

ANALYSIS OF ACTINIDES IN SAFEGUARDS SWIPE SAMPLES BY RADIOMETRIC AND MASS SPECTROMETRIC METHODS

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Ph.D. Theses

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Introduction

The safeguards system of the International Atomic Energy Agency (IAEA) aims to prevent the diversion of nuclear material from peaceful uses to nuclear weapons or other nuclear explosive devices. Swipe sampling - one of the implemented safeguards measures - has been routinely used by safeguards inspectors since 1996. Its objectives are to verify the declared nuclear activities and/or materials and to discover the traces of undeclared ones through the detection of U and Pu in the samples performed by either bulk or particle analysis.

While bulk analysis involves the determination of the U and Pu content of the whole sample after the separation of actinides by radioanalytical methods, particle analysis obtains that of individual particles originating from safeguards swipe samples. The U and Pu content is measured mostly by mass spectrometric techniques (e.g. inductively coupled plasma mass spectrometry (ICP-MS), secondary ion mass spectrometry (SIMS), thermal ionization mass spectrometry (TIMS)).

The results of the analysis - U and Pu content and isotopic composition - as a conclusion can either verify the declared nuclear activities and/or materials of the non-nuclear weapon member states or even reveal undeclared ones.

Objectives

The aim of this study was to develop sensitive radioanalytical methods for bulk and particle analysis of safeguards swipe samples to determine the actinide content (U, Th, Np, Pu, Am and Cm) in the whole sample by combining mass spectrometric and radiometric methods, and the U isotopic composition in radioactive particles originating from swipes by laser ablation ICP-MS (LA-ICP-MS).

By the determination of other actinides (i.e. Th, Np, Am and Cm) besides U and Pu more information on the sample can be obtained, thus the reliability of the safeguards conclusions can be improved.

In the analysis of safeguards swipe samples mass spectrometric methods are mostly used, however radiometric methods - such as alpha spectrometry - are capable of determining actinides, as well. Although the combination of these techniques is only rarely performed, it can not only improve the reliability of the results (through the comparison of the results on

isotopes which can be analyzed by both techniques) but more information can also be obtained (there are several isotopes which can be analyzed by only one technique).

Bulk analysis provides information only about the average composition of the samples however the artificial fissile material in the environment mostly occurs in the form of solid, radioactive particles. Particles containing alpha emitting and/or fissile material can be identified, localized and even micromanipulated. The U content of these 'hot particles' can be examined with high sensitivity excluding the effect of the sample as matrix. The information on single particles (such as isotope ratios of actinides) given by particle analysis offers a great possibility. According to the results, various origin scenarios can be distinguished based on the analysis of swipe samples, furthermore traces of undeclared activities can be detected even in case of attempts of concealments (e.g. releasing big amount of declared material on site). Moreover, the more precise information can improve the verification process of IAEA Safeguards.

Achievements

The literature overview of the dissertation gave only a very brief outline on the general aspects and focuses more on the special aspects of the topics that are closely related to the subject of the PhD dissertation. First, I introduced the safeguards system of the IAEA as the base of the current dissertation from the practical point of view of the analysis of safeguards swipe samples. Secondly, I shortly discussed the important properties of the actinides relevant to their separation. In the chapter on bulk analysis after the short description of the actinide separation techniques, I briefly summarized the sequential separation of actinides and the applied measurement techniques including alpha, beta (liquid scintillation counting), gamma spectrometry and ICP-MS. Finally, I also gave a brief overview of the particle analysis of actinides.

The experimental work of the dissertation covered two main topics: development of radioanalytical procedures for the determination of actinides by alpha spectrometry and/or ICP-MS, and the determination of U isotopic composition of individual particles originating from safeguards swipe samples by LA-ICP-MS.

The adaptation of a radiochemical separation method for the determination of actinides (Th, U, Pu and Am) by alpha spectrometry in safeguards swipe samples

I successfully adapted a radioanalytical method - originally designed for the analysis of small environmental samples - for the determination of actinides (Th, U, Pu and Am) in safeguards swipe samples by alpha spectrometry.

