

THE COMPARATIVE STUDY OF URANIUM ISOTOPES BY ALPHA SPECTROMETRY AND SECONDARY ION MASS SPECTROMETRY. PRELIMINARY RESULTS

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ABSTRACT

Kuruc J., Harvan D., Galanda D., Mátel Ľ., Aranyosiová M. & Velič D. **The comparative study of uranium isotopes by alpha spectrometry and secondary ion mass spectrometry. Preliminary results**

The paper presents the preliminary results of the first comparative measurements of uranium isotopes by two techniques – alpha spectrometry and secondary ion mass spectrometry (SIMS). Samples with specific activity of uranium isotopes were prepared by electrodeposition from aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, not directly from natural environment. We obtained linear correlation between SIMS intensities of uranium ions and their alpha activities. These correlations give a possibility to obtain linear correlation between SIMS intensities of uranium ions and surface weights of uranium isotopes. Preliminary results indicate the possibility to use SIMS for quantitative analysis of surface contamination by uranium isotopes. The obtained results are presented in this article.

Key words: alpha spectrometry; secondary ion mass spectrometry; uranium isotopes; electrodeposition; correlations; regression analysis; radiochemical analysis; radiometric analysis

INTRODUCTION

Principle of SIMS technique

Secondary ion mass spectrometry (SIMS) is a method founded for chemical composition analysis of different substances and materials [1]. It is not limited by origin or type of material. Basic principle of SIMS is resided in atomic bombardment of sample surface with high-energy primary ion beam (consisting from I^+ , Cs^+ , Au^+ i.e.). Primary ion beam penetrates by material, it transfers its energy to hit atoms and generates collision cascade. The result of collision cascade is emission of atoms, molecules and clusters from the surface. Emitted or sputtered particles convert into ions as secondary ions and secondary ions are analyzed in mass spectrometer.

The SIMS, with system for separate particle weights by time of fly (TOF–SIMS), is simple and the most effective. It works in pulse mode. Emitted secondary ions are extracted to time-of-fly column with potential, which are dispensed by the same kinetic energy. If the mass of ion is lower, then this ion flies faster through the column to the detector. This is the basic principle of separation of ions with TOF system. Measure of the depth profile is another possibility of analysis of sample surface. Depth profile affords information about composition inside the sample. It creates a three-dimensional picture of the sample.

Advantages [2]:

- High sensitivity (ppm, ppb)
- 1 nm depth resolution
- Collateral detection of all masses

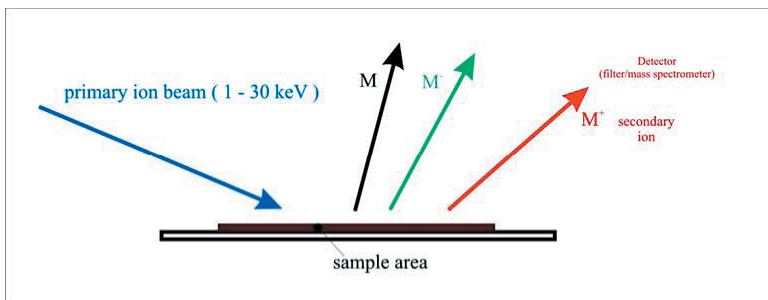


Fig. 1 Schematic diagram of atomic bombardment of sample surface by high-energy primary ion beam

- Weight range to 10000
- 100 nm laterally resolution in measure of two-dimensional distribution.

SIMS in nuclear research

In 1978 Shilling J. H. [3] was investigating to use this technique for analysis of trace elements and he showed that SIMS is not a universally appreciated analytical method. But this method found its utilization in most areas of research, especially in dating of surfaces, detection and migration of isotopes, isotopic analysis, contamination analysis of surfaces, and compositional changes in materials. SIMS found widely application in coupling with other analytical or nuclear methods such as XRF (X-Ray Fluorescence) [4], GC-MS (Gas Chromatography-Mass Spectrometry) [5], TIMS (Thermal Ionization Mass Spectrometry) [4], ICP-MS (Ion Coupled Plasma-Mass Spectrometry) [6], AMS

(Accelerator Mass Spectrometry) [7], NAA (Neutron Activation Analysis) [8], PIXE (Particle Induced X-Ray Emission) [9]. These methods were used for determination (especially isotopes ratios) of ^{238}U [10], ^{232}Th [11], lead isotopes [9, 12] and other isotopes [13].

