



Mass Spectrometry in Nuclear Forensics

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Overview

- ◆ Illicit trafficking/smuggling of nuclear materials is of great concern
- ◆ Measurements on interdicted materials to trace their origin and to detect undeclared nuclear activities
- ◆ Isotopic composition of U and Pu (depends on isotopic enrichments, reactor irradiation history, cooling)
- ◆ Variety of Nuclear Analytical Techniques being developed for Nuclear Forensics (mass spectrometry, radiometry, LIBS, portable XRF)
- ◆ Inorganic mass spectrometry occupies a unique place for determining isotopic composition, amount and trace constituents present
- ◆ Natural variations in the isotopic composition of O, S, Sr and Pb important for geolocation of the source material

Different Grades of Uranium and Plutonium

U grade	% of ²³⁵ U
DEPLETED U	< 0.71%
NATURAL U	About 0.71%
LEU (Low Enriched U)	> 0.71% to < 20%
HEU (High Enriched U)	> 20% to < 90%
Oralloy (Weapons Grade U)	90% or more

Pu grade	% of ²⁴⁰ Pu
REACTOR GRADE Pu	> 18%
FUEL GRADE Pu	> 7% to < 18%
WEAPONS GRADE Pu	< 7%

M.S. Technique Used	Application
Thermal Ionisation Mass Spectrometry (TIMS)	Isotopic composition and amount
Inductively Coupled Plasma source Mass Spectrometry (ICPMS)	Trace Impurities
Stable Isotope Ratio Mass Spectrometry (SIRMS)	Isotopic composition of Oxygen, Sulphur
Secondary Ion Mass Spectrometry (SIMS)	Particle Analysis
Gas Chromatography Mass Spectrometry (GCMS)	Residual Solvents/Chemicals

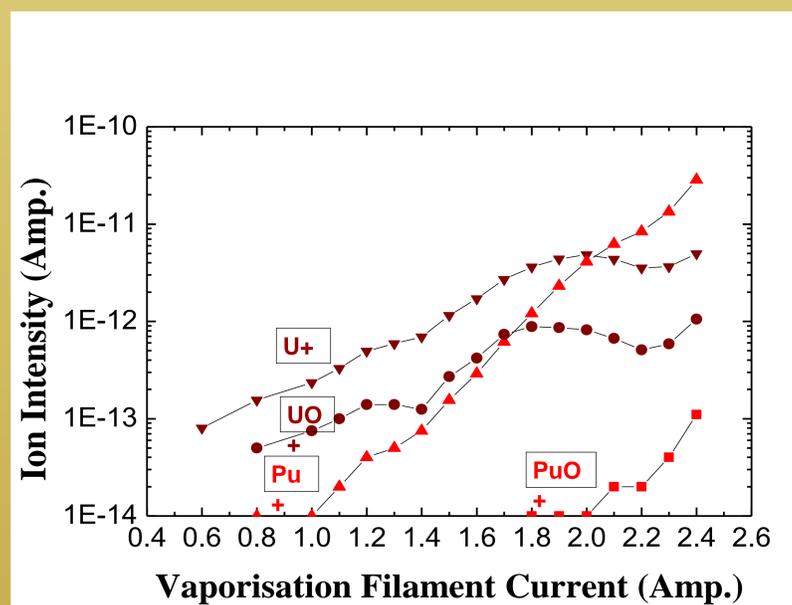
$$I(^{238}\text{T}) = I(^{238}\text{U}) + I(^{238}\text{Pu})$$

$$I(^{238}\text{Pu}) = I(^{238}\text{T}) - I(^{238}\text{U})$$

$$= I(^{238}\text{T}) - I(^{235}\text{U}) \times R(^{238}\text{U}/^{235}\text{U})$$

$$= I(^{238}\text{T}) - I(^{235}\text{U}) \times R(^{238}\text{UO}/^{235}\text{UO})$$

Evaporation and Ionization Behaviour of U and Pu in TIMS



Different Chronometers for Pu Age Determination

Parent (Half-life)	Daughter	Spikes Needed	Remarks
Pu-238 (87.7 yrs)	U-234	Pu-239, U-235	Low Abundance of Pu-238, Isobaric interference from U-238
Pu-239 (24110 yrs)	U-235	Pu-244, U-233	Pu-244 Spike availability restricted/limited
Pu-240 (6553 yrs)	U-236	Pu-244, U-233	Pu-244 Spike availability restricted/limited
Pu-241 (14.4 yrs)	Am-241, Np-237	Pu-244, Am-243	Spikes not available, Am-241 and Np-237 by ICPMS, γ spectrometry for ²⁴¹ Am
Pu-242 (3.76 x 10 ⁵ yrs)	U-238	-----	Long half-life of parent, not of interest

Mixture (SM-89)	²³⁸ Pu/(²³⁹ Pu+ ²⁴⁰ Pu) Alpha Activity Ratio	²³⁸ Pu/ ²³⁹ Pu Amount Ratio by	
		AS	TIMS
1	0.7956(0.15%)	0.003014	0.003014 (0.21%)
2	1.5468 (0.32%)	0.005860	0.005853 (0.23%)
3	3.0130 (0.69%)	0.011417	0.011524 (0.09%)
4	5.0848 (0.30%)	0.019267	0.019354 (0.07%)

CONCLUSION:

Pu-238 can be a useful chronometer for age determination of high burn-up Pu

Characterization of strong ^{241}Am sources

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Introduction

^{241}Am is a radionuclide that can be used in contexts such as ionization smoke detectors where ^{241}Am is used in small amounts. Stronger ^{241}Am sources are used in industrial gauging applications and in combination with low Z isotopes such as beryllium or lithium, as a neutron source. However, the useful applications of strong ^{241}Am sources in society also entails that the sources may be susceptible to theft or other illegal activities. By building national nuclear forensics libraries (NNFL), information about radioactive sources and nuclear material in a State can be kept in order to track the origin of a source when necessary. This information may, besides visual information and serial numbers, be information inherent in the source.

The aim of this work was to investigate the possibility of using gamma spectrometry to find inherent signatures in order to discriminate between different ^{241}Am sources in cases when visual signatures may not be accessible. The investigated signatures are age and impurities. Furthermore, Monte Carlo simulations have been used to clarify and explain the origin of the impurities seen in the gamma spectra.

Method

Measured sources:

- Source 1: Sealed 185 GBq ^{241}Am source
- Source 2: Sealed 185 GBq ^{241}Am source
- Source 3: Sealed 3.7 GBq ^{241}Am source
- Source 4: Electroplated ^{241}Am source
- Source 5: Smoke detector

Sources 1-4 were measured at a distance of about 30 cm using a portable p-type coaxial high purity germanium detector (Detective-EX, EG&G Ortec, Oak Ridge, TN, USA). Source 5, the smoke detector, was measured for comparison. This spectrum was acquired with a p-type coaxial HPGe detector (EG&G Ortec, Oak Ridge, TN, USA).

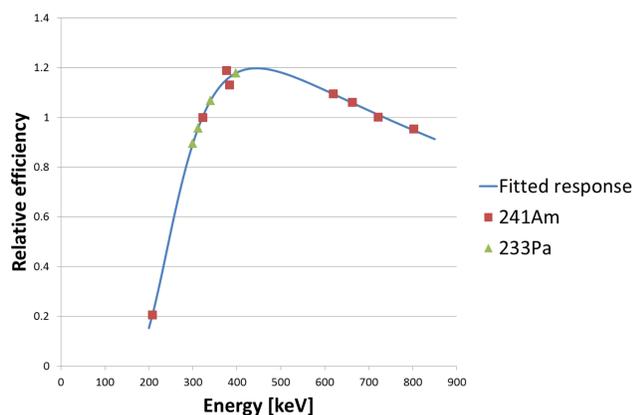


Figure 1. Fitted response; the line corresponds to the parameterization of the response curves

In order to characterize the response of these particular measurement setups, intrinsic response functions were established using a number of ^{241}Am gamma lines covering energies from 59.5 to 801.9 keV and the response, *i.e.* the relative efficiency, curves were fitted to an empirical polynomial, see Fig. 1.

Table 1. Some of the identified gamma lines from nuclides other than ^{241}Am and suggested reactions on impurities. The nuclides with an asterisk are emitting gamma rays due to de-excitation.

Energy [keV]	Reaction	$t_{1/2}$
440	$^{23}\text{Na} (\alpha, \alpha') ^{23}\text{Na}^*$	1110 fs
1129	$^{23}\text{Na} (\alpha, p\gamma) ^{26}\text{Mg}^*$	141 fs
	$^{23}\text{Na} (\alpha, n\gamma) ^{26}\text{Al}$	417 ky
1779	$^{23}\text{Na} (\alpha, p\gamma) ^{26}\text{Mg}^*$	6440 fs
1808	$^{23}\text{Na} (\alpha, p\gamma) ^{26}\text{Mg}^*$	476 fs
	$^{23}\text{Na} (\alpha, n\gamma) ^{26}\text{Al}$	417 ky

Conclusions

In this paper we have shown that it is possible to distinguish between five ^{241}Am sources that have been investigated using gamma spectrometry. This information may be useful when visual information of the sources is not available, for example in an investigation of attribution of an orphan source, or in a nuclear forensics investigation.