First of all, I studied several procedures (i.e. ignition, ashing, acid digestion and microwave digestion) to choose the most efficient one to decompose the matrix of the swipe sample, since the original procedure - fusion - was not appropriate for my purpose. Secondly, due to the relatively simple sample matrix of the swipes the step of the actinide preconcentration could be neglected, however, the oxidation state adjustment of Pu became more difficult. According to the modified procedure hydrazine had to be used besides Mohr's salt to perform the complete reduction of all actinides. This modification resulted in the presence of hydrazine excess in the load solution, therefore the procedure of adjusting Pu(IV) had to be also optimized by using excess amount of NaNO₂ compared to the expected amount of hydrazine.

The adapted radioanalytical method is capable of determining the following isotopes: ²²⁸Th, ²³⁰Th, ²³²Th, ²³⁴U, ²³⁵U, ²³⁸U, ²³⁸Pu, ^{239,240}Pu, ²⁴¹Am, ²⁴²Cm and ^{243,244}Cm. I determined the achievable detection limits (0.2 and 7.2 mBq/sample referring to counting times varying between 20 000 and 150 000 s), and the typical recoveries: 77% ± 5%, 67% ± 12%, 51% ± 16% and 73% ± 7% for Am, Pu, Th and U, respectively.

I also demonstrated the capability of the method for safeguards purposes by analyzing swipe samples taken during national safeguards inspections in several Hungarian nuclear facilities. I was able to detect the traces of the nuclear activities in some facilities, e.g., I detected U isotopes with natural isotopic composition at a company producing yellow cake.

Method development for the sequential separation of Th, U, Np, Pu and Am(Cm) on a single extraction chromatographic column

I improved the above radioanalytical procedure which resulted in the capability to sequentially separate Th, U, Np, Pu and Am(Cm) using only a single extraction chromatographic column while in the literature more extraction chromatographic and/or ion exchange columns have been used typically to achieve this objective. The method applied the combination of two measurement techniques, i.e., alpha spectrometry and ICP-MS, therefore

the list of nuclides that could be determined was extended and it covered ^{228}Th , ^{230}Th , ^{232}Th , ^{234}U , ^{235}U , (^{236}U), ^{238}U , ^{237}Np , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , ^{242}Cm and $^{243,244}\text{Cm}$ nuclides, furthermore the reliability of results was also increased.

I determined the achievable detection limits, e.g. 0.001, 0.004, 0.6, 0.4 and 0.5 mBq g⁻¹ for ^{235}U (ICP-MS), ^{238}U (ICP-MS), ^{238}Pu (alpha spectrometry), ^{239}Pu (ICP-MS) and ^{241}Am (alpha spectrometry), respectively, and the typical recoveries of each actinide: above 50% which can be regarded as good in case of a combined radioanalytical procedure. I validated the radioanalytical method by the analysis of certified reference material and standard swipe samples of the IAEA.

During method development some interesting properties of the TRU extraction chromatographic resin were revealed. I proved that on-column oxidation state adjustment of Np was possible on the TRU extraction chromatographic column only in case of certain oxidation states. Although tetravalent Np could be oxidized to Np(VI) with Ti(IV) and hexavalent Np could be reduced to Np(IV) with Ti(III) at a relatively high Ti concentration (>0.05 mol l⁻¹); Np could not be adjusted on-column to tri- and pentavalent oxidation states with any examined redox reagents ($\text{K}_2\text{S}_2\text{O}_5$, NaSO_3 , TiCl_3 ; KMnO_4 , NaNO_2 , $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$ and TiCl_4). Moreover, I proved that Ti improved the elution of tetravalent actinides. It was assumed that Ti as analogue helped remove Th by co-elution.

The modification of the standard procedure of the IAEA for the determination of U and Pu in environmental samples

I modified the standard procedure of the IAEA Clean Laboratory for the determination of U and Pu in environmental samples in order to be able to analyze ^{238}Pu by the combination of alpha spectrometry and ICP-MS. The amount of ^{238}Pu was calculated from the $^{238}\text{Pu} / ^{239,240}\text{Pu}$ ratio – determined by alpha spectrometry – in the view of the amount of ^{239}Pu and ^{240}Pu – determined by ICP-MS. I gave a very detailed uncertainty calculation in the dissertation, since the calculation of the uncertainty became more difficult due to the fact that the results originated from two independent measurements. I tested the method including the calculations by analyzing certified reference material and real samples originating from a safeguards inspection. The results demonstrated that less than 10 fg of ^{238}Pu could be determined within 6% of total uncertainty.

