Determination of uranium and transuranium elements in radioactive wastes of low and medium activity from a nuclear power plant

SUMMARY OF Ph.D. THESIS

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2002

Introduction

Radioactive wastes are inavoidable by-products of the production of electrical energy based on nuclear power. Treatment, temporary and permanent storage of radioactive wastes have to be solved in such a way that these materials are isolated from the environment so that they do not constitute unacceptable risks for humans and the nature in the present time or in the future.

In order to achieve this aim, wastes to be released or deposited are subjected to a strict check, the isotopic composition of the waste material and the activity concentrations of the individual radionuclides are to be known. For the determination reliable analytical methods with appropriate sensitivity producing reproducible results are required.

Subject of the Ph.D. Thesis

Development of a new analytical method for the investigation of the uranium and transuranium elements in the low- and medium-activity liquid radioactive wastes (evaporation residues, exhausted ion-exchange resins, active sludges and other contaminated technological liquids), and in waste waters to be released into the environment in the nuclear power plant in Paks, by means of alpha-spectrometric method.

Timeliness of the researh

- During the operation of the VVER-440 type reactor of the nuclear power plant in Paks α-emitting isotopes may get into the primary coolant - owing to the surface contamination of fuel elements, leakage or damage of the enclosure, or as activation products - and these radionuclides may then get into regeneration wastes formed during the purification of primary coolant water, and into other wastes via intended or unintended leakage.
- Radioactive wastes produced by different reactor types have reactor-specific matrix, which explains why different procedures are needed to the determination of the alpha-emitting isotopes present.

Description of the problem

Alpha-emitting isotopes formed in nuclear power plants include isotopes of uranium and their activation and decomposition products. When uranium-based fuel elements are used, uranium and plutonium constitute the major part, while americium and curium the smaller part of the alpha-emitting isotopes occurring in the waste materials. These radionuclides appear in the regeneration wastes of the purifiers of primary water coolant in concentrations depending on their amounts, chemical forms and solubilities.

The aim of my research was to develop analytical methods for routine application for the determination of uranium and transuranium isotopes in the radioactive waste materials of different states and present in different matrices formed during the operation of the VVER-440 type reactor of the nuclear power plant in Paks and intended for permanent storage, and in waste waters to be released into the environment.

Analysis of α-emitting isotopes in radioactive wates from nuclear power plants is not a simple task technically, since in some cases due to the low radioactive concentration (in waste waters for ^{238}U 0.5-1.0μg/l), in others to the difficult matrix environment (for ion-exchange resins and sludges) highly efficient enrichment or complicated chemical separation operations become inevitable. Hence, the heel of Achilles of the analytical procedure here is sample preparation.

Enrichment and separation methods described in the relevant literature were developed mainly for the reprocessing of fuel elements and for the treatment of the reprocessing wastes, where the radiochemical concentrations of the alpha-emitting isotopes are relatively high. Modified versions of these methods are adapted and used to the determination of the activity concentrations which are several orders of magnitude smaller in environmental and waste samples. The success of these modified analytical procedures depends first of all on the sample preparation method applied.

The other crucial point of transuranium analysis is the production of a thin-layer preparate for energy-selective α-spectrometric measurement. The small sample obtained after enrichment is to be spread on a highly polished stainless steel disc in a well-adhering form in a uniform layer of a thickness which is infinitely small with respect to the transmission of α-rays. The amount of sample deposit is stricly limited by the surface area of the disc and the allowable layer thickness. No appreciable self-absorption is allowed, hence the layer thickness may not exceed a few μm. The best solution, which is also the most difficult to realize is in which the radionuclide to be measured is situated on the surface of the sample holder disc. Procedures which meet these requirements of the preparation of an ideal sample usually involve time consuming and complicated operations, and require good technical background and skill.