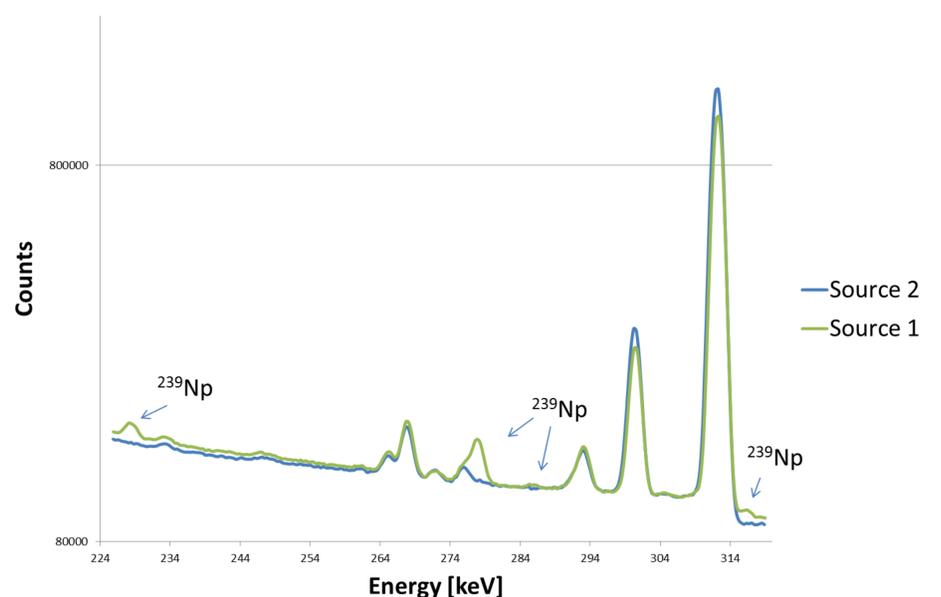


Figure 2. Excerpt of spectra of source 1 and 2

Results

The gamma spectra of Sources 1-3 have a number of peaks that cannot be derived from ^{241}Am . Some of these energies together with suggested reactions are presented in Tab. 1. Many of these peaks do not have a Gaussian shape but are doppler broadened. This is in itself an indication that there are other, light, elements present and that there are nuclear reactions taking place within the source.

The calculated ages of the sources are presented in Tab. 2. The 322.6 keV ^{241}Am line and the 311.9 keV gamma line of ^{233}Pa were used for the age determination. The combined uncertainty includes uncertainties in decay constants, photon yield, counting statistics and the fitted response. The age of Source 4 was known; the separation and the subsequent electroplating was performed in 2001, which is in good agreement with the measured age.

Two of the spectra (from Source 1 and Source 3) showed peaks that can be identified as ^{239}Np . This could imply that these sources contain some ^{243}Am as an impurity, since ^{239}Np is the daughter of ^{243}Am . The gamma lines of ^{243}Am are too weak to be measured directly in these sources with gamma spectrometry. The Source 2 spectrum did not show these peaks, see Fig. 2.

Table 2. Results from the age determination of the different sources

Source	Age [y]	Uc [y] k=2	Separation date
Source 1	31.4	2.0	1982-01-06
Source 2	40.8	2.6	1972-07-18
Source 3	43.9	3.6	1969-07-06
Source 4	12.2	2.3	2001-06-25
Source 5	21.5	6.9	1985-07-09

European
Commission

REIMEP-22: Interlaboratory Comparison on U Age Dating

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European Commission • Joint Research Centres/ ¹ Institute for Reference Materials and Measurements (IRMM), Geel, Belgium/ ² Institute for Transuranium Elements (ITU), Karlsruhe, Germany

REIMEP-22 in details

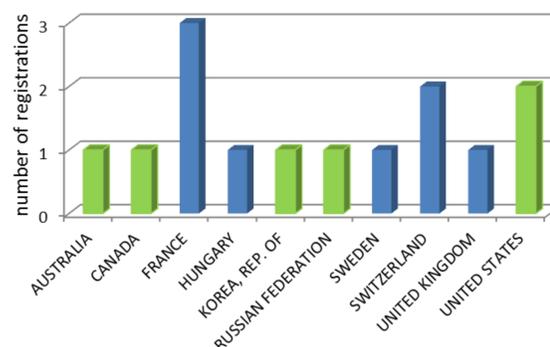
Prior to the release of a novel uranium Reference Material (IRMM-1000) to be certified for the production date, the EC-JRC-IRMM launched in compliance with ISO 17043 a new Inter-laboratory Comparison REIMEP-22 (Regular European Inter-laboratory Measurement Evaluation Programme) on "U Age Dating - Determination of the production date of a uranium certified test sample" based on this material. (see presentation IAEA CN-218/29 on IRMM-1000)

Participants in REIMEP-22 were asked to take part in two comparisons either on a 20 mg and/or 50 mg uranium certified test sample with an undisclosed value for the production date depending whether they applied a mass spectrometric or a radiometric technique.

Based on the use of the natural radioactive decay and disequilibrium of radionuclides from the U-series in the sample, they were asked to measure, using their routine laboratory procedures, the $^{230}\text{Th}/^{234}\text{U}$ (compulsory) and $^{231}\text{Pa}/^{235}\text{U}$ (optional) amount or activity ratios in a 20 mg or 50 mg uranium certified test sample respectively and report its production date.

Registrations and Participants

REIMEP-22 particularly targeted laboratories and institutes from the Nuclear Forensics International Technical Working Group (ITWG) but also other laboratories in the field of nuclear science or geochemistry worldwide.



In total, 14 laboratories registered for REIMEP-22 with 2 laboratories participating in the two comparisons (20 mg and 50 mg uranium certified test samples)

Finally, 9 laboratories reported results for the 20 mg uranium sample (using spectrometric methods and reporting amount ratios) and 4 laboratories for the 50 mg uranium sample (using radiometric methods and reporting activity ratios).

Reporting results – $^{230}\text{Th}/^{234}\text{U}$

- Report the amount/activity ratios in 3 replicates as measured on the 6th March 2013.
- Report the average value of the replicates for the 6th March 2013 as well.
- Using the average ratio, calculate the age of the material and report the production date as dd/mm/yyyy and the uncertainty in days (with coverage factor $k=1$ or 2).

Comparison on 20 mg REIMEP-22 sample



20mg REIMEP-22 zeta scores

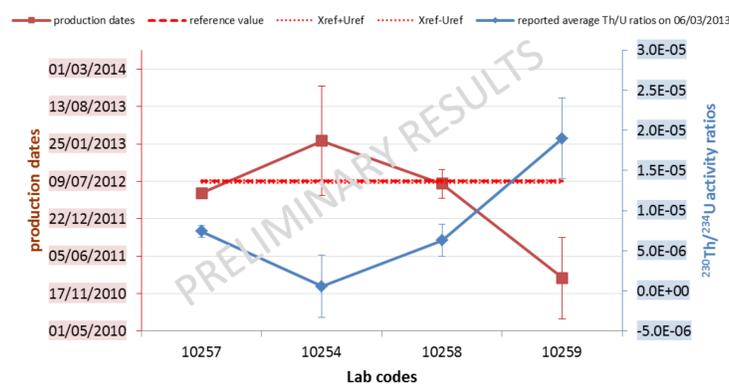


$$\text{zeta - score} = \left| \frac{X_{ref} - X_{lab}}{\sqrt{(U_{ref}/k)^2 + (U_{lab}/k)^2}} \right|$$

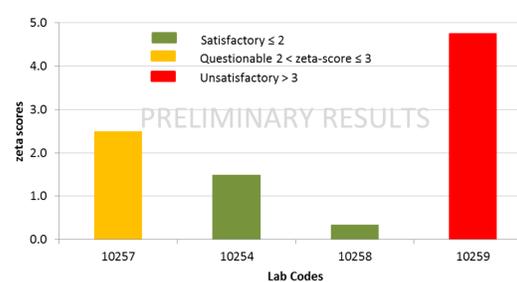
X_{ref} reference value (date) and U_{ref}
 X_{lab} reported production date and U_{lab}

- Four labs reported production dates that agree well with the reference value, so separation of the ^{230}Th from the ^{234}U in the certified test sample was successful.
- The other labs either underestimated the uncertainties on the production date or found "younger" ages (perhaps due to an incomplete recovery of the thorium in the certified test sample using their analytical method).
- For two labs, reported ratios do not match with the reported production dates, either ratios were not reported for the reference date and/or these labs had problems in calculating the production dates from the average ratio.

Comparison on 50 mg REIMEP-22 sample

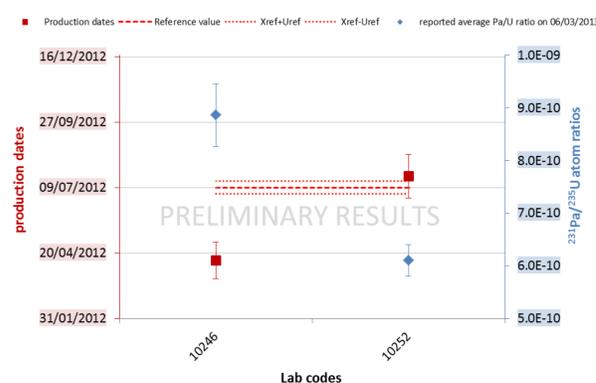


50mg REIMEP-22 zeta scores



- Good agreement between reported activity ratios and the production dates.
- 2 labs reported production dates that agree well with the reference value.