The combination of alpha spectrometry and ICP-MS applied in this study enabled the ^{238}Pu determination which could enhance the reliability of the final conclusions of the

analytical results of the safeguards inspection samples. The method has got application in the practice of the IAEA Clean Laboratory.

Method development for the determination of U isotopic composition of single particles originating from safeguards swipe samples by LA-ICP-MS

I developed a complex method for the determination of the U isotopic composition of single particles originating from safeguards swipe samples. The method consisted of several, individual procedures.

The particles were removed from the swipe samples by an impactor which enabled to transfer them directly onto an appropriate sample holder, i.e. membrane filter that was designed to fit all the further procedures.

I applied solid state nuclear track detectors (SSNTD) to identify the particles of interest (POIs, particles containing alpha emitting material). I thoroughly tested and optimized each step (i.e. exposition, etching and analysis in optical microscope) of this procedure to make it as effective as possible for safeguards purposes.

The use of SSNTDs allowed me to localize the identified particles by 6-point algorithm and relocalize them by 3-point algorithm. The use of these algorithms resulted in very precise localization. The mathematical basis of these calculation methods was given in the dissertation, as well. I also tested, optimized and determined the achievable accuracy and precision: $10 \pm 7 \mu\text{m}$ and $7 \pm 6 \mu\text{m}$ for localization by 6-point and relocalization by 3-point algorithm, respectively.

I developed methods for the micromanipulation of particles. These methods were tested, optimized and applied in a research project on the examination of particles originating from the primary and the secondary coolant of the Nuclear Power Plant of Paks.

I determined the U isotopic composition of the POIs by LA-ICP-MS and recommended two calculation methods to obtain the U isotope ratios and the U isotopic composition given in atom or mass percent. I thoroughly tested and optimized the procedure and the calculation methods.

I also tested the whole method with different combinations of the procedures mentioned above to prove that the procedures can be combined ad-libitum and the method can be effectively applied for safeguards purposes. I validated the method with different combinations using test particles containing natural U and particles originating from confiscated nuclear fuel pellets with known U isotopic composition.

Novel contributions

1. I have successfully adapted a combined radioanalytical method - originally designed for the analysis of small environmental samples - for the determination of actinides in safeguards swipe samples. The following isotopes can be determined by the method based on alpha spectrometry: ^{228}Th , ^{230}Th , ^{232}Th , ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am , ^{242}Cm and $^{243,244}\text{Cm}$. The achieved detection limits were as low as 0.2 and 7.2 mBq/sample (in case of counting times of 20 000 and 150 000 s), and the typical recoveries were $77\% \pm 5\%$, $67\% \pm 12\%$, $51\% \pm 16\%$ and $73\% \pm 7\%$ for Am, Pu, Th and U, respectively. I have demonstrated the effectiveness and the capability of the method for safeguards purposes by analyzing swipe samples taken during national safeguards inspections in several Hungarian nuclear facilities.
2. I have improved the above mentioned radioanalytical method. The new method is capable of the simultaneous separation of Th, U, Np, Pu, Am(Cm) on a single TRU extraction chromatographic column based on selective, on-column oxidation state adjustment of actinides. The method involves the combination of two measurement techniques, i.e., alpha spectrometry and ICP-MS, therefore the list of nuclides that can be determined has been extended and it covers ^{228}Th , ^{230}Th , ^{232}Th , ^{234}U , ^{235}U , (^{236}U), ^{238}U , ^{237}Np , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , ^{242}Cm and $^{243,244}\text{Cm}$ nuclides, furthermore the reliability of results has been increased. The achieved detection limits were as low as 0.001, 0.004, 0.6, 0.4 and 0.5 mBq g^{-1} for ^{235}U (ICP-MS), ^{238}U (ICP-MS), ^{238}Pu (alpha spectrometry), ^{239}Pu (ICP-MS) and ^{241}Am (alpha spectrometry), respectively. The typical recoveries of each actinide were above 50% which can be regarded as good in case of a combined radioanalytical procedure.
3. I have proved that on-column oxidation state adjustment of Np is possible on the TRU extraction chromatographic column only in case of certain oxidation states. I have proved that tetravalent Np can be oxidized to Np(VI) with Ti(IV), hexavalent Np can be reduced to Np(IV) with Ti(III) at a relatively high Ti concentration ($>0.05 \text{ mol l}^{-1}$), and Np cannot be adjusted on-column to tri- and pentavalent oxidation states with any examined redox reagents ($\text{K}_2\text{S}_2\text{O}_5$, NaSO_3 , TiCl_3 ; KMnO_4 , NaNO_2 , $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$ and TiCl_4). Moreover, I have proved that Ti - as an analogue of Th - improved the elution of tetravalent actinides.

