



Participation of Czech laboratories in isotopic, structural, and elemental characterization of uranium nuclear forensic samples within the 7th collaborative material exercise

Jan Lorincik¹ · Kristina Sihelska^{1,3} · Daniela Vesela¹ · Ivan Elantsev^{1,3} · Klara Rezankova¹ · Claudia Aparicio¹ · Thi Minh Do¹ · Jan Kucera² · Jan John³ · Mojmir Nemeč³ · Miriam Mindova³ · Vlastimil Miler⁴ · Daniel Gotz⁴ · Jiri Janda⁵ · Alena Kelnarova⁶

Received: 11 October 2023 / Accepted: 19 December 2023 / Published online: 19 January 2024
© Akadémiai Kiadó, Budapest, Hungary 2024

Abstract

This paper describes the nuclear-forensic characterization of materials provided by the Nuclear Forensic International Technical Working Group within the 7th Collaborative Material Exercise. The characterized materials were two powdered uranium material samples labelled ES-1 and ES-3 and two uranium metal samples labelled ES-2 and ES-4. A combination of several analytical techniques was used by a group of Czech laboratories to the identification of chemical compounds and the determination of the uranium isotopic and elemental composition of all four samples. Those results allowed for an unambiguous conclusion that ES-1 was depleted uranium trioxide, ES-2 was depleted uranium-vanadium alloy, ES-3 was depleted uranium nitrate, and ES-4 was depleted uranium metal. A further conclusion was that ES-2 cannot originate from the same source as the other three samples and that ES-1, ES-3, and ES-4 had a common source material. The highlights of this work were in obtaining the isotopic composition of uranium, including minor isotopes, in the early (24-hour) phase of the exercise using the Secondary Ion Mass Spectrometry in a single-particle measurement mode and in the application of the Neutron Activation Analysis with uranium separation prior to irradiation for the elemental screening of the uranium samples.

Keywords Nuclear forensics · Uranium · Uranium materials · Trace elements in uranium compounds · Uranium isotopic composition · Collaborative material exercise · Secondary ion mass spectrometry · Neutron activation analysis

Introduction

A country that is advanced in nuclear technology needs a nuclear forensic capacity to support an investigation of criminal acts that involve nuclear or radioactive substances, to deter or combat illicit trafficking of nuclear material, and to verify the correctness and completeness of material holdings reported by the licensees. In the Czech Republic (CR), most seized materials out of regulatory control (MORC) were abandoned legacy samples of uranium compounds or radioactive sources found at various institutions or public areas during cleanup or decommissioning processes or by chance. Those MORC were identified and categorized by first responders, then stored or disposed of under the supervision of the regulatory body. In most cases, the criminal investigation and thereby specialized nuclear forensic laboratories were not involved.

In the absence of frequent criminal cases nuclear forensic laboratories need regular exercises to sustain or improve

✉ Jan Lorincik
jan.lorincik@cvrez.cz

¹ Research Centre Rez, Husinec-Rez, Czech Republic

² Czech Academy of Sciences, Nuclear Physics Institute, Husinec-Rez, Czech Republic

³ Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Prague, Czech Republic

⁴ Nuclear Research Institute, Husinec-Rez, Czech Republic

⁵ NBC Defence Institute, University of Defence, Vyskov, Czech Republic

⁶ National Radiation Protection Institute, Prague, Czech Republic

their skills in nuclear forensics and to demonstrate credible nuclear forensic performance that can serve as a deterrent against nuclear smuggling.

To that end, a group of Czech laboratories with nuclear forensic capabilities has been assembled to cover a broad range of skills, know how, and analytical infrastructure and to take part in the 7th Collaborative Material Exercise (CMX-7) organized by the Nuclear Forensic International Technical Working Group (ITWG).

The nuclear forensic investigation involves a broad range of techniques, including chemical and physical analytical methods and radio analytical methods [1] and relies on knowledge in areas such as radiochemistry, reactor physics, material science, and nuclear fuel cycle. The aim of the nuclear forensic investigation is to answer questions on the origin of the investigated nuclear material, its production process, its owner, the smuggling route, and the intended use. The key characteristics to answer those questions are isotopic, elemental, and molecular composition, microscopic structure, as well as macroscopic features.

In this work, the nuclear forensic characterization of uranium materials, the analytical workflow, and the decision-making leading to answering the investigator's questions from the exercise scenario are described. The CMX-7 exercise had also a conventional forensic part, but its description is beyond the scope of this paper.

Experimental

Samples and exercise investigative questions

Four samples were received by a shipping Point of Contact (POC), who was not participating in the exercise and did not share the information about the samples from the packing list with the members of the participating laboratories. The POC transported samples to Research Centre Rez, where the boxes with the samples were opened and the exercise on the Czech side began.

After initial inspection and setting up the radiation protection measures the materials in transparent glass bottles were taken out of the transport containers and the first physical characteristics were recorded. The sample labelled ES-1 was a yellow powder in a glass vial. Sample ES-2 was composed of four pieces of black foil in a glass bottle. Sample ES-3 was a green-yellow powder in an Erlenmeyer flask. Sample ES-4 was composed of two rectangular ~1 mm thick dark pieces in a glass vial.