Summary of the research results

I developed a new analytical procedure for the alpha-spectrometric determination of uranium (^{238}U,^{235}U,^{234}U) and transuranium isotopes ($^{239+240}Pu$, ^{244}Cm) in low-and medium-activity liquid radioactive wastes, including exhausted ion-exchange resins, sludges and evaporation residues formed during the operation of the VVER-440 reactor of the nuclear power plant in Paks, and in waters to be released into the environment, which are, according to technological intentions, inactive.

I tested the accuracy of the results of determinations carried out by means of the chemical separation and analytical methods developed in the framework of the international QUALITY ASSESSMENT PROGRAM (QAP) organized by the U.S.Department of Energy Environmental Measurements Laboratory (U.S. DOE EML) for evaluating the results of environmental radiological measurements.

I participated in international control measurements, in which 139 laboratories tested their measurement results, on three occasions (programs QAP-49, QAP-50 and QAP-51).

I determined the concentrations and activity concentrations of ^{238}U; ^{234}U; and ^{239}Pu radionuclides in soil samples (which are similar to sludge samples) and water samples (which are similar to the liquid samples from nuclear power plants) using the analytical procedures described in my thesis. The results of the tests indicate that the accuracy of the results meets the strict requirements of the QAP program, and reaches the international standard.

Summary of the assessment results of the QAP program

Measurement and EML evaluation results for QAP soil samples

Name of sample (No.)	Radionuclide determined	Measurement result sent	Estimated error of measurement result sent	EML measurement result	Estimated error of EML measurement result	EML evaluation
QAP-50 (9903SOHT)	**U** chemical concentration	**12.0** (μg/g)	±1.0	**11.8** (μg/g)	±0.3	**A**
QAP-50 (9903SOHT)	**U** activity concentration	**293.2** (Bq/Kg)	±21.0	**291.0** (Bq/Kg)	±3.0	**A**
QAP-50 (9903SOHT)	^{238}**U**	**148.0** (Bq/Kg)	±10.0	**145.0** (Bq/Kg)	±1.732	**A**
QAP-50 (9903SOHT)	^{234}**U**	**145.0** (Bq/Kg)	±10.0	**140.67** (Bq/Kg)	±1.155	**A**
QAP-51 (9909SOHT)	^{239}**Pu**	**2.34** Bq/Kg)	±0.2	**3.2** (Bq/Kg)	±0.5	**W**

Measurement and EML evaluation results for QAP water samples

Name of sample (No.)	Radionuclide determined	Measurement result sent	Estimated error of measurement result sent	EML measurement result	Estimated error of EML measurement result	EML evaluation
QAP-50 (9903WAHT)	**U** chemical concentration	**0.0191** (μg/ml)	±0.002	**0.0212** (μg/ml)	±0.001	**A**
QAP-50 (9903WAHT)	**U** activity concentration	**0.47** (Bq/L)	±0.05	**0.541** (Bq/L)	±0.0246	**W**
QAP-50 (9903WAHT)	^{238}**U**	**0.236** (Bq/L)	±0.02	**0.262** (Bq/L)	±0.016	**A**
QAP-50 (9903WAHT)	^{234}**U**	**0.225** (Bq/L)	±0.020	**0.269** (Bq/L)	±0.015	**W**
QAP-49 (9809WAHT)	^{239}**Pu**	**1.1** Bq/L)	±0.15	**1.41** (Bq/L)	±0.04	**N**

EML evaluation: **A**=Acceptable, **W =** Acceptable with Warning, **N**= Not Acceptable

New scientific results

The new scientific results achieved in the development of sample preparation methods for the alpha-spectrometric analysis of liquid radioactive wastes from a nuclear power plant are summarised as folows:

- I was the first to apply a procedure for the digestion of ion-exchange resins involving decomposition in an oxygen atmosphere at overpressure in a closed calorimeter bomb. I have found no paper in the literature on the use of such technique for the sample preparation of radioactive wastes.
- I processed the solid fraction of radioactive sludge samples, following decomposition, by extraction ad re-extraction, using an extractant with apolar solvent base and containing tributyl phosphate. Although tributyl phosphate is widely applied as an extractant, this type of procedure was first developed and applied as a reactor-specific method by myself to the determination of uranium and plutonium in low- and medium-activity radioactive liquid waste (sludge) samples from the nuclear power plant in Paks.
- I worked out a new selective method for the determination of the alpha-emitting costituents in evaporation residues containing both organic and inorganic compounds and saturated with boric acid.
- I carried out the decomposition of the organic compounds present in radioactive sludges, evaporation residues and waters to be released into the environment in an Erdey-Jankovits digestor modified by myself for my specific purposes. The modified digestor, in which the entire sample preparation procedure involving chemical separation can be carried out, is universally applicable for sample preparation for the determination of alpha-emitting isotopes in any type of low- and medium-activity liquid radioactive waste occurring in a nuclear power plant.
- I developed on the basis of literature experiences, and was the first to apply an electrodeposition technique for the production of thin-layer preparates to alpha-spectrometric analysis of radioactive waste streams in the nuclear power plant in Paks. Uranium and transuranium isotopes were deposited by electrolysis in a device designed and constructed in our laboratory with thermostation and controlled cathode potential adjusted at different values for each element to be deposited.

New elements of the application-technical aspects of the analysis of α-spectra and of waste assessment

- I prepared an automatic spectrum evaluation program for the α-spectrometric analysis of radioactive wastes. The program is simple, easy to handle and is working with a template composed in EXCEL workbook. The importance of the program written in Turbo Pascal 7 lies in the fact that it converts the files with MCA extension registered by the multi-channel analyser to text files with PRN extension. To these files, when loaded into EXCEL tables, all functions of EXCEL (calculation, built-in functions, chart creation) can be applied in order to evaluate overlapping peaks often occurring in alpha-spectra.
- Based on the measurement results of uranium and transuranium activity concentration determinations in the radioactive wastes of the nuclear power plant in Paks carried out using the methods described in my thesis I made scaling factor and correlation analysis calculations. The calculations show that the scaling factors obtained for the transuranium elements in the final products (evaporation residues, ion-exchange resins, other liquid radioactive wastes) appearing in the technological branches of the nuclear power plant generally agree with the internationally known values, but no exact analytical information is available for the determination of the transuranium concentrations. Studies of the scaling factor point to the fact that α-spectrometry may not be replaced by model calculations. α-spectrometry is at present the most reliable technique for the determination of the activity concentrations of transuranium radionuclides in radioactive wastes.

Application

- Using the new analytical methods developed, we regularly measure the uranium and transuranium radionuclides in the radioactive liquid wastes, released water, and in the water in test wells bored around the nuclear power plant in Paks.

- Using the methods developed and the experiences gathered in Hungary in the field, we take part in research and development projects for waste assessment in nuclear power plants in Slovakia.

Publications and lectures

Publications serving as the basis of the Ph.D thesis

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8. S.Tölgyesi, I.Gresits,T. Past L.,Szabó,G.Volent,T.Pintér: Determination of Alpha-emitting Isotopes in Radioactive Wastes of Nuclear Power Plant Paks. Journal of Radioanalitical and Nuclear Chemistry, Vol. 254, No.2 pp 357-361 (2002)

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1. Gresits Iván, Szabó Levente, Tölgyesi Sándor, Volent Gábor, Solymosi József, Nagy Lajos György: Tórium bomlástermékeinek alfa-spektrometriás meghatározása levegő-mintákból. (Determination of the decomposition products of thorium in air samples by alpha-spectrometry) Eötvös Loránd Fizikai Társulat Sugárvédelmi Konferencia. Balatonkenese 1993. máj. 12-14.
2. Gresits Iván, Solymosi József, Tölgyesi Sándor, Ormai Péter, Past Tibor, Szabó Levente: Alfa-sugárzó izotópok szelektív kémiai elválasztása a PA Rt. folyékony hulladékaiból. (Selective chemical separation of alpha-emitting isotopes from liquid wastes from the nuclear power plant in Paks) Eötvös Loránd Fizikai Társulat Sugárvédelmi Konferencia. Balatonkenese 1994. május 3
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