- 4.** I have modified the standard procedure of the International Atomic Energy Agency (IAEA) Clean Laboratory for the determination of U and Pu in environmental samples in order to analyze ^{238}Pu - after purification on an anion exchange resin - by combining alpha spectrometry with ICP-MS. The amount of ^{238}Pu is calculated from the $^{238}\text{Pu} / ^{239,240}\text{Pu}$ ratio - determined by alpha spectrometry - in the view of the amount of ^{239}Pu and ^{240}Pu – determined by ICP-MS. The results demonstrated that 10 fg of ^{238}Pu can be determined within 6% of total uncertainty. The ^{238}Pu determination can enhance the reliability of the final conclusions of the analysis of the safeguards inspection samples. The method has got application in the practice of the IAEA Clean Laboratory.
- 5.** I have developed a complex method for the determination of the U isotopic composition of single particles originating from safeguards swipe samples. The method consists of several, individual procedures for (1) particle removal from swipe samples by vacuum impactor technique, (2) the identification of particles containing alpha emitting material using solid state nuclear track detectors, (3) the localization and relocalization of identified particles based on basis transformation, (4) the micromanipulation of particles and (5) the analysis of single particles ($>10 \mu\text{m}$) by LA-ICP-MS. The procedures can be combined ad-libitum. The method was used for the examination of particles originating from confiscated nuclear fuel pellets.

Publications related to the PhD dissertation

Refereed Journal Publications

1. Mácsik, Z., Groska, J., Vajda, N., Vogt, S., Kis-Benedek, G., Kim, C.S., Maddison, A., Donohue D. (2012) *Improved radioanalytical method for the simultaneous determination of Th, U, Np, Pu and Am(Cm) on a single TRU column by alpha spectrometry and ICP-MS.* **Radiochimica Acta**, Accepted for publication
2. Mácsik, Z., Shinonaga, T. (2010) *Accuracy and precision of ²³⁸Pu determination at fg level by alpha spectrometry using ²³⁹Pu and ²⁴⁰Pu amount analyzed by inductively coupled plasma mass spectrometry.* **Applied Radiation and Isotopes**, 68 2147-2152
3. Vajda, N., Törvényi, A., Kis-Benedek, G., Kim, C.K., Bene, B., Mácsik, Zs. (2009) *Rapid method for the determination of actinides in soil and sediment samples by alpha spectrometry.* **Radiochimica Acta**, 97 395-401
4. Mácsik Zs., Vajda N., Bene B., Varga Zs. (2009) *Radioanalitikai módszer fejlesztése dörzsmintákban található aktinidák elemzésére.* **Sugárvédelem on-line folyóirat**, II. évf. 1. szám 14-18