In the fictional scenario of the exercise, ES-1 and ES-2 were found on the crime scene as MORC, ES-3 was found also as MORC during the follow-up investigation in the workplace of the main suspect, and ES-4 was retrieved for comparison from a laboratory licensed to handle nuclear

material [2]. The investigator requested the support of the investigation by answering the following questions:

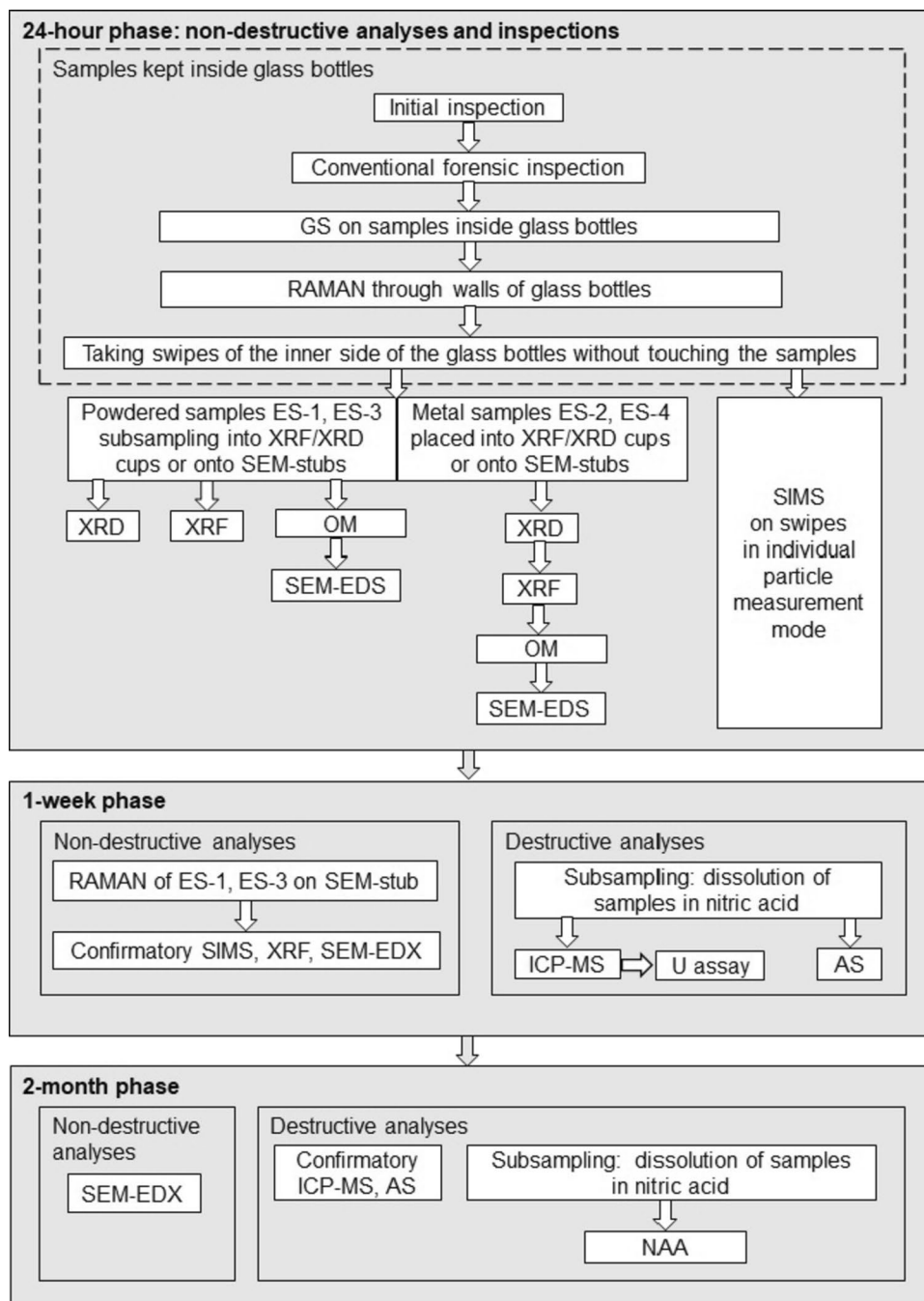
- (1) Can the yellow powder of ES-1 be linked with the black foils of ES-2?
- (2) Can either ES-1 or ES-2 be associated with the green-yellow powder of ES-3?
- (3) Are any MORC (ES-1, ES-2, ES-3) consistent with the dark pieces of comparative sample ES-4?
- (4) What is the chemical composition/phase of the samples?

The answers were sent to the investigator played by the ITWG organizers after the completion of each of the three phases of the exercise (24-hour, 1-week, 2-month).

Analytical plan and the exercise workflow

A generic analytical plan prepared for the exercise following the guidelines from the ITWG [3] has been continually adjusted as the exercise was evolved. The final version of the analytical plan is in Fig. 1. Within the initial inspection in the 24-hour phase, basic dosimetry measurements (dose rate, surface contamination) were conducted. Within the conventional forensic inspection step, the photographic evidence, fingerprints, and basic physical description were recorded and relevant information was inserted into the chain of custody forms. Then the samples in unopened bottles were transported to the Gamma Spectroscopy (GS) laboratory and after finishing the GS measurement to the Micro-Raman Spectroscopy (RAMAN) laboratory. Then each bottle was opened in a flow box or fume hood in a different radiochemical laboratory to avoid cross-contamination and the swipes of microscopic particles released from the samples were taken from the inner surface of the neck of the glass bottles without touching the samples inside. The swipes went to the Secondary Ion Mass Spectrometry (SIMS) laboratory. Next, sets of subsamples from the powdered samples (ES-1, ES-3) were prepared for the X-Ray Fluorescence (XRF), the X-Ray Diffraction (XRD), and the Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (SEM–EDS). The latter subsamples were shared with the visible-light Optical Microscopy (OM). The XRF and the XRD subsamples were placed using a micro-spatula inside the cups made of a Mylar-foil forming a circular base fixed on a Teflon ring. The OM/SEM–EDS subsamples were placed also with a spatula onto a double-sided carbon tape attached to an aluminum alloy SEM stub. In the case of the metallic pieces (ES-2, ES-4) no subsampling was needed in the 24-hour phase. The metallic pieces were simply placed inside the cups or onto a double-sided carbon tape on a SEM stub.