Reporting results - $^{231}\text{Pa}/^{235}\text{U}$



Even the Pa/U clock in the IRMM-1000 could be used to determine the production date, although IRMM-1000 will not be certified for this specific clock.

<https://ec.europa.eu/jrc/en>

<https://ec.europa.eu/jrc/en/interlaboratory-comparison/reimep-22>

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Joint
Research
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Measurement of organic residues of uranium ore concentrates (yellow cakes) for nuclear forensics

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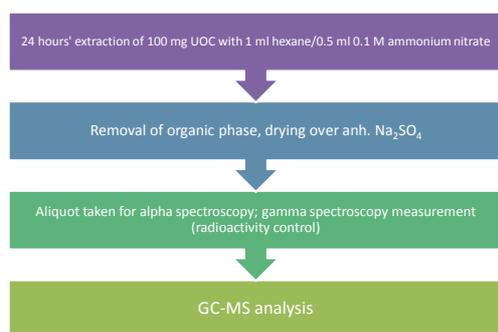
Introduction

Uranium ore concentrates (UOC, commonly known as yellow cakes) potentially contain organic impurities in various forms. They can derive from the original ore (e.g. bitumens, humic acid, coal) or from the industrial production process (e.g. tertiary amines, TBP). The analysis of such organic traces are still unexploited for nuclear forensics to identify the source of the ore or the production process.

Objectives

- ✓ Method development for the analysis of organic residues in UOCs
- ✓ Target analytes: TNOA: tri-n-octylamine; TBP: tri-butylphosphate; TOPO: trioctyl-phosphine oxide
- ✓ Test for UOC samples from various production routes
- ✓ Application for origin assessment in nuclear forensics

Proposed sample preparation

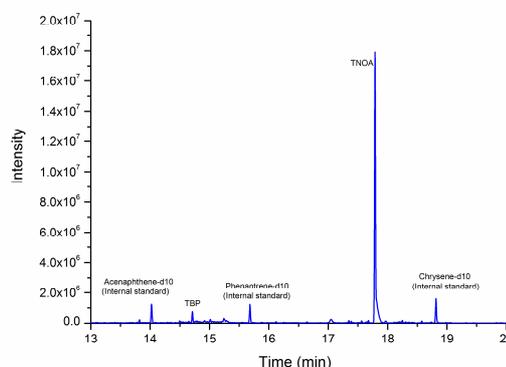


Instrumentation

Large Volume Injection gas chromatography mass spectrometry (LVI-GC-MS). Column: DB-5ms UI, 30m x 0.25mm x 0.25µm.



Chromatogram of organic extract from yellow cakes



Organic extract from a uranium ore concentrate processed with solvent extraction method using tertiary amine. TNOA was detected at a concentration of 150 ng/g.

Major findings

- Aqueous phase is necessary to extract the target analytes
- Method is appropriate to measure trace-level organic residues in UOCs
- Trace-level organics was detected in a few UOCs in agreement with the known production way

Nuclear Families



— an extension to is it DU, NU, LEU or HEU

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Uranium is usually categorised by isotopics as either:

- Depleted Uranium
- Natural Uranium
- Low Enriched uranium
- High Enriched uranium

Type	% U-235
DU	< 0.72
NU	0.72
LEU	>0.72, <20
HEU	>20

Uranium can be characterised by the analysis of all the isotopes present.

Natural Uranium Isotopics, %			
U-234	U-235	U-236	U-238
0.0054	0.7204	$\sim 1 \times 10^{-11}$	99.2742

A major proportion of the worlds processed uranium has been irradiated in nuclear reactors as fuel or blankets:

- Irradiated Depleted Uranium, IrDU
- Irradiated Natural Uranium, IrNu
- Irradiated Low Enriched Uranium, IrLEU
- Irradiated High Enriched Uranium, IrHEU

The effect of irradiation is

- to reduce U-234 concentration by conversion to U-235,
- to reduce U-235 concentration by fission and conversion to U-236,
- to increase U-236 concentration by conversion of U-235
- to reduce U-238 concentration by conversion to Pu-239

Due to the presence of highly active fission products this material is not in circulation.

A significant proportion of the irradiated fuel has been reprocessed.

Leads to 4 extra categories:

- Reprocessed Irradiated Depleted Uranium, ReProDU
- Reprocessed Irradiated Natural Uranium, ReProNU
- Reprocessed Irradiated Low Enriched Uranium, ReProLEU
- Reprocessed Irradiated High Enriched Uranium, ReProHEU

Should therefore be possible to categorise uranium into 8 categories

– the starting materials, and the reprocessed materials.

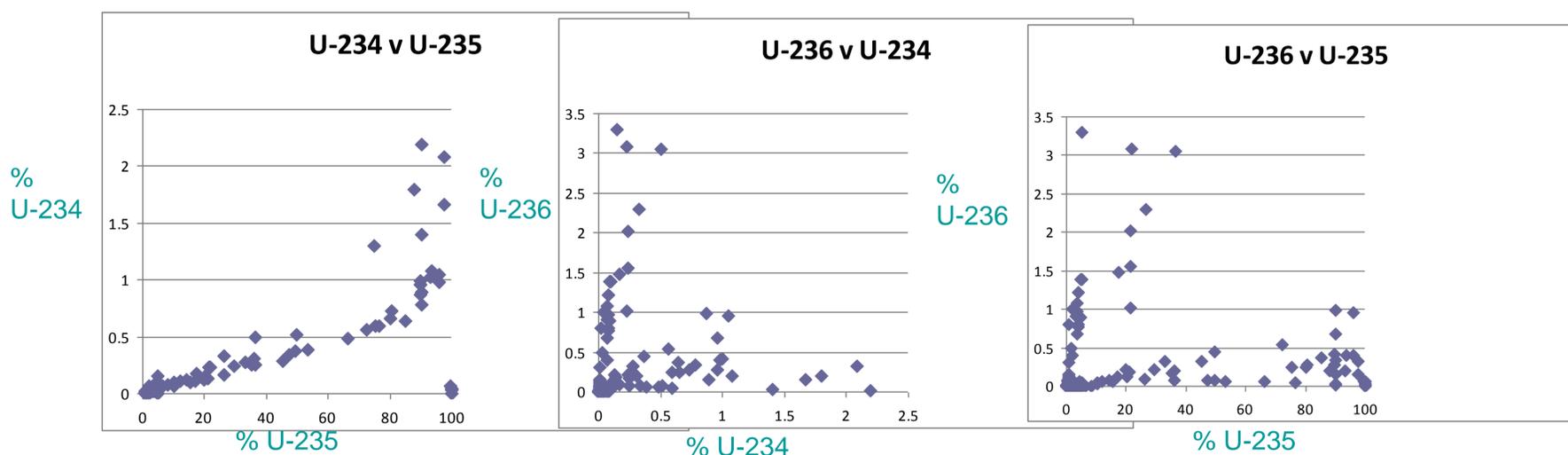
Irradiation and reprocessing cycles can be repeated several times, including re--enrichment.

Where this has happened U-236 contaminates the manufacturing plants allowing U-236 to be detected in any new uranium entering the fuel cycle – called perfuming.

It is very difficult to find any uranium isotopic data in the open literature that is U-236 free.

The world supply of uranium has been well perfumed. This, together with the extensive use of blending in the nuclear industry, makes the study of uranium isotopic fingerprints very complex.

URANIUM ISOTOPE PLOTS USING DATA FROM THE OPEN LITERATURE



Neutron-Dose Control of First Responders under Sampling and Categorization

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Abstract

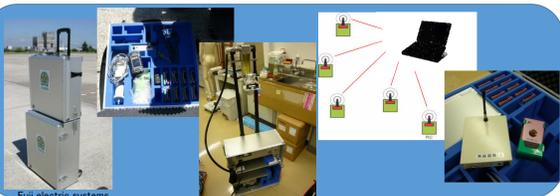
Nuclear materials and RDDs, which makes criticality field, emit neutrons whose energy range can vary from thermal to several MeV. In particular, the fast neutrons around over 1MeV have a strong damage for human body. Portable equipment and radiation protection for radiological emergency response team to achieve emergency tasks safely at the incident sites have been developed and evaluated in National Research Institute of Police Science (NRIPS, JAPAN). In this report, we introduce fast neutron shield with water and wireless network personal dosimeters under sampling and categorization. Described next in this report are evaluation tests of real-time neutron dosimeters using low-scatter room (neutron irradiation field) in Pacific Northwest National Laboratory. We evaluated them under fast neutron field and thermal neutron field.

1. Development of neutron shield and neutron dose monitoring system



Neutron shield with water

The thickness of water shield in developed prototype equipment is 10cm, which decrease to 1/3 fast neutrons and 1/2 gamma-rays (Co-60). The neutron shield is mounted on an electric cart with DC motor, which maximum speed is 3km/h. A long tong is set to the center of shield, with which first responders can collect samples safely.