Conference papers

5. Mácsik Z., Széles É., Stefánka Zs., Vajda N. *Method development for analysis of single particles for safeguards purposes* – conference paper and presentation; **33rd ESARDA Annual Meeting – Symposium on safeguards and nuclear material management**, 16-20 May 2011, Budapest, Hungary
6. Mácsik, Z., Vajda, N., Széles, É., Katona, R. *Method development for analysis of single hot particles in Safeguards swipe samples* – conference paper and poster; **Symposium on International Safeguards: Preparing for Future Verification Challenges**, 1-5 November 2010, Vienna, Austria
7. Mácsik Zs., Vajda N., Széles É., Katona R. *Módszerfejlesztés nukleáris biztosítéki célú dörzsmintákban található egyedi forró részecskék analízisére* – conference paper and presentation; **Őszi Radiokémiai Napok 2010**, Hevesy prize special award, 20-22 October 2010, Keszthely, Hungary
8. Vajda, N., Molnár, Zs., Mácsik, Z., Széles, É., Hargittai, P., Tóth Pintér Csordás, A., Pintér, T. *Corrosion particles in the primary coolant of VVER-440 reactors* – conference paper and presentation; **Nuclear Plant Chemistry Conference**, 3-7 October 2010, Quebec City, Canada
9. Mácsik, Zs., Shinonaga, T. *Környezeti minták Pu tartalmának nagy pontosságú meghatározása biztosítéki ellenőrzések céljából* – conference paper and presentation; **Őszi Radiokémiai Napok 2009**, Hevesy prize 2nd place, 14-16 October 2009, Pécs, Hungary
10. Mácsik Zs., Vajda N., Bene B., Varga Zs. *Radioanalitikai és mikroanalitikai módszerek fejlesztése dörzsmintákban található aktinidák elemzésére* – conference paper and presentation; **Őszi Radiokémiai Napok 2008**, 28-30 October 2008, Hajdúszoboszló, Hungary
11. Mácsik, Z., Vajda, N., Bene, B., Varga, Zs. *Development of Radioanalytical and Microanalytical Procedures for the Determination of Actinides in Environmental Samples* – conference paper and presentation; **International Youth Nuclear Congress 2008** (IYNC 2008), ENEN prize, 20-26 September 2008, Interlaken, Switzerland

Conference and seminar presentations and posters

12. Mácsik Zs., Vajda N., Groska J., Széles É. *Th, U, Np, Pu és Am egymás melletti elválasztása egyetlen extrakciós kromatográfiás oszlopon* – presentation; **Őszi Radiokémiai Napok 2011**, 26-28 October 2011, Sopron, Hungary
13. Mácsik Z., Széles É., Stefánka Z., Vajda N. *Localization and analysis of single uranium particles by LA-ICP-SFMS* – poster; **European Winter Conference on Plasma Spectrochemistry**, 30 January - 4 February 2011, Zaragoza, Spain
14. Mácsik Zs., Széles É. *Módszer fejlesztése forró részecskék azonosítására és lokalizálására biztosítéki részecske-analízis céljára* – presentation; **XXXV. Sugárvédelmi Továbbképző Tanfolyam**, 27-29 April 2010, Hajdúszoboszló, Hungary
15. Mácsik, Z. *IAEA Fellowship at the Clean Laboratory, SAL - 10/11/08–08/05/09* – presentation; **Seminar in the Safeguards Analytical Laboratories (SAL), International Atomic Energy Agency (IAEA)**, 15 May 2009, Seibersdorf, Austria
16. Mácsik, Z. *Experiences on environmental sampling and analysis for safeguards purposes in Hungary* – presentation; **International Training Course on Implementation of State Systems of Accounting for and Control of Nuclear Material**, 23 June - 4 July 2008, Moscow, Russia
17. Vajda, N., Törvényi, A., Kis-Benedek, G., Kim, C.K., Mácsik, Z., Bene, B. *Method development for the simultaneous determination of actinides using mass spectrometric and LSC techniques* – presentation; **LSC 2008 – Advances in Liquid Scintillation Spectrometry**, 25-30 May 2008, Davos, Switzerland
18. Mácsik Zs., Bene B., Vajda N.: *Környezeti minták elemzése biztosítéki (safeguards) célból* – presentation; **XXXIII. Sugárvédelmi Továbbképző Tanfolyam**, 6-8 May 2008, Hajdúszoboszló, Hungary
19. Mácsik, Z., Vajda, N., Surányi, G.: *Method development for the determination of actinides and studies on actinide speciation in coolant* – poster; **ACTINET Plenary Meeting**, 18-20 March 2008, Avignon, France