METHODS AND EXPERIMENT

The most common procedures are co-precipitation and electrodeposition for preparation samples [14]. Radionuclides are deposited by electro-chemical procedures on metallic plate in deposition cell by the effect of electrochemical process in solution by electrical flow [15]. Metallic plate is a disc (sample for measure) and electrode, too. Frequently used discs are platinum, tantalum, nickel discs and stainless steel discs. Uniform distribution of particles on disc's surface is an advantage and it is the most

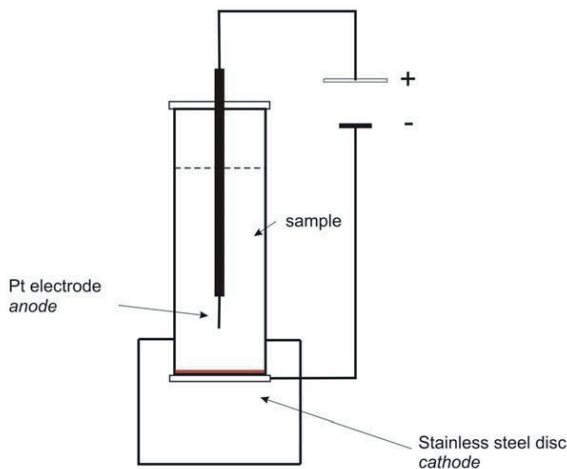


Fig. 2 Schematic diagram of electrodeposition cell [14]

important for SIMS measurement. Losses are low as uncertainty of weighting [14]. Brightening stainless steel discs were used in this experiment. Electrodeposition cell is presented in Fig. 1.

Preparation of discs with electrodeposited uranium was performed by methodology from Galanda D. [14] and Eichrom Industries, Ltd. [16]. After preparation, discs were measured by low-level alpha spectrometer. Recovery of electrodeposition was accepted as a value 86 % in accordance to literature [16]. Our calculations of weights of deposited uranium confirmed this value. Weights of deposited uranium isotopes were calculated from their alpha activities. After alpha spectrometry, discs were analyzed by the machine TOF-SIMS IV at International Laser Center in Bratislava.

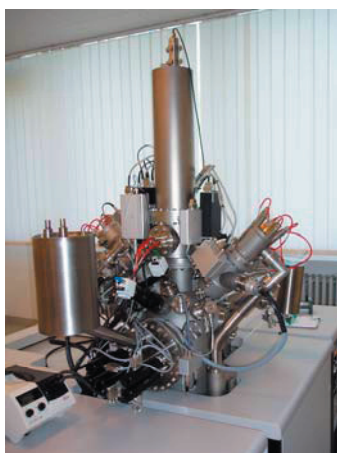


Fig. 3 TOF-SIMS IV at International Laser Center in Bratislava [1]

Characteristics of the used instrument:

Alpha spectrometry

Instrument: Ortec Dual Alpha Spectrometer 576 A – 919 (Ortec®, U.S.A.); Efficiency: Discs

1–3, $\varepsilon = 0.18$, Discs 4, 5, $\varepsilon = 0.203$; Background: <30 counts/day; 300 to 450 mm² active area, <40 counts/day, 600 mm² active area; Measure time: Discs 1–3, $t = 60000$ s, Discs 4, 5 $t = 3000$ s; Software: AlphaVision 32.

SIMS:

Instrument: TOF-SIMS IV (ION TOF GmbH, Germany); Ion gun: Au; Primary ions: Bi⁺; Ion energy: 25 keV; Samples current: 1 pA; Area: 150×150 mm²; Number of ions: 5×10^{12} ions·cm⁻²; Polarity: positive; Software: IonSpec.