Fig. 1 The analytical plan of the Czech laboratories for the CMX-7 exercise



The analyses in the 1-week and 2-month phases were designed to refine the answers or to increase the level of confidence in the answers either by repeating the analyses from the 24-hour phase at different measurement conditions or by employing other methods. In the 1-week phase, the other methods were the Alpha Spectrometry (AS) and the Inductively Coupled Plasma Mass Spectrometry (ICP-MS), in the 2-month phase it was the Pre-Irradiation Separation–Neutron Activation Analysis (PS-NAA).

Methods and instruments

The instruments and methods used in the exercise are listed in Table 1, including a basic description of instrumental specifications and the main parameters or settings used in the exercise. The procedures using SIMS and PS-NAA will be described in more detail in the next sections.

The sample characteristics obtained using the methods in Table 1 were processed using the Graded nuclear forensic

Table 1 Instruments and methods used in the exercise

Method	Purpose	Instrument/Model/ Software	Parameters used in the analyses
AS	Isotopic composition	Camberra AlphaAnalyst, GENIE 2000™ software	uranium CeF ₃ microprecipitation, filter source counting time 24 hours
GS	Isotopic composition, initial identification, and categorization	BEGE (Camberra) 1,7 keV energy resolution at 1332 keV, detector efficiency 60%, counting time per sample 6 h, GENIE 2000™ software	U-235 was determined from lines at 143.8 keV and 185.7 keV, U-238 concentration from lines of Th-234 at 63.3 keV and 92.6 keV, and Pa-234m at 766.4 keV and 1001 keV
ICP-MS	Isotopic composition, uranium assay	Thermo Element XR sector field instrument used for isotopic uranium, Thermo iCap RQ, Qtegra software used for uranium assay	Isotopic composition: 0.01 s dwell time per isotope, 5×2500 passes. Uranium assay: 0.05 s dwell time, 25 sweeps, 3×. Quantification by external calibration to NBS U960 and IRMM-056
PS-NAA	Elemental composition (minor, trace)	Coaxial BEGE (Camberra) detector, relative efficiency 20%–78%, nuclear research reactor LVR-15 at Rez, CR	Pre-irradiation separation of uranium matrix using UTEVA resin *
OM	Size, shape (powders)	BX-51P (Olympus)	Objective 5x, 10x, Eyepiece 10x
RAMAN	Compound identification	DXR2 Raman Microscope (Thermo Scientific), Diode-pumped solid-state laser (532 nm, 10W), multichannel CCD, OMNIC™ software	Measured at 1 mW, 2 s, accumulation of 100 spectra, 3500–50 cm ⁻¹ , 50 μm confocal slit apertures
SEM	Size, shape, surface morphology	FIB-SEM LYRA3 GMU (TESCAN), SE, BSE detectors	Electron beam 20 kV, 0.5 nA, working distance 9 mm
EDS	Elemental composition (major, minor)	SDD detector 80 mm ² X-MaxN (Oxford instruments) integrated with FIB-SEM LYRA3, AZtec™ software	electron beam 20 kV, 0.7 nA, detector live time 40–240 s, 5–10 eV/channel, working distance 9 mm
SIMS	Isotopic composition	IMS 7f (CAMECA), ion sources: DUO-PLASMA-TRON and Cs ⁺ , APM and WinCurve™ software	Primary ions: O ₂ ⁺ , positive secondary ions, *
XRD	Compound identification	Empyrean diffractometer (Malvern Panalytical), Co X-ray tube (0.1789 nm, 40 kV and 40 mA), detector PIXcel3D, HighScore Plus™ software	Samples ES-2 and ES4: Single scan in Bragg–Brentano geometry, 2θ range 2.5–135°, step size 0.0263°
XRF	Elemental composition (major, minor)	ARL QUANT'X (Thermo Scientific), Rh X-ray source (50 kV, 1.98 mA), SDD detector (area 30 mm ² , resolution < 150 eV at 5.9 keV), UniQuant™ software	Samples ES-1 and ES-3: Single scan in transmission mode, 2θ range 15–82°, step size 0.0263° Operated in the air (detects elements from Na)
GDF	Assignment of the level of confidence to conclusions	GDF, MS Excel™	p-values separating the confidence levels: 0.05, 0.1
Cluster analysis	Evaluation of linkage among samples, based on trace elements	STATISTICA, StatSoft software	Linkage is defined as a Euclidean distance

*See more detail in the text of the next two sections

decision framework (GDF) [3] – a statistical tool that enabled to assign a level of confidence to answers to investigative questions. A clustering analysis was used to quantify linkage among samples in terms of Euclidean distance $(x, y) = \left[\sum (x_i - y_i)^2 \right]^{1/2}$, where x_i and y_i were concentrations of element “ i ” in samples x and y .