10 wireless network personal dosimeters

- Real time monitor system for personal dose with wireless network in the field.
- Maximum range : 100m at open space

3 handheld devices Radioisotope identification, neutron detection, high-dose rate and contamination check

Air sampling : 50L/min at 1m height

2. Past evaluation of personal dosimeters

SILENE 2002 [1]

Nuclear criticality field

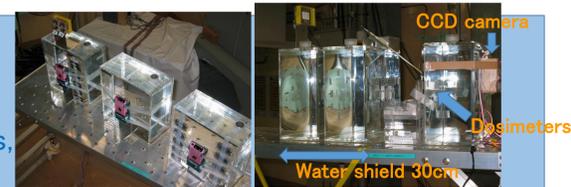
This reactor allows the simulation of various criticality accidents, pulse mode, free evolution and steady state. 71% of personal dosimeters are within $\pm 25\%$ of reference dose value.



TRACY(JAEA)-NRIPS 2010 [2]

Nuclear criticality field

Tested are real-time personal neutron dosimeters of different types, NRG13 (Fuji Electric Systems, Japan), ADM-353(Aloka, Japan) and DMC2000GN (MGP, USA). These solid state dosimeters have digital displays of dose, and a warning function using light, sound and/or vibration. The dosimeters were attached on a 30*30*15cm³ phantom, and located at the distances of 1.35m and 5.5m from the TRACY core. The dosimeters at 1.35m were irradiated directly (bare condition). On the other hand, a 30cm-thickness water shield was set in front of the dosimeters at 5.5m (water shield condition). The dose indicated by ADM-353 was 2 times by NRG13 in bare condition, whereas the dose indicated by ADM-353 was over 8 times by NRG13 in water shield condition(Figure.1). They are caused by the energy responses of dosimeters and variation of neutron spectra at the location.



Irradiation (1) Bare
Irradiation (2) Water shield (Displays on dosimeters were observed with a CCD camera)

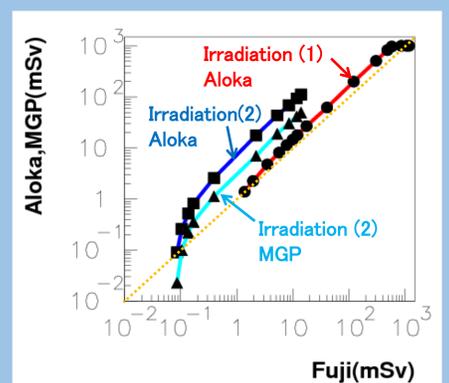


Fig.1 Comparisons between dose indicated by each dosimeters[2]. Aloka and MGP for Fuji Electric Systems

Passive Dosimetry

Active Dosimetry

3. Evaluation of neutron dosimeters

The dosimeters were attached on a 40 × 40 × 15cm³ phantom and located at the distances of 30cm, 55cm and 100cm from the neutron sources (Am-Be, bare Cf-252, and moderated Cf-252), respectively. The dose rates were 0.866mSv/h, 3.41mSv/h and 3.68mSv/h, respectively.

We decided irradiation time in which the accumulated doses were set to about 0.5mSv.

We compared the response for each dosimeters under direct irradiation and irradiation with neutron shield (10cm thickness polyethylene corresponded to water). A 10cm-thickness shield was set 10cm in front of the dosimeters. The neutron spectrum with neutron shield was thermalized to lower energy, which intermediate neutrons increased.

	Aloka PDM313	Aloka ADM353	Thermo EPD N2	MGP(MIRION) DMC2000GN	Fuji NRF31	Fuji NRG13
Detector type	Neutron	Neutron/gamma	Neutron/gamma	Neutron/gamma	Neutron/gamma	Neutron/gamma
Resolution	10uSv	100uSv	1uSv	10uSv	1uSv	100uSv
Dose range	10uSv-100mSv	100uSv-1000mSv	1uSv-16Sv	10uSv-10Sv	1uSv-10Sv	300uSv-1000mSv
Size (mm)		110*52*18	86*63*19	87*48*31	60*78*27	
Weight (g)		90	108	80	<100	
# of dos.	#1,#2	#3,#4	#5-#7	#8-#10	#11-#13	#14

Table.1 Tested neutron dosimeters

Fig.2 Schematic view of evaluation geometry

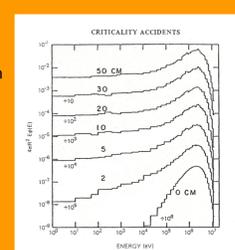
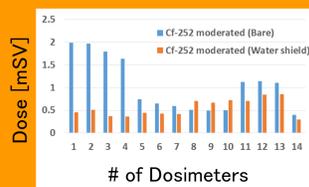


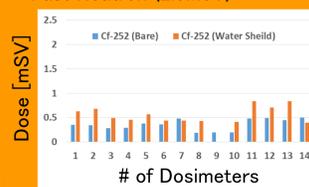
Fig.4 Neutron spectra penetrated in water. [IAEA Tec. Rep. Ser. No.211(1982)]

Thermal Neutron (around 0.025eV)



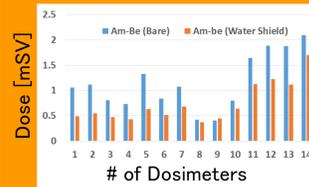
Field Neutron Dose (0.5mSv)

Fast Neutron (2.3MeV)



Field Neutron Dose (0.5mSv)

Fast Neutron (4.4MeV)



Field Neutron Dose (0.5mSv)

Fig.5 Response of different neutron Dosimeters.

4. Results and Summary

Under thermal neutron field (moderated Cf-252 source), responses of Aloka dosimeters were 2-4 times higher than those of other dosimeters. We can see same situation in the past results (at criticality field^[2], around a spent fuel cask^[4], EVIDOS Project^[5]). However the significant difference of each dosimeter's responses was not confirmed under moderated Cf-252 source with neutron shield. Under Cf-252 irradiation which mean energy is 2.3MeV, doses of Aloka and Thermo dosimeters are lower than those of Fuji dosimeters, whereas the opposite tendency for Am-Be irradiation which mean energy is 4.4MeV. This is owe to the difference of calibration source (Cf-252 or Am-Be) for each dosimeters at factory setting. The difference is consistent with the past result^[6], which we lead to the correct dose using the correction factor for neutron energy.

[Reference]

- [1]R. Medioni et al. "Criticality accident dosimetry systems: an international intercomparison at the silene reactor in 2002" Radiation Protection Dosimetry 110(1),429-436 ,2004
- [2]K.Tsuchiya et al. "Evaluation of Personal Dosimeters and Electronic Modules under High-Dose Field" IEEE Nuclear Science Symposium 2010, Knoxville, USA Conference Records pp506-507, 2010
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- [4]S.Mayer et al. "Intercomparison of the response of different photon and neutron detectors around a spent fuel cask" Radiation Measurements 47, pp.634-639, 2012
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- [6]K.Tsuchiya et al. "Radiation-induced failures and degradation of wireless real-time dosimeter under high-dose-rate irradiation" Proceedings of SPIE Defense, Security, and Sensing 2010 Vol.7665 76651G, 2010

Fig.3 Relative dose equivalent response for normally incident neutrons as a function of neutron energy[3].

Novel Method for Rapid Extract of Radionuclides Using Polymer Ligand Film for Nuclear Forensics Applications

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Introduction

Accurate and fast determination of radionuclides activity in a sample is critical for nuclear forensics analysis. Radioanalytical techniques are well established for radionuclides measurement; however, they are slow and labor intensive, requiring extensive radiochemical separations and purification prior to analysis. With these limitations, there is great interest for a new technique to rapidly process samples. This poster presents a development of Polymer Ligand Film (PLF) for rapid extraction of plutonium and uranium. PLF is a thin polymer medium with ligands incorporated onto its structure to enable selective extraction of analytes from a solution. The PLFs developed in this research were designed to facilitate fast isolation of radionuclides from solutions for screening samples. The main focus was to shorten and simplify the procedure for separating radionuclides from solutions onto a surface appropriate for radiometric counting. To achieve this goal, PLFs were synthesized to perform direct sorption of analytes onto its surface for direct counting using radiometric techniques. A diagram comparing the classical method and PLF technique is shown in Figure 1. The new technique combines column chromatography and electrodeposition into a single step for samples.

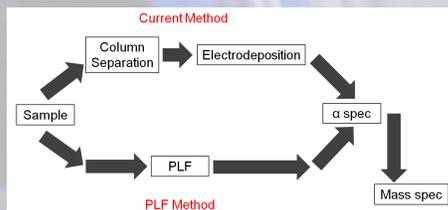


Figure 1 Diagram comparing conventional sample preparation method and PLF method

Method

Materials

- Bis(2-ethylhexyl) methanediphosphonic acid ($H_2DEH[MDP]$) was obtained from Eichrom Technology Inc
- Polystyrene beads were obtained from Sigma-Aldrich.
- Tetrahydrofuran (THF) was obtained from Acros Organics.

Alpha Spectroscopy

- An Octet Plus system from Ortec, equipped with 900 mm² ion implanted silicon detectors.
- Each detector was for calibrated energy and efficiency using a secondary NIST traceable source.

