

**DETERMINATION OF DIFFICULT TO MEASURE
RADIONUCLIDES IN NUCLEAR POWER PLANT WASTES
PhD thesis**

Author: Szabolcs Osváth

Supervisor: Nóra Vajda

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Context of research

The majority of long-lived radionuclides produced in the nuclear fuel cycle can be regarded as “difficult to measure” nuclides due to the low activities (e. g. activation product ^{94}Nb) and/or the absence of γ radiations of medium or high energies in the decay schemes (e. g. fuel components or activation product actinoids are α -emitters, fission and activation product ^{93}Zr and fission product ^{90}Sr are pure β -emitters, activation product $^{93\text{m}}\text{Nb}$ emits X-rays). These isotopes are important because of the possible long-term environmental effect due to their long half-lives. That is why their analysis is necessary, but chemical separation is needed before the nuclear measurement of all the isotopes mentioned above.

As a university and PhD student, I participated in the development of a complex radioanalytical method for the simultaneous determination of the radionuclides mentioned above (especially $^{93\text{m}}\text{Nb}$, ^{94}Nb , ^{237}Np and ^{93}Zr) from a single aliquot of liquid nuclear power plant samples.

The method for determination of $^{93\text{m}}\text{Nb}$ and ^{94}Nb is based on three publications: the idea of using Nb_2O_5 precipitation for separation was taken from Espartero (1998), anion exchange chromatography is based on Hegedűs' (1985) results, and Lederer's (1992) work was used when developing the separation of Nb from Sb. In the last half century, many papers were published about analysis of actinoids, for example my supervisor's combined procedure [6]. That makes separation and measurement of many radionuclides (especially actinoids) possible. This is why analysis of ^{237}Np was combined with that of Th, U, Pu, Am and Cm. The extraction chromatographic material UTEVA is well known, thanks to Horwitz (1992). According to the oxidation of actinoids, best results were achieved following Ward's (1954) ideas, using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and AgNO_3 catalyst. Behavior of Zr on UTEVA was most detailed described by Maxwell (1998).

Objectives

Importance of reliable and accurate methods for determination of difficult to measure radionuclides is nowadays increasing. Analysis of components of radioactive wastes is necessary before deposition. Analysis of materials of dismantled nuclear facilities is a challenging job, as low activity concentrations have to be determined, the result can allow even the clearance of the material. As environmental protection is of major concern today, there is a need for radioanalysis of environmental samples and foodstuff. The need for radioanalysis has been emphasized by the severe accident of the Fukushima Daiichi nuclear power plant.

Objective of my PhD studies was to develop radioanalytical methods for separation and determination of difficult to measure radionuclides ($^{93\text{m}}\text{Nb}$, ^{94}Nb , ^{237}Np és ^{93}Zr) from liquid radioactive wastes using effective extraction chromatographic techniques. A combined radioanalytical procedure (analyzing the isotopes of as many as possible elements) is a general intention in order to save work, money and time. This is why I wanted to analyze ^{237}Np with other actinoids together, and I wanted to combine my methods with each other.

Method development included optimization of steps of radioanalysis, testing different reagents and reaction conditions. Recoveries, decontamination factors and activity concentrations were experimentally determined. The reliability of the methods was checked by comparing the measured activity concentrations with calculated ones.

Methods

Model experiments were performed to develop radioanalytical procedures for determination of ^{93m}Nb , ^{94}Nb , ^{237}Np and ^{93}Zr , and to optimize the reaction parameters. The methods were tested on liquid radioactive waste samples (evaporator concentrates) from a nuclear power plant. For separation of elements (groups of elements) precipitation, co-precipitation, anion exchange and extraction chromatography were performed. To follow the chemical losses (to determine the recoveries) tracers (^{95}Nb , ^{239}Np , ^{95}Zr) were used.

Nb was pre-concentrated by precipitating Nb_2O_5 after repeated evaporation with HNO_3 and dispersion in HCl . Nb ions were retained from HF and eluted with HBr/HF . Actinoids were pre-concentrated from dilute acidic solutions on $\text{Fe}(\text{OH})_2$ and – after dissolving the precipitate – oxidized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of AgNO_3 catalyst. UTEVA column was used for extraction chromatographic separation of actinoids, as they can be selectively eluted using different acids in different concentrations. $\text{Fe}(\text{OH})_2/\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ precipitate was used for pre-concentration of ^{93}Zr , HF for dissolution of the precipitate, and H_3BO_3 to complex the excess F^- ions. ^{93}Zr was isolated on UTEVA also.

Quantitative determination of the mentioned radionuclides was performed using α , γ , and X-ray spectrometers with semiconductor detectors as well as ELEMENT2 type inductively coupled mass spectrometer (ICP-MS).

New scientific results

1. I developed a method for the determination of ^{93m}Nb and ^{94}Nb which is based on precipitation of niobium oxide, anion exchange chromatography, gamma and X-ray spectrometry. Using this method, I analyzed nuclear power plant evaporator concentrates; limits of detection are 10^{-4} - 10^{-3} Bq/mL ^{94}Nb and 10^{-2} - 10^{-1} Bq/mL ^{93m}Nb (if measuring time is 4 hours). I confirmed the reliability of the results by comparing the measured $^{93m}\text{Nb}/^{94}\text{Nb}$ activity ratios with calculated ones. [1, 4, 5]
2. I developed a relatively fast and simple method for the determination of Th, U, Pu, Am, Cm radionuclides and ^{237}Np which is based on oxidation of actinoids, chromatographic separation on UTEVA, alpha spectrometry or ICP-MS measurement. Using this method, I analyzed nuclear power plant evaporator concentrates. In case of ICP-MS measurement of ^{237}Np , limit of detection is 2×10^{-10} Bq/L, background equivalent concentration is 10^{-10} Bq/L, in case of other actinoids, limit of detection is 1 mBq/L. I confirmed the reliability of the results by comparing the measured $^{237}\text{Np}/^{239,240}\text{Pu}$ activity ratios with calculated ones. I showed that in 1 M HNO_3 with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in presence of AgNO_3 catalyst even Am can be oxidized, but due to the circumstances of the chromatography, it is reduced back and is not retained on UTEVA. [2, 3, 4]
3. I developed a relatively fast and simple method for the determination of ^{93}Zr which is based on precipitation of zirconium oxide, chromatographic separation on UTEVA, and ICP-MS measurement. Using this method, I analyzed nuclear power plant evaporator concentrates; limit of detection is 0.02 Bq/L, background equivalent concentration is 0.05 Bq/L. [3,4]
4. Combining the method for the determination of isotopes of Nb, the method for the determination of actinoids and the method for the determination of ^{93}Zr , I developed a complex procedure, that can be used for the simultaneous determination of Th, U, Np, Pu, Am, Cm radionuclides, ^{90}Sr , as well as ^{93}Zr or ^{93m}Nb and ^{94}Nb . [4]

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Utilization of the results

The results presented above were utilized by foremost determining the activity concentrations of ^{93m}Nb , ^{94}Nb , ^{237}Np and ^{93}Zr in a few evaporator concentrate samples from the Paks Nuclear Power Plant [8].

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