SIMS in a 24-hour phase of nuclear forensic investigation

The SIMS as a destructive technique and a demanding method in many respects (throughput, cost of ownership, availability) is usually employed in the 2-month phase or the 1-week phase at best of a nuclear forensic investigation. Here, the use of SIMS in the 24-hour phase is described. The procedure is based on the experience obtained in the

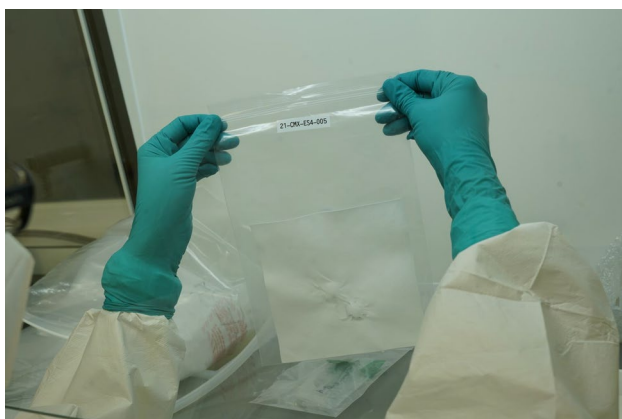


Fig. 2 Swipe from inner surface of the neck of a bottle containing a CMX-7 sample. Note circular areas corresponding to the diameter of the bottle neck

analyses of individual dust particles containing uranium for international nuclear safeguards [4].

Shortly after removing the cap, swipe samples were taken from the inner surface of the neck of each bottle (Fig. 2). This was done without touching or disturbing the samples inside the bottles. The extraction of particles from the swipes onto silicon planchets (1" wafers) was done with a vacuum impactor [5]. This method consists of impacting particles on a silicon planchet beforehand covered with an organic compound, polyisobutylene in nonane, acting as a sticky agent [6]. This operation was carried out in a disposable plastic glove bag. Each sample had its own glove box to prevent cross-contamination.

Then the SIMS performed two-dimensional image scans $500 \mu\text{m} \times 500 \mu\text{m}$ for ^{235}U and ^{238}U isotopes (Fig. 3) and an automated sample-stage movement in discrete steps of $500 \mu\text{m}$ to cover a sufficiently large part of the planchet— $2 \text{ mm} \times 2 \text{ mm}$ composing of 16 fields in the center of the silicon planchet (Fig. 4). The coordinates and preliminary enrichment of uranium particles was the result of that step. Additionally, various enrichment populations of particles can be observed if the sample is not isotopically homogenous. Next, several representative particles were chosen one by one, and an accurate and precise measurement of isotopic composition, including minor isotopes ^{234}U and ^{236}U , of each individual particle was obtained.

The calibration of the isotopic measurement was carried out using the certified reference material of uranium oxide particles CRM U010 (New Brunswick Laboratory, Argonne, IL, USA) analyzed under identical conditions as the samples.

The main difference in the SIMS procedure used in this work compared to [4] was in speeding up the particle search and identification step by screening substantially smaller areas of the planchets. Thus, the SIMS measurements for all

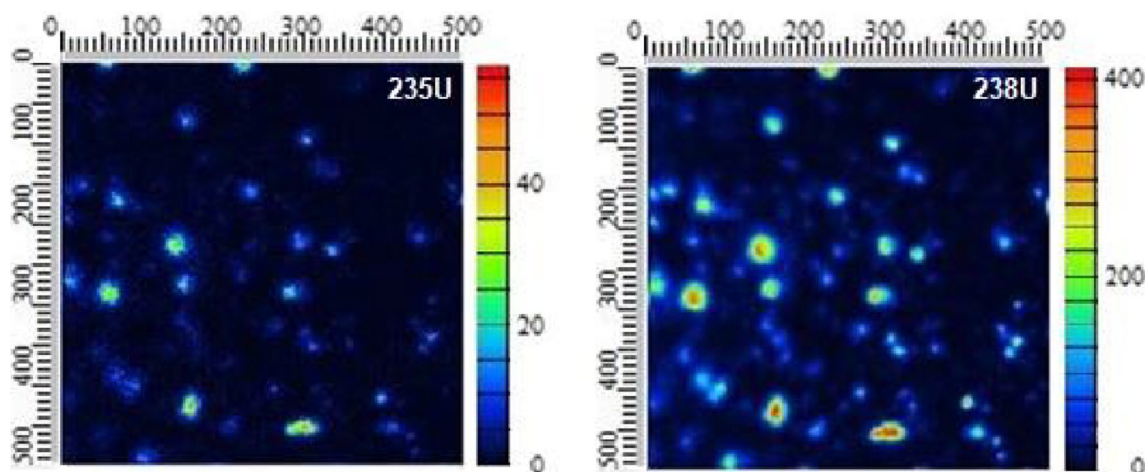


Fig. 3 SIMS images $500 \mu\text{m} \times 500 \mu\text{m}$ of ^{235}U and ^{238}U in particles deposited on a single-crystal Si planchet

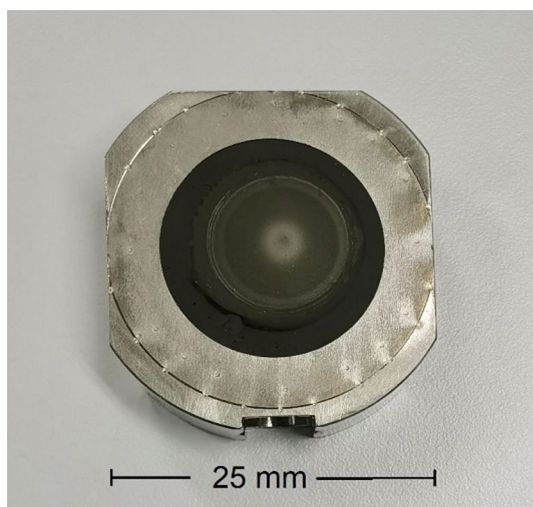


Fig. 4 Particles deposited on a single-crystal silicon plachet and fixed in a SIMS sample holder. The denser central part was scanned for the presence of uranium particles

four samples could have been completed within a “record-breaking” time of ~ 14 hours.