PLF Preparation and Experimental Conditions

- Polymer ligand films were prepared by incorporating $H_2DEH[MDP]$ in the polystyrene structure.
- The stock solution was prepared by dissolving the ligands and the polystyrene beads in Tetrahydrofuran (THF).
- The solution was directly deposited onto a 40 mm diameter stainless steel substrate then dried.
- 1:5, 1:10, 1:15, 1:20, and 1:25 (wt/wt) $H_2DEH[MDP]$ PLFs were tested over 0.01 to 8M nitric acid solutions.
 - The PLF composition is described as the ratio between ligand and the entire solid mass. For example, PLF with one part ligand and one part polystyrene was assigned 1:2 (w/w) ratio.
- The physical appearance of the PLFs changed depending on the amount of ligand in the film.
- ²³⁹Pu tracer was directly stippled on the PLF surface, allowing the analyte to equilibrate for 3 hours before removing the solution.
- The plutonium activity of each sample was measured by direct alpha counting to quantify the plutonium recovery by $H_2DEH[MDP]$ PLF.



Figure 2 PLF stock solution (A) with un-dissolved polystyrene, (B) with polystyrene completely dissolved



Figure 3 PLF prepared with solvent casting method

Acknowledgements

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Results

Pu Sample Recovery

- 1:10, 1:15, and 1:20 PLFs were all effective in plutonium extraction from 0.01 to 1M nitric acids.
- The highest recovery for these PLFs all occurred at 1M tracer solution.
- The percent recoveries were 50.44 ± 8.27 and 47.61 ± 7.17 for 1:10 and 1:20 PLF, respectively.
- The plutonium recovery for 1:5 PLF was noticeably lower than the other PLFs from 0.01 to 1M.

U Sample Recovery

- The uranium extraction behavior was entirely different than the plutonium extraction.
- Neither 1:10 nor 1:20 PLF was effective in uranium extraction over all nitric acid ranges tested.
- 1:5 PLF showed the highest recovery of ~30% with 1M nitric acid and 22.5% with 0.1M nitric acid.
- 1:5 PLF, uranium can be co-extracted along with plutonium at 0.1 or 1M nitric acid. At the same nitric acid concentration, 1:20 PLF can be used to extract plutonium over uranium.

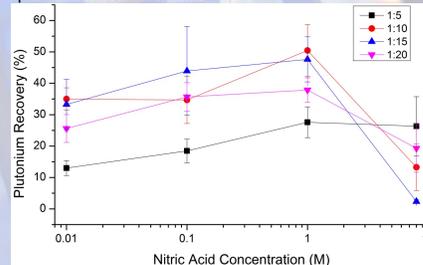


Figure 4 Plutonium recovery

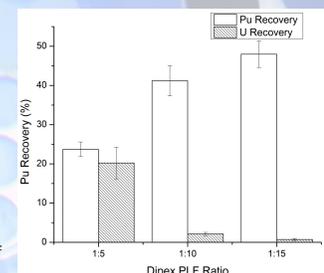


Figure 5 Pu & U recoveries with PLF

Mass spectroscopy Analysis

- Analyte + ligand complexes were removed from PLF with isopropanol.
- Hydrogen peroxide and sodium vanadate were added to destroy the plutonium complexes.
- The ²⁴⁰/²³⁹Pu ratio measured with TIMS were accurate when compared to the known values.

Environmental Sample Analysis

- Analytes from soil samples were first leached with nitric acid.
- Nitric acid solution was filtered then stippled directly onto PLF to extract plutonium.
- Water samples were first treated with nitric acid, then plutonium was extracted with PLF.
- PLF was able to extract Pu from environmental samples with minimal sample preparation.

Conclusions

The PLF technique simplified the procedure and offered considerably reduced sample analysis time. The entire sample preparation to analysis was done within one to two days. The classical method takes two days to a week in comparison. The technique also requires minimal chemicals and it is also field deployable. The reduction in time and simplified procedure make this technique ideal for post-detonation nuclear forensics. Sample processing procedures for alpha spectroscopy and mass spectroscopy were established. Environmental samples were effectively processed with the PLF system using the established procedure.

NUCLEAR FORENSICS VIA MACHINE LEARNING LASER BASED SPECTRAL ANALYSIS AND IMAGING

IAEA-CN-218

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International Conference on Nuclear Forensics: Enhancing Global Efforts, IAEA, Vienna, Austria, 7-10 July 2014

INTRODUCTION & BACKGROUND TO THE STUDY

The limitations of classical nuclear forensic analysis methods calls for innovative approaches for rapid noninvasive detection and accurate quantification and attribution of illicit trafficking of nuclear and radiological materials against nuclear security threat.

This is enabled by combining machine learning and laser based spectroscopy and spectral imaging techniques which we are developing to elucidate trace isotopic, molecular and elemental (trace impurities) composition, as well as the microstructure (as each step in the fuel cycle creates and/or modifies these signatures) of nuclear materials.

We focus on analysis of samples of limited sample size for responding to environmental releases of NORM and illicit trafficking activities in our region, which is a hub for trade in radioactive 'conflict' minerals and counterfeit nuclear materials, with high possibility of radiological dispersal devices (RDD) and improvised nuclear devices (IND).

Key advantages of the approach: small samples (mg) can be evaluated with minimal sample preparation; samples can be remotely analyzed very rapidly (ms-seconds) and method can utilize multivariate calibration and exploratory analysis.

Attribution (origin, method of production, probability that more of the material exists, transit route, and means by which administrative control over the material was lost) i.e. especially enabled by this approach. Multivariate interpretation is the crucial factor in this exercise.

While Laser Induced Breakdown (LIBS) reveals the atomic (and sometimes molecular and isotopic) emission spectra of elements in micro-plasma obtained from samples, laser Raman microspectroscopy reveals the molecular configuration by active vibrational spectra of polyatomic ions in samples as well as structure and morphology. These methods are targeted for their versatility, high sensitivity, speed, simple operation and *in situ* capabilities.

MATERIALS & METHODS

Current Analytical Challenges

Standard nuclear forensics methods are limited by the complexity of samples and of the often multivariate signature interpretation.

Mostly destructive, and consuming large amounts of sample.

Complex matrix and contamination during sampling and treatment make determination of especially trace REE complicated.

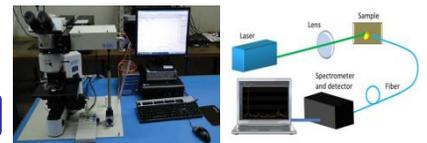
Information that must be interpreted (using expert knowledge) is often not meaningful (often subjective) to the attribution assessment.

The Practical Approaches

Machine learning (ML) is used to reduce the analytical complexity and increase the information gained.

Attribution is being achieved and will be improved via ML fuzzy logic and exploratory analysis/modeling.

Need for spectral resolution of system are significantly relaxed via computational intelligence (ML) techniques.



• Minimally invasive. • Rapid. • Simultaneous analysis. • No chemical treatment. • Sample shape irrelevant.

- LIBS 2500 PLUS (Ocean Optics) - Q-Switched Nd: YAG
- Confocal Laser Raman Microspectroscopy.
- ML techniques for data compression and modeling

We analyzed and imaged uranium oxide as well as several U-bearing ores and radiological (HBRA) samples and also interpreted natural variability between uranium ore-bearing rocks and soils from HBRA.

SELECTED RESULTS & DISCUSSION

The chemical composition of uranium oxide was found, via two unique peaks, to be an indicator to which part of the nuclear fuel cycle the material belongs.

The two nuclear forensic signatures we successfully used to reconstruct the composition of high background radiation area (HBRA) ore samples.

We have successfully designed a hyperspectral imaging (HSI) scheme for non-contact analysis of nuclear forensic traces, to obtain both high (1 μm diffraction limit) spatial and spectral information from small micron scale samples such as 'hot' aerosol particulates.

This enables us to analyze the chemical and/ structural composition of nuclear traces and simultaneously visualize their spatial distribution.

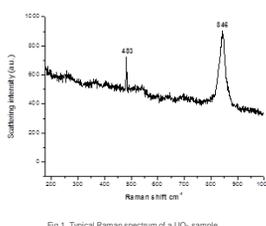


Fig 1. Typical Raman spectrum of a UO₂ sample.

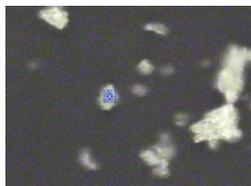


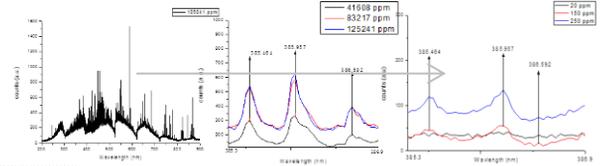
Fig 2. Microscopic image of the UO₂ bearing particle (~0.7 μm) showing 25 spot sizes from which Raman spectra and spectral images of the 423 and 848 cm^{-1} peaks were imaged to construct HSI for chemical imaging.

Table1. Identification of lines for quantitative analysis of U using LIBS

U-I	356.659 nm
U-II	367.007 nm
U-III	383.146 nm
U-IV	385.464 nm
U-V	385.957 nm
U-VI	386.592 nm
U-VII	417.159 nm

LIBS has demonstrated potential for the detection and quantification and evaluation of characteristics of trace evidence found at a nuclear/radiological crime scene as signals from ppm concentration are obtained.