RESULTS AND DISCUSSION

In accordance to the method described in part Methods and experiments, discs with electrodeposited isotopes of uranium from solution of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ were prepared. Tab. 1 shows the basic properties of natural uranium isotopes [17, 18]:

The Figure 4 shows the disc after electrodeposition.



Fig. 4 Stainless disc after electrodeposition

Tab. 1 Basic properties of natural occurrence of uranium isotopes

<i>Uranium isotopes</i>	<i>Natural occurrence [%]</i>	<i>Relative atomic weight</i>	<i>Half time of decay</i>	<i>Emitted radiation; Energy [MeV]</i>	<i>Decay product</i>
²³⁴ U	0.0055	234.0409456	245500 y	α ; 4.859	²³⁰ Th
²³⁵ U	0.7200	235.0439231	$7.038 \cdot 10^8$ y	α ; 4.679	²³¹ Th
²³⁸ U	99.2745	238.0507826	$4.468 \cdot 10^9$ y	α ; 4.270	²³⁴ Th

Alpha spectrometry

Alpha spectrometry with Dual alpha spectrometer was realized before SIMS analysis. Activities were obtained from counts and calculated from Equation 1:

$$A = \frac{(n_d - n_b)}{\varepsilon \cdot R}, \quad (1)$$

where A is an activity of sample [Bq]; n_d is a count rate of isotope [s^{-1}]; n_b is a count rate of background [s^{-1}]; ε is efficiency of detector; R is recovery of electrodeposition ($R = 0.86$ according to [16]). Uncertainties of alpha activity measurements were calculated from Equation 2:

$$u_A = \pm \frac{A}{\sqrt{N_D}} \cdot 1.96, \quad (2)$$

where A is alpha activity [Bq]; N_D is number of counts obtained from alpha spectrometry measurements. Results obtained from Eq. 1 and Eq. 2 are described in Tab. 2:

Tab. 2 Results from alpha spectrometry

		^{234}U	^{235}U	^{238}U	$^{234}\text{U}/^{238}\text{U}$	$^{235}\text{U}/^{238}\text{U}$
Disc # 1	A [Bq]	0.0068	0.0002	0.0042	1.619	0.0476
	u_A [\pm Bq]	0.0017	0.0003	0.0013		
Disc # 2	A [Bq]	0.0124	0.0003	0.0102	1.216	0.0294
	u_A [\pm Bq]	0.0023	0.0004	0.0021		
Disc # 3	A [Bq]	0.0202	0.0014	0.0173	1.168	0.0809
	u_A [\pm Bq]	0.0029	0.0008	0.0027		
Disc # 4	A [Bq]	0.5687	0.0153	0.5152	1.1038	0.0297
	u_A [\pm Bq]	0.0646	0.0090	0.0615		
Disc # 5.	A [Bq]	1.086	0.0267	1.128	0.9628	0.0237
	u_A [\pm Bq]	0.089	0.0127	0.091		

Tab. 3 Values of weights and surface's weights of uranium isotopes

Disc No.	^{234}U		^{235}U		^{238}U	
	m [g]	m_s [$g \cdot cm^{-2}$]	M [g]	m_s [$g \cdot cm^{-2}$]	m [g]	m_s [$g \cdot cm^{-2}$]
Disc # 1	$2.95 \cdot 10^{-11}$	$2.93 \cdot 10^{-12}$	$2.69 \cdot 10^{-9}$	$9.07 \cdot 10^{-10}$	$3.38 \cdot 10^{-7}$	$1.14 \cdot 10^{-7}$
Disc # 2	$5.38 \cdot 10^{-11}$	$1.81 \cdot 10^{-11}$	$4.04 \cdot 10^{-9}$	$1.36 \cdot 10^{-9}$	$8.23 \cdot 10^{-7}$	$2.77 \cdot 10^{-7}$
Disc # 3	$8.79 \cdot 10^{-11}$	$2.96 \cdot 10^{-11}$	$1.75 \cdot 10^{-8}$	$5.90 \cdot 10^{-9}$	$1.39 \cdot 10^{-6}$	$4.70 \cdot 10^{-7}$
Disc # 4	$2.47 \cdot 10^{-9}$	$8.32 \cdot 10^{-10}$	$1.91 \cdot 10^{-7}$	$6.44 \cdot 10^{-8}$	$4.14 \cdot 10^{-5}$	$1.39 \cdot 10^{-5}$
Disc # 5	$4.72 \cdot 10^{-9}$	$1.59 \cdot 10^{-9}$	$3.34 \cdot 10^{-7}$	$1.13 \cdot 10^{-7}$	$9.07 \cdot 10^{-5}$	$3.06 \cdot 10^{-5}$