NAA in the 2-month phase of nuclear forensic investigation

NAA can be used for the screening and determination of trace elements in various materials. However, in the case of uranium matrix, number of fission products is created on neutron irradiation, so that their activity prevents determination of other major, minor, and trace elements. Therefore, uranium must be selectively separated from the samples prior to irradiation, which is a challenging task [7].

Within this work, uranium powdered samples ES-1 and ES-3 with masses of 30–50 mg were dissolved in 3M HNO_3 . The chunks with masses of 50–70 mg cut out of the metal samples ES-2 and ES-4 were first etched to lose about 5–10% of their mass to remove a possible external contamination and then dissolved. Three 2-ml-columns of UTEVA resin in succession in Fig. 5 were used for pre-irradiation removal of uranium from the samples. A quality control sample Chanterelle (powdered U_3O_8) [9] with mass of ≈ 50 mg was analyzed in the as received state. The same analytical procedure was used for a processing blank. Aliquots of the effluent were transferred into cleaned polyethylene and quartz (Suprasil®, Heraeus) tubes for short- and long-time

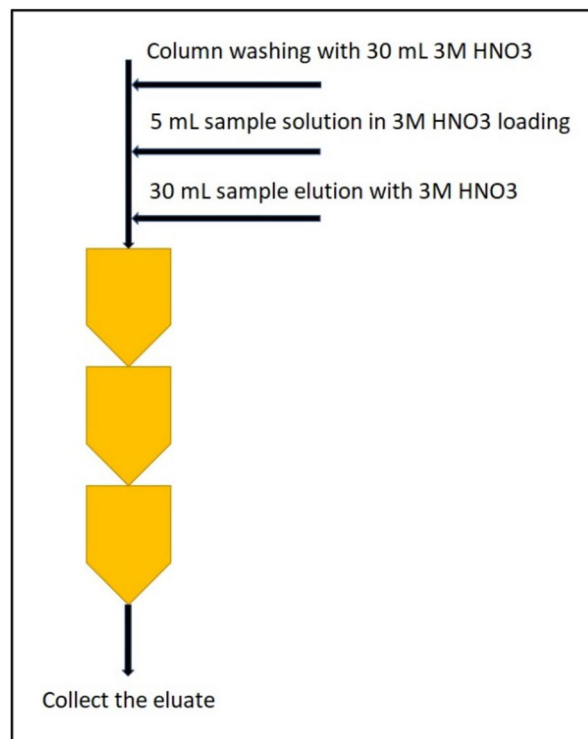


Fig. 5 3-stage separation columns to remove the uranium matrix from the sample solutions

irradiation, respectively, and sealed. A separation factor of uranium between 10^3 and 10^4 was achieved.

All laboratory ware (Teflon, Polypropylene, Polyethylene) was soaked for several days in sub-boiled 3M HNO₃ and washed with demi-water. For sample dissolution and uranium separation using UTEVA resin, 3M HNO₃ prepared from sub-boiled HNO₃ was used. All operations were performed in a Clean Lab ISO 5–6.

The irradiation has been performed in the LVR-15 reactor in Rez, Czech Republic [8]. The thermal neutron flux density and the timing for the short-time irradiation were $\Phi_{th} = 3 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, $t_i = 90 \text{ s}$ (irradiation time), $t_d = 600 \text{ s}$ (decay time), $t_c = 600 \text{ s}$ (counting time), respectively. The thermal neutron flux density and the timing for long-time irradiation were $\Phi_{th} = 4 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, $t_i = 3 \text{ hours}$, $t_d = 2\text{--}3 \text{ days}$ or $25\text{--}30 \text{ days}$, $t_c = 1 \text{ hour}$, or 3 hours , respectively.

The quantification was carried out by the comparator method with in house calibrators prepared from solutions Astatol with certified element contents (Analytika, s.r.o., Czech Republic) irradiated and counted as the samples.

The counting of short-lived radionuclides of the elements Al, V, Mn, and Cu was done with a coaxial BEGE detector (PGT, FWHM 1.75 keV, relative efficiency 20.3%, both for 1332.5 keV line of ⁶⁰Co) using dual LFC module to perform dynamic correction of dead time and pile-up losses. The counting geometry was 3 cm from the detector cap. For the counting of medium- and long-lived radionuclides of the elements Na, As, Sb, W, Cr, Fe, Co, Ni, Zn, Sb and Ba another coaxial BEGE detector (Canberra, FWHM 1.87 keV, relative efficiency 77.8%, both for 1332.5 keV line of ⁶⁰Co) was used, again with the LFC module in the associated electronic chain. The counting geometry was 2 cm from the detector cap.

The cluster analysis was employed to quantify linkage among the samples analyzed using Euclidean distance $(x, y) = \left[\sum (x_i - y_i)^2 \right]^{1/2}$, where x_i and y_i were concentrations of element “i” in samples x and y.

Results and discussion

24-hour phase

The measurements, data interpretation, and creation of the report for each analysis from Fig. 1 were running in parallel with continually streaming the data to the coordinator of the engaged laboratories.

The very first results came from the GS laboratory indicating that all samples contained depleted uranium (DU).