Interest in LIBS lies in analysis of REE – to determine e.g., the degree of enrichment, and trace elements (varying concentrations of impurities exist in every material) present.



Figs 5. LIBS spectra obtained from UO₂ in cellulose. The figs show (a) the spectrum obtained, (b) regions of spectral interest of selected lines delineated at major concentration and (c) analytical line responses at ppm level U.

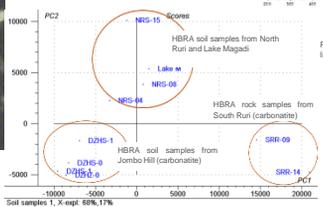


Fig 3. PCA score plot of HBRA soils and rock samples analysed by LIBS. The hypothesis of presence of an underlying uranium-rich rock in the Lake Magadi basin is strengthened by this result.

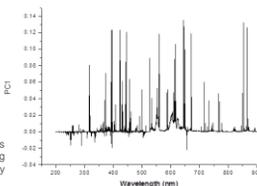


Fig 4. The loadings spectra for figs 4 above showing the spectral features responsible for the clustering in Fig 3. The clusters correspond to mostly U, Th, and REE lines.



Fig 6. Sample slide used for spectral mapping of individual particles.

Microstructural features from laser Raman microspectroscopy are very informative: shape of particles or the surface structure gives hints of the sample origin. E.g. surface roughness may also be needed to determine when the material was last chemically processed in relation with altitude of enrichment.

CONCLUSIONS AND PROSPECTS

- The combined utility of ML-assisted laser spectral and imaging techniques via LIBS and laser Raman microspectroscopy provides complementary information and adds novelty to a comprehensive analytical picture in nuclear forensics: ML extracts subtle relevant information from the complex spectra/images and affords multivariate data reduction as well as exploratory analyses of the nuclear forensic investigation. Fusing data from the two techniques is essential for the success of nuclear forensics investigations and subsequent subsequent attribution.
- The obtained PCA multivariate models have capacity for constraining the geological models of uranium deposits as well as for genetically discriminating new uranium discoveries.
- The challenge for the future is to develop and apply ML tools for data interpretation that provide combined and credible determinations of locations and methods of materials production.
- Analysis of the temporal behavior of spectra will give insight in the chemical changes within specimens, which can be used for age estimation purposes.

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In-field detection and analysis of α radiation

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Motivation and present status

Alpha-particle-emitting nuclides are very radiotoxic if inhaled or ingested. The short range of alpha particles in air (a few cm) makes the non-destructive screening of alpha emitters at a crime scene difficult and time consuming. The same limitation in range is also present in the alpha-particle screening of collected evidences in a forensic laboratory.

The thermalization of alpha particles in air, and the subsequent excitation of air atoms and molecules, produces UV-light that can be detected over long distances, see Fig. 1 [1]. (Alpha particles generate 19 ± 3 photons per one MeV in air [2].) Therefore, compared to the current state-of-the-art screening methods, UV-imaging is a significant step forward for alpha-particle screening in forensics.

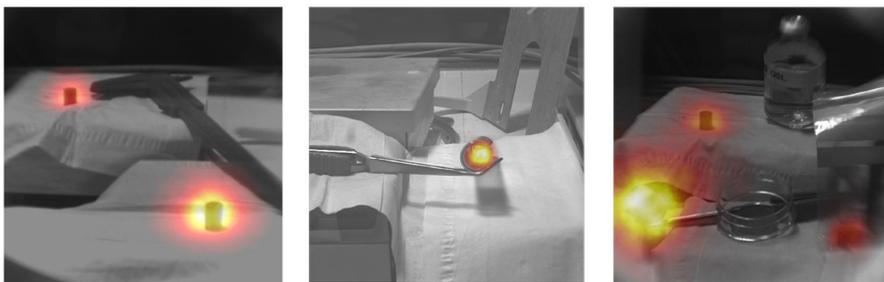


Fig. 1. UV imaging of multiple alpha sources.

Further characterization of alpha particle emitting radionuclides causing the UV-light can be continued with a position-sensitive UV-gated gamma-spectrometry technique (Fig. 2), jointly developed by STUK and the Technical University of Tampere, Finland [3, 4].

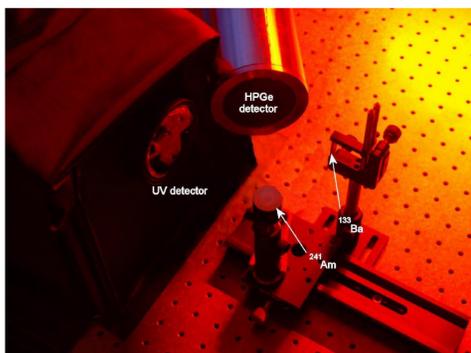
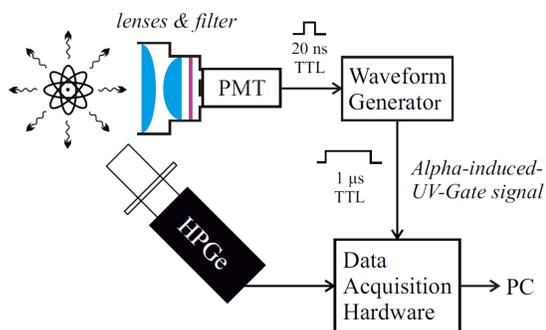


Fig. 2. UV-gamma coincidence test setup.

An additional advantage related to these new techniques is that the UV-light penetrates several materials, including many plastics. Therefore, these techniques allow, for example, the analysis of samples without removing them from their sealed plastic bags, i.e. without jeopardizing the integrity of the collected samples.

In conclusion, UV-based methods for remote detection and analysis of alpha-particle emitting radionuclides have the potential to both speed up the crime scene investigation and increase the safety of the personnel.

Future work

In UV imaging, the research emphasis lays on extending the image area and improving the tolerance to external lighting. Namely there are also other sources of UV light, which are often overwhelming. Our sun, for example, prevents the straightforward measurements in day light. Approach to reduce the sensitivity to the background lighting is based on restricting UV imaging to the wave lengths covering only the main peaks of nitrogen (310-390 nm), see Fig. 3. Another research line investigates the possibility to apply the so-called solar-blind part of the spectrum (240-280 nm) for imaging. Namely, atmospheric ozone absorbs radiation within this band, preventing it to reach the surface of the earth. Automated panorama imaging is studied for extending the image area.

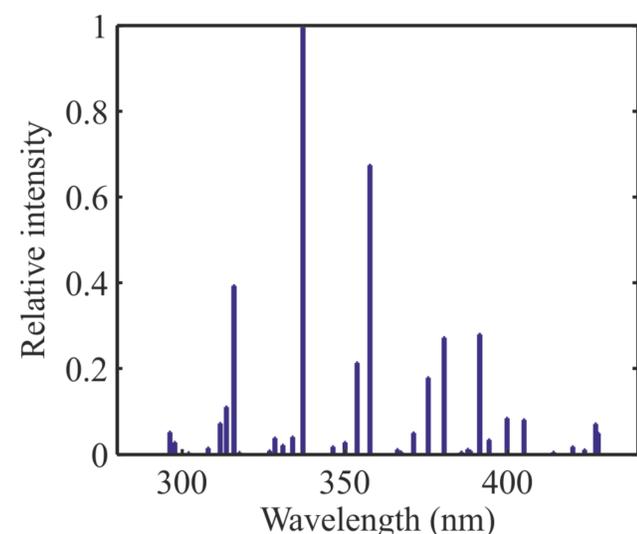


Fig. 3. Spectrum of N_2 [5].

Earlier studies employing HPGe gamma-ray detectors have proved the superiority of the UV-gamma-coincidence technique for the analysis of low-activity samples [3, 4]. In the future, liquid nitrogen or electrically cooled HPGe detector will be replaced with a fast scintillator detector that is capable to operate in room temperature. This development will improve detection capability by reducing the random coincidence rate, and it makes the UV-gamma coincidence technique more user-friendly to operate in the field.

The UV-based measurement techniques will be developed in Finland using standard calibration sources. Validation of the techniques will be made at the Institute for Transuranium Elements (JRC-ITU) using nuclear-security relevant sources not available in Finland, such as plutonium and MOX fuel.

The above described work will be carried in two EU funded projects (GIFT and MetroDECOM).

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Center for Strategic Studies

The Feasibility Analysis of the Materials of the Nuclear Explosion with the Fission Product Xenon

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Introduction

The identification of the fissile material of a nuclear explosion is quite an important part of the post-explosion nuclear forensics investigation, and it is also very important in nuclear non-proliferation field. The fissile materials used in nuclear weapons are usually Highly Enriched Uranium(HEU) and Plutonium(Pu). It is possible to distinguish U-235 and Pu-239 by analyzing the isotopic components of the fissile fragments due to the slight difference of the fission products between U-235 and Pu-239 in the same neutron energy. One series of these characteristic isotopes are the Xenon isotopes, including Xe-131m, Xe-133m, Xe-133, and Xe-135, which are easy-spreading, stable and easy-detectable. By analyzing the ratio of Xenon isotopes, U-235 and Pu-239 may be distinguished. In this poster, with the demonstration of the difference of the ratio of Xenon isotopes between U-235 and Pu-239, the feasibility to identify the fissile material of a nuclear explosion is analyzed. Besides, by numerically simulating other fissile fragments, the fissile materials may be further confirmed.