Relatively high difference between relationships $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ are caused by low activities of uranium isotopes at low-active samples. These low-active samples were close to background.

Conversions of activities to weights by Eq. 3 are summarized in Tab. 3:

$$m = \frac{A \cdot A_r}{N_A \cdot \ln 2} \cdot T_{1/2}, \quad (3)$$

where m is weight of uranium isotope [g]; A is activity [Bq]; A_r is relative atomic weight; N_A is Avogadro's constant; $T_{1/2}$ is half time of decay [s]. Surface area after electrodeposition was 2.97 cm^2 . Values of surface's weights of uranium in $g \cdot \text{cm}^{-2}$ are summarized in Tab. 3.

SIMS results

Discs prepared by electrodeposition after alpha spectrometry were measured at the International Laser Center in Bratislava by TOF-SIMS IV

with Au ion gun. Bi^+ ions with energy 25 keV and sample current 1 pA were used. The result of measurement is mass spectra with intensity vs. m/z . Figures 5 and 6 show some examples of these SIMS spectra.

ce's weights. Intensities (counts) were obtained by using of IonSpec software. Figure 7 shows the linear correlation of SIMS intensity vs. activities of uranium isotopes.

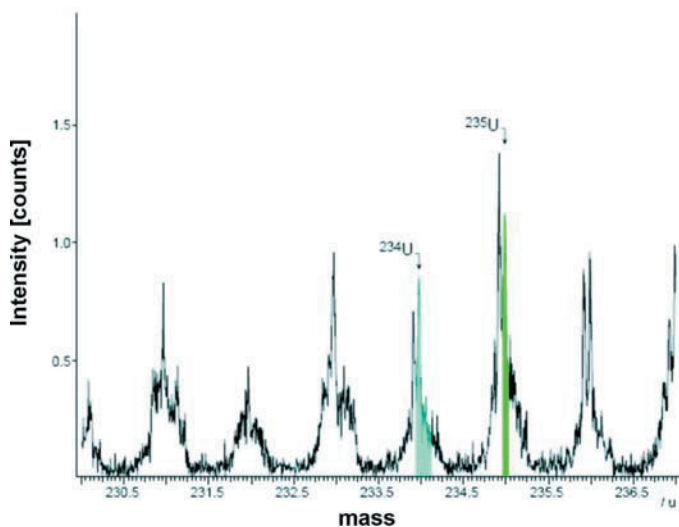


Fig. 5 SIMS spectrum of ^{234}U and ^{235}U

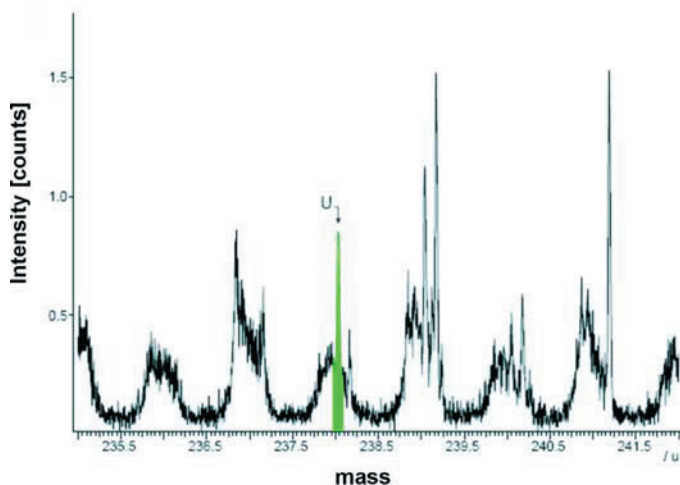


Fig. 6 SIMS spectrum of ^{238}U

We studied SIMS intensities of ^{234}U , ^{235}U and ^{238}U ions in dependence with its activities obtained from alpha spectrometry and its calculated surfa-

In the Tab. 4 the results of dependence of SIMS intensity of ions of uranium isotopes on surface weights of uranium isotopes are presented.