The RAMAN laboratory provided the first clue about the composition of the powdered samples while keeping

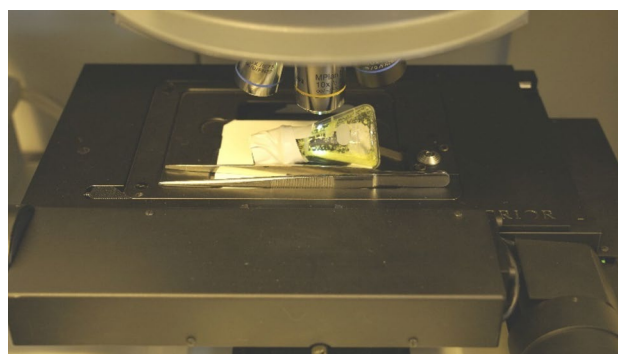


Fig. 6 Raman measurement of powdered material ES-3 inside Erlenmeyer flask

Table 2 Compound identification in the 24-hour phase using RAMAN and XRD. Only compounds with the two highest scores are listed. ES-2 and ES-4 were not analyzed with RAMAN. It was conjectured that in the case of ES-2 and ES-4 the XRD results might not represent the bulk of the samples

Sample	RAMAN	XRD
ES-1	UO ₃	UO ₂ (OH) ₂
	UO ₂ (OH) ₂	UO ₃
ES-2		UO ₂
		Fe
ES-3	UO ₂ (NO ₃) ₂ ·nH ₂ O	UO ₂ (NO ₃) ₂ ·3H ₂ O
	Unresolved peak at 121 cm ⁻¹	UO ₂ (NO ₃) ₂ ·6H ₂ O
ES-4		UO ₂
		Fe

the materials inside the glass bottles (Fig. 6). After the receipt of the XRD data the main composition of ES-1 and ES-3 could be determined with high confidence due to the match between RAMAN and XRD data in Table 2. ES-1 was identified as a mixture of uranium trioxide UO₃ and uranium oxo hydroxide UO₂(OH)₂ with the possible presence of minor elements or compounds containing N or Na (not shown in Table 2 due to low score). It should be noted that the stoichiometry of UO₂(OH)₂ from the XRD/RAMAN databases is identical to that of uranium trioxide monohydrate UO₃·H₂O. ES-3 was identified as a mixture of trihydrate and hexahydrate of uranyl nitrate UO₂(NO₃)₂·nH₂O (n = 3, 6). In the case of ES-2 and ES-4, XRD identified UO₂ and Fe but if the ductility of the samples and possible contamination from the manipulating metallic tools was considered, it was conjectured that both samples were uranium metals with oxidized surfaces and trace Fe surface contamination. XRF added Cu, Zn, and V to the list of possible surface contaminants. SEM–EDS did not add any new information besides confirming uranium, oxygen, and in the case of ES-2 nitrogen as well.

The SEM together with the OM allowed for morphological characterization of the material. However, these generally important characteristics did not contribute to answering the investigator's questions.

The most important information came from the SIMS laboratory in the third quarter of the 24-hour phase. In the automated particle screening mode, the SIMS identified 1540 particles containing ^{235}U and ^{238}U from the ES-1 sample, 330 particles from ES-2, 218 particles from ES-3, and 1012 particles from ES-4. The outputs of that step were coordinates of uranium particles on the plachets and preliminary estimates of the enrichments. It was found that all four samples contained particle population with only one enrichment, i.e., the samples were isotopically homogeneous. Several uranium particles from each sample were chosen for isotopic measurement at high precision mode. The choice was based on the ^{235}U signal intensities. The results in the graphical form are in Fig. 7. Each point corresponds to one analyzed particle. The difference between

the uranium isotopic composition of ES-2 and the other samples has been clearly established.

To summarize the 24-hour phase, it was found (at various levels of confidence) that

- All samples are made of depleted uranium and are isotopically homogeneous
- ES-1, ES-3, and ES-4 have the same isotopic composition, but different from ES-2
- ES-1 is a mixture of uranium trioxide UO_3 and uranium oxo hydroxide $\text{UO}_2(\text{OH})_2$
- ES-2 is an oxidized uranium metal
- ES-3 is a mixture of trihydrate and hexahydrate of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- ES-4 is an oxidized uranium metal
- The same isotopic composition of ES-1, ES-3, and ES-4 gave rise to the conjecture that ES-3 could have been made from ES-4 and ES-1 from ES-3.

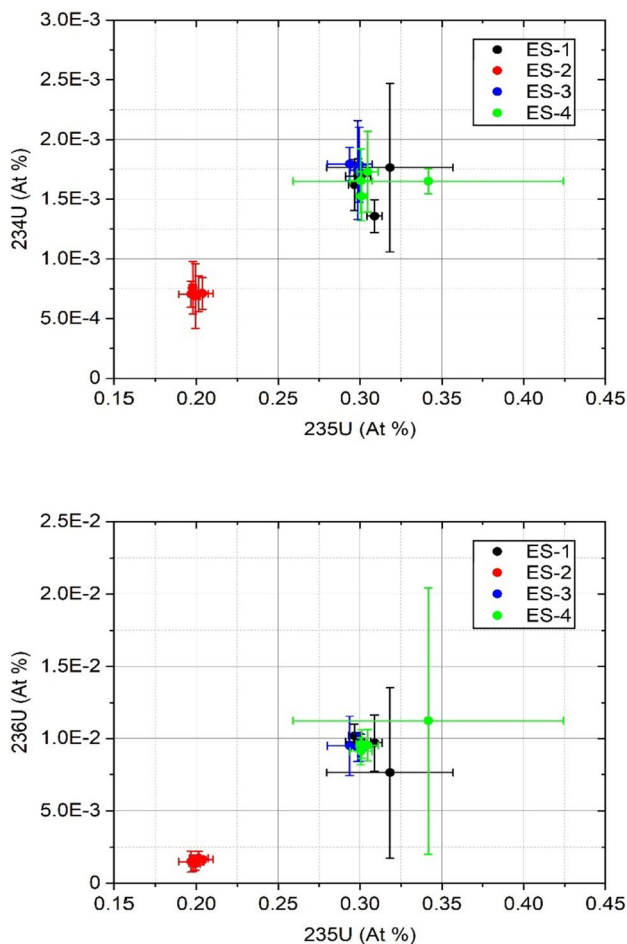


Fig. 7 Scatter diagrams of uranium isotope concentrations in individual particles. Each symbol represents a measurement of one particle. The error bars correspond to standard deviations 1σ based on the counting statistics

