. 52, no. 1–2, pp. 153–157.
15. Nicholson S., Sanders T., Blaine L. The determination of low levels of ⁹⁹Tc in environmental samples by inductively coupled plasma-mass spectrometry. *Science of Total Environment*, 1993, vol. 130–131, pp. 275–284.
16. Garraway J., Wilson P. The technetium-catalysed oxidation of hydrazine by nitric acid. *Journal of the Less Common Metals*, 1984, vol. 97, pp. 191–203.
17. Shi K., Qiao J., Wu W., Roos P., Hou X. Rapid determination of technetium-99 in large volume seawater samples using sequential injection extraction chromatographic separation and ICP-MS measurement. *Analytical Chemistry*, 2012, vol. 84, no. 15, pp. 6783–6789.
18. Kuz'menkova N. V. et al. Raspredeleniye radionuklidov mezhdru bioticheskimi i abioticheskimi komponentami radioaktivno-zagryaznennykh vodoyomov V-17 i V-4 [Radionuclide Distribution Between Biotic and Abiotic Components of Radioactively Contaminated Reservoirs V-17 and V-4]. *Voprosy radiatsionnoy bezopasnosti — Issues of Radiation Safety*, 2017, no. 1, pp. 54–66.
19. Fifield L. Accelerator mass spectrometry of long-lived heavy radionuclides. *Radioactivity in the Environment*, 2008, vol. 11, pp. 263–293. DOI: 10.1016/S1569-4860(07)11008-1.
20. Rokop D., Schroeder N., Wolfsberg K. Mass spectrometry of technetium at the subpicogram level. *Analytical Chemistry*, 1990, vol. 62, no. 13, pp. 1271–1274.
21. Shi K., Hou X., Roos P., Wu W. Determination of technetium-99 in environmental samples: a review. *Analytica Chimica Acta*, 2012, vol. 709, pp. 1–20. DOI: 10.1016/j.aca.2011.10.020.
22. Lyman J., Fleming R. Composition of sea water. *Journal of the Marine Research*, 1940, vol. 3, no. 2, pp. 134–146.
23. Aliyev R. A. et al. Opredeleeniye Tc-99 v zagryaznennykh prirodnykh vodakh [Determination of

Tc-99 in Contaminated Natural Waters]. *Voprosy radiatsionnoy bezopasnosti — Issues of Radiation Safety*, 2007, no. 3, pp. 10–16.

24. Hou X. Radioanalysis of ultra-low level radionuclides for environmental tracer studies and decommissioning of nuclear facilities. *Journal of Radioanalytical and Nuclear Chemistry*, 2019, vol. 322, pp. 1217–1245. DOI: 10.1007/s10967-019-06908-9.

25. Lozano J., Fernandez F., Gomez J. Preparation of alpha-spectrometric sources by coprecipitation with

Fe(OH)₃: application to uranium. *Applied Radiation and Isotopes*, 1999, vol. 50, no. 3, pp. 475–477.

26. Lozano J., Fernandez F., Gomez J. Preparation of Alpha-spectrometric sources by coprecipitation with Fe(OH)₃: Application to actinides. *Applied Radiation and Isotopes*, 1997, vol. 48, no. 3, pp. 383–389.

27. Maxwell S. L., Culligan B. K., Kelsey-Wall A., Shaw P. J. Rapid radiochemical method for determination of actinides in emergency concrete and brick samples. *Analytica Chimica Acta*, 2011, vol. 701, no. 1, pp. 112–118. DOI: 10.1016/j.aca.2011.06.011.

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