The theoretical analysis of the radioactivity change of the Xenon isotopes

For the fissile fragment, its activity composes of the fissile contribution, and the decay contribution both from the mother nuclides and the daughter nuclides. Taking Xe-135 for example, and ignoring the short-half-life intermediate products, we can get the nucleon densities of I-135 and Xe-135 as shown below.

$$\frac{dN_I(t)}{dt} = \gamma_I \sum_f \phi \delta(t-t_0) - \lambda_I N_I(t)$$

$$\frac{dN_{Xe}(t)}{dt} = \gamma_{Xe} \sum_f \phi \delta(t-t_0) + \lambda_I N_I(t) - (\lambda_{Xe} + \sigma_a^{Xe} \phi \delta(t-t_0)) N_{Xe}(t)$$

For the nuclear explosion, the original nucleon densities of I-135 and Xe-135 are both 0. So we solve the equations above with the assumption that the nuclear explosion begins at $t=0$ and the neutron flux density reaches the maximum and then fall back to 0 immediately. Thus the nucleon densities of I-135 and Xe-135 can be shown as

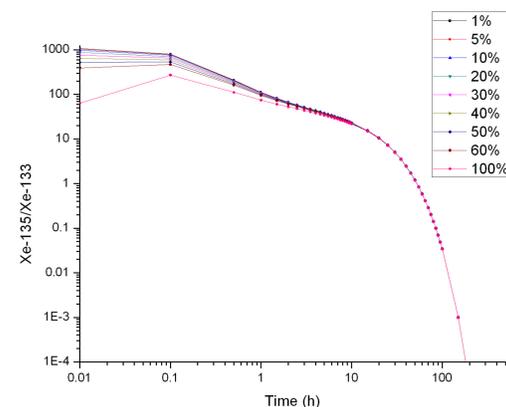
$$N_I(t) = \begin{cases} \gamma_I \sum_f \phi & t = 0 \\ \gamma_I \sum_f \phi e^{-\lambda_I t} & t > 0 \end{cases}$$

$$N_{Xe}(t) = \begin{cases} \gamma_{Xe} \sum_f \phi & t = 0 \\ \frac{\lambda_I}{\lambda_{Xe} - \lambda_I} \gamma_I \sum_f \phi (e^{-\lambda_I t} - e^{-\lambda_{Xe} t}) + \gamma_{Xe} \sum_f \phi e^{-\lambda_{Xe} t} & t > 0 \end{cases}$$

For U-235 and Pu-239, the cumulative yield of Xe-135 is almost the same, so it is extremely difficult to distinguish U-235 and Pu-239 from each other after the peak point. Thus the time zone which can be used to derive the fissile material is limited, and the sampling work should be done as soon and near as possible to get an accurate estimation.

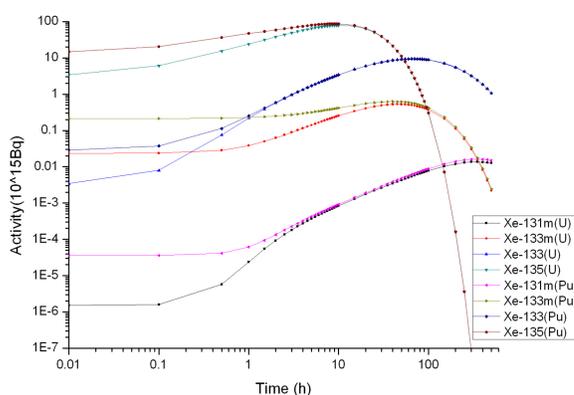
The influence of the nuclear loading efficiency to the simulation

In a nuclear explosion, the bomb requires higher neutron flux to get higher nuclear loading efficiency. And for fissile product like Xe-135, which has a relatively high neutron-absorption cross-section, the higher the neutron flux is, the higher the probability of neutron-absorption reaction is. So it will affect the ratio of Xenon isotopes, for example, Xe-135/Xe-133. But by the result of the numerical simulation, as is shown below, we know that in the low nuclear loading efficiency area, the ratio Xe-135/Xe-133 doesn't change much with the nuclear loading efficiency. What's more, after a few hours, the ratio Xe-135/Xe-133 nearly doesn't change with nuclear loading efficiency, and goes consistently. In the real situation, the loading efficiency of a nuclear explosion usually stays low, so the influence of the nuclear loading efficiency can be ignored in the numerical simulation.

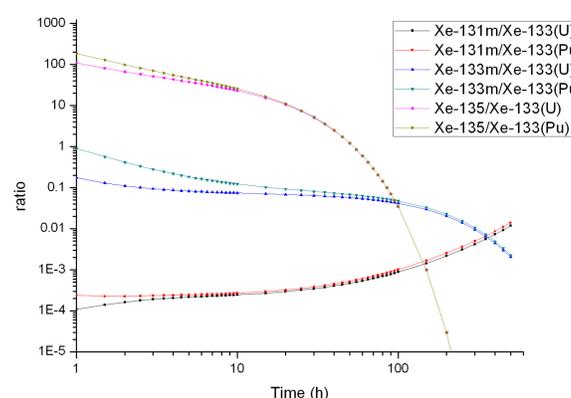


The simulation for the radioactivity change of the Xenon isotopes

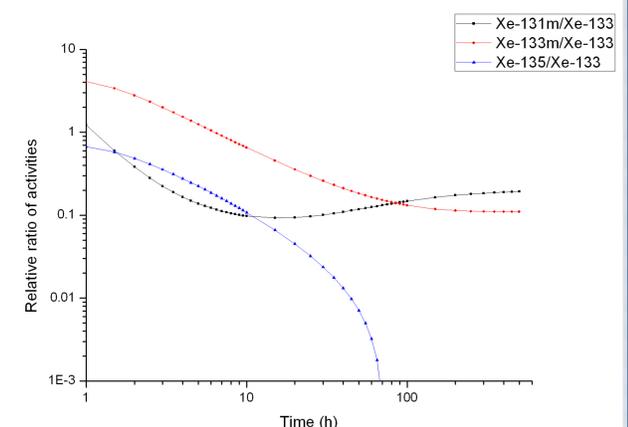
With all that discussed above, we can do numerical simulations about same-yield nuclear bombs with pure U-235 or pure Pu-239. The activities of the Xenon isotopes changing with time can be shown as below.



It is easy to see that the Xe-133 curves coincide soon, so it is difficult to get the difference from these curves. But Xe-133 can be used as a reference isotope, and we can get the ratios of other isotopes with Xe-133 as shown below.



As is shown, it is possible to distinguish U-235 and Pu-239 with activity ratio in theory if one could detect the isotopes quickly enough. And the theoretical distinguish ability can be decided by the relative ratio of Xenon isotopes between U-235 and Pu-239, which is shown below.



Conclusion

So there is indeed possibility to identify the fissile material by the ratio of Xenon isotopes, but it requires quick response ability and high-accuracy instruments. And its real degree of confidence should be decided by the sampling method and detection accuracy. What's more, there are some other nuclides that can be used to distinguish U-235 and Pu-239, including Kr, Ba, Ru, and so on. And their isotopic ratios can be used to further confirm the result or even be used to distinguish U-235 and Pu-239 alone. But there are still some limits and the operability of these nuclides is different depending on these limits. And this requires further discussion.

A technical nuclear forensics capability to support the analyses of illicit radiological and nuclear materials



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Nuclear Forensics @ AWE

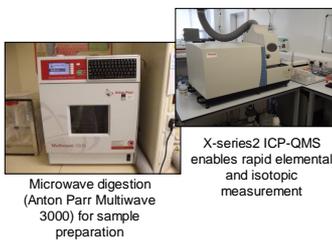
Intercepted materials can be analysed using nuclear and conventional forensic techniques to provide information to first responders and law enforcement.