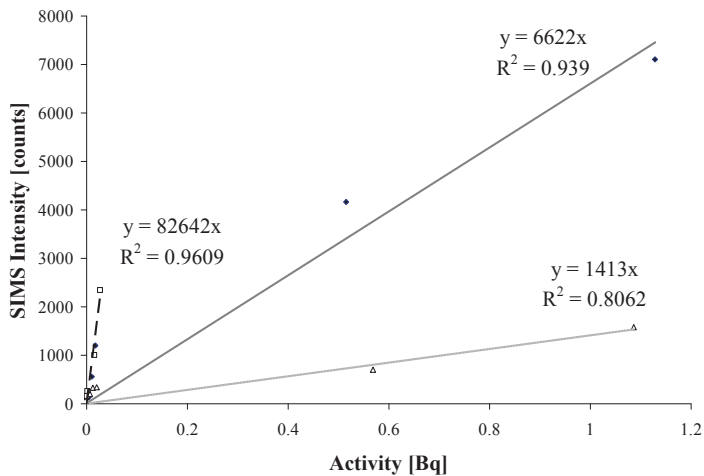


Fig. 7 The correlation between SIMS intensity of ions with $m/z = 234$ vs. ^{234}U alpha activity

Tab. 4 Table with correlated values SIMS intensity vs. Uranium isotopes surface's weights

Isotope	m_s [g·cm ⁻²]	Intensity [Counts]	Linear correlation	
			$y = b \cdot x$ $y = 965.42x$	R^2 0.8065
^{234}U	2.93.10⁻¹²	202	$y = 19.63x$	0.9607
	1.81.10⁻¹¹	331		
	2.96.10⁻¹¹	339		
	8.32.10⁻¹⁰	701		
^{235}U	1.59.10⁻⁹	1578	$y = 244.52x$	0.9389
	9.07.10⁻¹⁰	134		
	1.36.10⁻⁹	162		
	5.90.10⁻⁹	263		
	6.44.10⁻⁸	1003		
^{238}U	1.13.10⁻⁷	2347		
	1.14.10⁻⁷	132		
	2.77.10⁻⁷	560		
	4.70.10⁻⁷	1200		
	1.39.10⁻⁵	4165		
	3.06.10⁻⁵	7105		

As we can see, it's possible to plot the calibration curves of SIMS intensities [counts] vs. surface's weights of uranium isotopes by Equation 3, which permits to use the SIMS measurements as a quantitative method for measurement of surface contamination by uranium isotopes.

CONCLUSIONS

The main objective of the paper is to find the correlation between two sensitive techniques—alpha spectrometry and SIMS for natural isotopes of uranium and to determine the possibility of using

of SIMS for quantitative measurement of uranium isotopes and contaminated metal surfaces by natural uranium. Linear correlation between the SIMS maximum ion intensity vs. alpha activity as well as of SIMS maximum ion intensity vs. surface's weight were obtained according to Fig. 7 and Tab. 4, respectively. We can see from these correlations the deviation from linearity of low-level activity discs, which is caused by low count rates in SIMS. These are evidently near background of SIMS device. Measurements of minimal detection mass (MDM) of uranium isotopes and uncertainties of the counts in SIMS need to carry out additional experiments, but they were not realized for time demandingness yet. Preliminary results indicate the possibility to use SIMS for quantitative analysis of surface contamination by uranium isotopes. From SIMS measurement it may be expected the acquirement of information about depth profiles of distribution of uranium as well as about distribution uniformity on a metal surface.

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