1-week phase

The most important contribution in the 1-week phase of the exercise came from the ICP-MS measurements. Besides confirming the isotopic composition of the samples at a high level of confidence, it provided uranium assay for all four samples in Table 3. Though almost an exact match between the measured uranium assay for ES-1 and the theoretical value for UO_3 must have been incidental, it narrowed down the compound identification to UO_3 . The uranium assay for ES-3 is in between the theoretical values for the trihydrate and hexahydrate of uranyl nitrate, suggesting a refinement of ES-3 identification to a mixture of the trihydrate/ hexahydrate = 2/3.

For comparison, the samples were also measured using AS, but the uncertainties of isotopic concentrations were much larger than those for SIMS or ICP-MS, so the AS results were not considered in solving the exercise questions.

Table 3 Uranium assay measured with ICP-MS with estimates of maximal uncertainties compared to the theoretical uranium content in the selected compounds

Sample	U assay, g/kg	Compound	Theory, g/kg
ES-1	832 ± 83	UO_3	832.19
		$\text{UO}_2(\text{OH})_2$	782.86
ES-2	1050 ± 105	U metal	1000
ES-3	494 ± 49	$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	531.22
		$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	474.04
ES-4	983 ± 98	U metal	1000

2-months phase

After the completion of 24-hour and 1-week phases of the nuclear forensic part of the exercise the only missing critical information was the trace element content in ES-1, ES-3, ES-4, which could provide further confirmation about the established linkage among the samples or disprove it.

The chosen method for the trace-element screening—PS-NAA provided concentrations of more than 10 elements at ppm levels for all four samples. Due to an unfavourable operation schedule of the LVR-15 reactor (usually 10–11 operation campaigns of 4 weeks with breaks for 2–3 weeks for the reactor maintenance and the active core adjustment for upcoming experiments) during the CMX-7 exercise and a long decay time needed for the determination of long-lived radionuclides (4–5 weeks), only the results for the short-lived radionuclides were available before the end of the exercise. However, since the measurement of long-lived radionuclides was completed only a couple of days after the end of the 2-months phase (and in the case of a more favourable LVR-15 operation schedule could be managed within 2-months phase), the results obtained from the measurement of both short- and long-lived radionuclides have also been included in this work for the sake of completeness. These results are presented in Table 4, which shows a completely different elemental composition of sample ES-2 compared to samples ES-1, ES-3 and ES-4, especially much higher V content. The results for the quality control sample—reference material Chanterelle agree with the CETAMA certified values within uncertainty margins, proving the accuracy of our PS-NAA results, which also means that none of elements determined was significantly retained in uranium separation

by UTEVA resin. No significant element levels in the processing blank were found (indicating good contamination control), so that no correction was needed.

The cluster analysis of the PS-NAA data (cf. dendrogram in Fig. 8) revealed short linkage distance (a high similarity of elemental composition) between the ES-4 metal and the ES-3 powder, which supported the conjecture that the uranium nitrate powder ES-3 was created from the uranium metal ES-4. The other powdered sample ES-1 exhibits somewhat longer linkage distance to both ES-3 and ES-4, therefore the proposed reaction path between the uranium nitrate powder and the uranium trioxide powder remained neither confirmed nor excluded. The ES-2 metal forms a unique, completely separated cluster, indicating completely different elemental composition. Noteworthy, the PS-NAA results obtained on bulk samples, and results of the subsequent cluster analysis, are fully consistent with the results of uranium isotopic composition in individual particles of the samples achieved by SIMS already in the 24-hour phase of the CMX-7 exercise (cf. Fig. 1).

Conclusions

Coordinated application of a range of analytical methods allowed for answering all nuclear forensic investigator's questions within 24 hours at varying level of confidence.

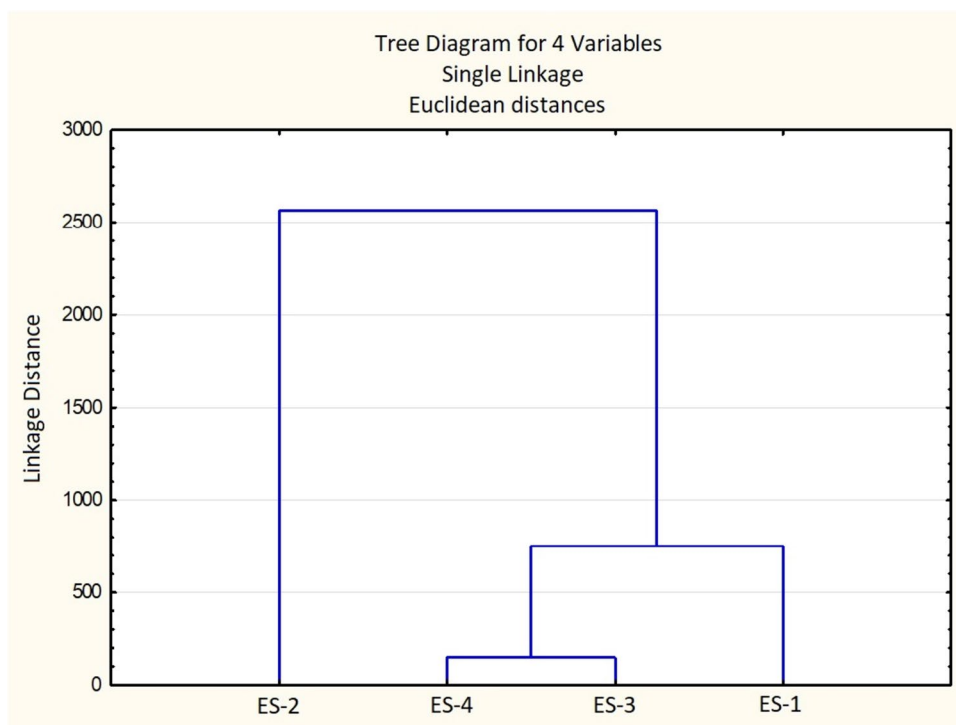
A notable point of this work was the application of the SIMS technique in the earliest phases of the exercise in a non-destructive manner using the sub-sampling via swiping the surfaces of the samples or their transport containers. Besides precise isotopic composition, the SIMS results