Intercepted materials and associated evidence

Technical Nuclear Forensics

Development of new and existing capabilities

- Modern instrumentation enables enhancement of capability to meet nuclear forensics requirements



X-series2 ICP-QMS enables rapid elemental and isotopic measurement

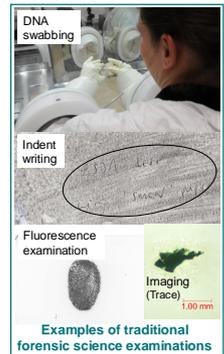
Collocated refurbished facilities



Conventional Forensics on contaminated items

Broad range of traditional forensic science examinations capabilities:

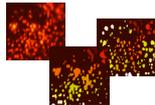
- Record photography
- Swabbing for DNA
- Trace evidence recovery
- Digital data recovery
- Fingerprint Development
- Questioned Documents



Cameca 1280 HR HMR SIMS

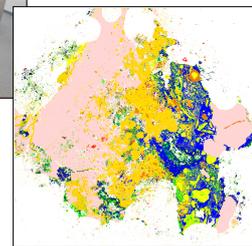
Large Geometry Double Focusing (HMR) Secondary Ion Mass Spectrometer with simultaneous multi-ion detection

Nuclear safeguards applications using LG-SIMS with automated screening capabilities.
 P. Peres, N Montgomery et al. *Surface and Interface Analysis*. Volume 45, Issue 1, p. 561-565, (January 2013)

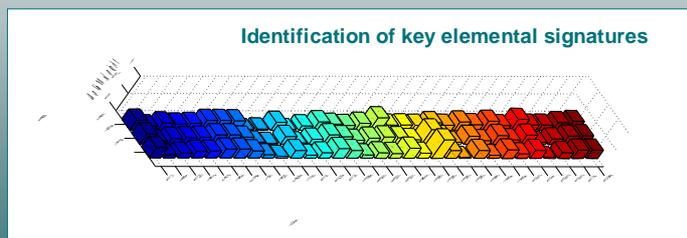
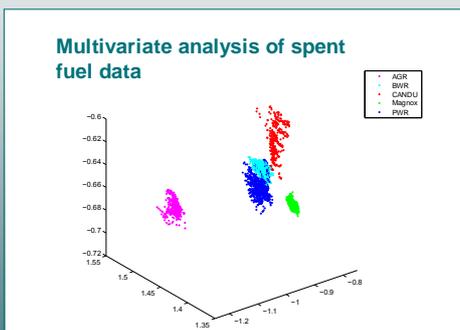
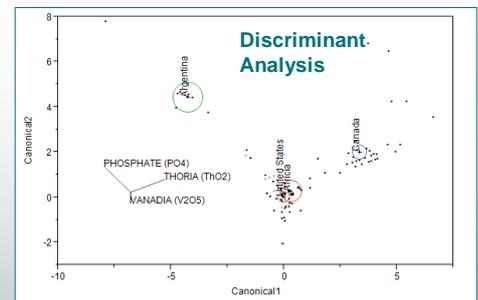
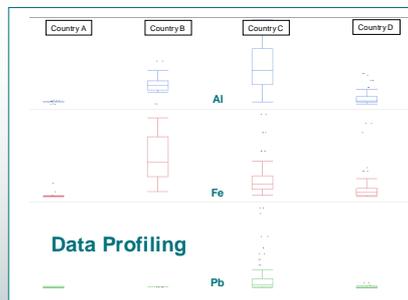


Quantitative Mineralogy - QEMSCAN

Characterises associated particulate material to support geolocation of items.



An advanced nuclear forensics capability supports the analysis of the material data, and associated evidence data, identifying and utilising forensic signatures.



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POTENTIAL AND LIMITATIONS OF ICP-QMS TECHNIQUE FOR THE MEASUREMENT OF ^{230}Th

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INTRODUCTION

The age of a material, defined as the time elapsed since its last processing was performed, is a valuable signature for a nuclear forensic investigation. In the case of uranium containing materials, this parameter can be obtained from the parent/daughter $^{230}\text{Th}/^{234}\text{U}$ ratio that determines when the complete separation of ^{234}U from ^{230}Th was held. The proper application of this chronometer is based on the following premises: i) U and Th total separation during the manufacture, ii) from this time the sample has remained a closed-system.

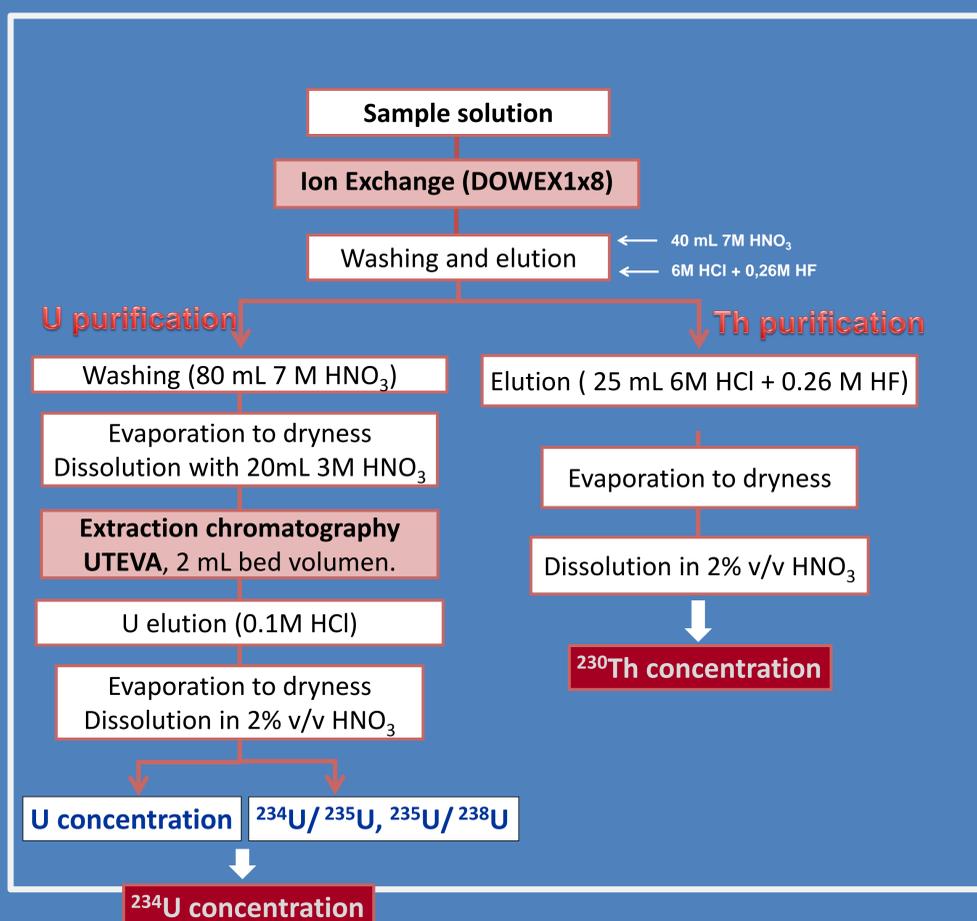
Alpha spectrometry has been used for more than 30 years for measuring U and Th isotopes. One of the great disadvantages of this technique is the large counting time necessary to achieve a good

statistics and, consequently, a lower associated uncertainty. A way to face this difficulty is the use of the mass spectrometry, in particular, plasma inductively coupled mass spectrometry (ICP-MS), since it allows the detection and measurement at ultratrace concentration of isotopes of uranium (^{234}U), thorium (^{230}Th) and fission products.

Recent developments in quadrupole based instruments (ICP-QMS) have led to considerable increase in sensitivity and precision, allowing performing the measurement of ^{230}Th at environmental levels. Based on these assumptions, this work presents the analytical procedure for the detection and measurement of ^{230}Th and ^{234}U and its application to standard reference uranium materials.

METHODS

SAMPLES: Uranium Isotope SRM (U-150 and U-850) distributed by National Bureau of Standards (supplier Union Carbide Nuclear Company)



INSTRUMENT : iCap Q (Thermo) with a high transmission interface, 90° ion optics and collision/reaction cell with “cut-off” of mass.

Plasma		
RF power	1550 W	
Gas flow rates (L min ⁻¹)	Cool, 14 – Auxiliary 0,80 – Nebulizer, 0,94	
Inlet system		
Nebulizer	Meinhard 0,1 mL.min ⁻¹	
Spray chamber	Cross flow Peltier cooled	
Data acquisition		
Concentration	Isotopes	^{238}U , ^{230}Th
	Runs- Replicates	20 - 5
	Dwell time (s)	0.05
Isotope ratios	Isotopes	^{234}U , ^{235}U , ^{238}U
	Runs- Replicates	100 - 5
	Dwell time (s)	0.1

Decay Constants (per y)	^{230}Th 9.15771E-06	^{234}U 2.82629E-06
Half-life (years)	7.569E+04	2.4525E+05

RESULTS

Sample	^{230}Th (g/g)	$^{234}\text{U}/^{238}\text{U}$	^{234}U g/g	Estimated age (years)	Age (years) (Date of production)
U-150	2.3512×10^{-11}	0,00118	1.6874×10^{-7}	$56,69 \pm 1,45$	55,33 (January 1959)
U-850	1.6690×10^{-11}	0,04664	1.1489×10^{-7}	$58,01 \pm 1,16$	56,36 (December 1957)

Concentrations and isotope ratio in the sample solution of each SRM material

CONCLUSIONS

- A method of U–Th dating applicable to uranium materials have been presented, including a preparative chemistry (AG1-X8 and UTEVA column) associated with an isotopic and elemental measurement of U and Th using ICP-MS with quadrupole mass analyzer.
- Calculated ages indicate production dates earlier than those recorded in documents. This discrepancy is associated with an excess of ^{230}Th often attributed to incomplete removal during purification. Nevertheless, in this work can also be due to the uncertainty associated with the measurement of the concentration of ^{230}Th .
- The stability and signal to noise ratio of modern generations of ICP-QMS allows to obtain elemental and isotopic measurements of U and Th with 1-3% uncertainties, which makes this technique comparable to the well-established α -spectrometry to measure these isotopes. Moreover, the speed of this technique suggests the suitability of their use to obtain a first approximation to the dating of a material.