Table 4 Elements contents in the samples analyzed and in Chanterele reference material in mg kg^{-1} with their expanded uncertainties (coverage factor $k=2$)

Element	ES-1	ES-2	ES-3	ES-4	RM CEA CETAM chantere- relle [9]	
					This work	Certified ^a
Na	9.03 ± 0.10	3.84 ± 0.05	5.95 ± 0.02	4.93 ± 0.08	273 ± 2	NA
Al	23.8 ± 3.6	14.8 ± 5.6	17.7 ± 2.8	23.6 ± 3.8	60.0 ± 11.2	56 ± 7
V	<0.13	2550 ± 52	<0.09	<0.12	10.7 ± 0.6	9.4 ± 1.3
Cr	3.65 ± 0.09	0.57 ± 0.03	1.78 ± 0.08	4.16 ± 0.12	45.2 ± 2.9	49.6 ± 4.1
Mn	8.56 ± 0.70	4.15 ± 0.78	5.12 ± 0.56	11.6 ± 0.8	8.60 ± 1.6	9.9 ± 1.7
Fe	115 ± 8	321 ± 29	50.5 ± 5.0	59.6 ± 5.9	118 ± 18	122 ± 10
Co	0.098 ± 0.010	0.055 ± 0.004	0.064 ± 0.008	0.117 ± 0.010	5.33 ± 0.55	5.2 ± 1.1
Cu	12.2 ± 5.4	15.3 ± 5.6	11.1 ± 1.5	12.9 ± 1.6	29.3 ± 1.2	26.4 ± 3.4
Ni	14.0 ± 0.6	10.9 ± 0.3	7.30 ± 0.42	18.8 ± 0.6	47.5 ± 1.2	50 ± 3
Zn	9.2 ± 0.3	6.4 ± 0.2	19.9 ± 0.4	7.0 ± 0.2	44.6 ± 0.6	44 ± 4
As	0.016 ± 0.003	0.033 ± 0.002	0.014 ± 0.003	0.017 ± 0.003	1.25 ± 0.06	NA
Sb	0.121 ± 0.014	0.043 ± 0.005	0.104 ± 0.011	0.088 ± 0.012	0.088 ± 0.008	NA
Ba	420 ± 8	101 ± 3	133 ± 16	251 ± 6	1230 ± 125	NA
W	0.044 ± 0.005	0.132 ± 0.004	0.081 ± 0.004	0.085 ± 0.004	14.8 ± 2.4	18.1 ± 2.6

^aNA: Not available

Fig. 8 Dendrogram of hierarchical cluster analysis among the samples obtained from the PS-NAA results



showed that the particles released from each sample contained only a single enrichment. In case of the presence of several enrichments in the sample, early use of SIMS could give valuable clue for the next investigative steps.

Another innovative part was the application of PS-NAA to the trace-element screening of the uranium samples, which supported the SIMS results. Though the potential of PS-NAA for survey analysis has not been fully explored in this work, it can be already concluded that PS-NAA could be a useful tool for trace level elemental screening of samples with high content of uranium and its application potential in nuclear forensics deserves further exploration.

Acknowledgements The larger part of the presented results was obtained using the CICRR infrastructure, which is financially supported by the Ministry of Education, Youth and Sports—project LM2023041.

Data availability The data that support the findings of this study are available within the article or from the corresponding author, Jan Lorincik, upon reasonable request.

Declarations

Conflict of interest All authors have no conflicts of interest.

References

- Mayer K, Wallenius M, Ray I (2005) Nuclear forensics—a methodology providing clues on the origin of illicitly trafficked nuclear materials. *Analyst* 130:433–441
- Project Hebenon - Inject 1, Collaborative Materials Exercise 7, ITWG, December 2020
- Taylor F, Higginson M, Marsden O, Schwantes J (2020) Participant information package collaborative materials exercise. *J Radioanal Nuclear Chem* 323:415–430
- Peres P, Hedberg PML, Walton S, Montgomery N, Cliff JB, Rabemananjara F, Schuhmacher M (2012) *Surf Interface Anal* 45:561–565
- Donohue DL (2002) Peer reviewed: strengthened nuclear safeguards. *Anal Chem* 74(1):28A–35A
- Esaka F, Watanabe K, Fukuyama H, Onodera T, Esaka KT, Magara M, Sakurai S, Usuda S (2004) *J Nucl Sci Technol* 41:1027–1032
- Rosenberg RJ (1993) *J Radioanal Nucl Chem* 169:113–124
- Koleška M, Lahodová Z, Šoltés J, Viererbl L, Ernest J, Vinš M, Stehno J (2015) *J Radioanal Nucl Chem* 305:51–59
- (2018) Reference materials catalogue, chanterelle, CEA, CETAMA, 30207 bagnois-sur-cèze cedex, France

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.