

Identification of Unknown Nuclear Material

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Abstract. An isotopic fingerprinting method has been demonstrated to discriminate spent fuels of the same origin. The method, demonstrated for conceptual and real spent fuels through their isotopic compositions obtained from simulations and Post-Irradiation Examinations, was sensitive enough to resolve spent fuels from: different reactor types, the same reactor but with different charge composition and of the same charge composition but from different reactors. Furthermore, the simulation of spent fuel composition when ^{236}U is considered in fresh fuel has shown that the inclusion of ^{236}U does not affect the clustering. Spent fuels have been resolved on the basis of U and Pu or only Pu isotopic composition.

1. Introduction

Nuclear forensics is primarily concerned with the timely interception of nuclear material seized away from its designated areas. Identification of the provenance of this material could indicate the trafficking route from its diversion to its interception. Then, appropriate measures could be taken to combat possible future diversions of nuclear material away from designated areas. The objective of this work is to demonstrate a sensitive enough isotopic fingerprinting procedure cluster spent fuels of the same origin [1-6]. The term origin refers to the type of the reactor where the fuel was irradiated and the spent fuel final burnup at the end of irradiation, as well as the composition of the fuel charged to the reactor.

2. Materials and methods

Spent fuel/reactor compositions should ideally cover all possible origins. The information can be drawn from Post-Irradiation Examination studies rendering isotopic composition information on the spent fuels. Such spent fuels from PWR and BWR nuclear reactors, which have been considered in this study, are shown in Table 1. The isotopic composition data, given at the End-of-Irradiation of these fuels, have been obtained from Post-Irradiation Examination and are available in the OECD/NEA SFCOMPO databank (<http://www.oecdnea.org/sfcompo/Ver.2/Eng/index.html>). Alternatively, in the absence of suitable experimental data on U and Pu compositions of spent nuclear fuels, these were simulated for the reactor-commercial nuclear fuel combinations considered (Table 2). These were simulated using the zero-Dimensional isotope generation and depletion code ORIGEN-2.2 [7]. The simulations performed were coupled with burnup-dependent cross-section libraries resembling, as closely as possible, the fuel type and neutron spectrum of irradiation. The composition of spent fuel depends on, and hence reflects, the charge composition of the fuel, its irradiation history and the neutron spectrum, hence carrying information uniquely related to the origin of the fuel.

The discrimination of the spent fuel is based on the use of the uranium and/or plutonium isotopic composition as the forensic signatures. The isotopic ratios considered were in the case of U and/or Pu:

$^{242}\text{Pu}/^{240}\text{Pu}$, $^{238}\text{Pu}/\text{Pu}$, $^{235}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$, $^{241}\text{Pu}/^{240}\text{Pu}$, $^{239}\text{Pu}/^{235}\text{U}$, $^{242}\text{Pu}/^{238}\text{U}$. Then, these ratios are compared, using the multivariate statistical technique of factor analysis, in order to cluster on a 3D representation, spent fuel of the same origin, through their similarities and differences in the isotopic compositions [1,2].

Table 1. PWR and BWR UO_2 fuels considered from the SFCOMPO data bank.

Reactor		Fresh fuel	Burnup range
name	type	(enrichment in ^{235}U)	(GWd/tU)
Mihama-3	PWR	3.21%	21 - 32.
Genkai-1	PWR	3.415%	38.1, 38.7
Calvert Cliffs-1	PWR	2.453%	31 - 46
Calvert Cliffs-1	PWR	2.72%	26, 33.17
Calvert Cliffs-1	PWR	3.038%	27 - 44
Monticello	BWR	1.87%	44 - 55
Monticello	BWR	2.14%	49 - 54
Gundremmingen	BWR	2.53%	21 - 25

Table 2. Simulated reactors, fuels and targeted burnup values.

Reactor	Fresh fuel	Burnup range (GWd/tU)
PWR	3 - 5% ^{235}U	40 - 55
PWR	3.5% ^{235}U + Gd	40 - 55
	thermal MOX [95% U depleted, 5% Pu*]	35 - 50
	MTR high enriched (90 % ^{235}U)	100 - 300
	MTR low enriched (25 % ^{235}U)	50 - 100
BWR	UO_2 , 2.5 - 4% ^{235}U	20 - 40
	2.75% ^{235}U + Gd	20 - 40
CANDU-N	natural U	4 - 10
CANDU-S	slightly enriched UO_2 , 1 - 2% ^{235}U	7 - 30
LMFBR	MOX [74% U depleted, 25% Pu*]	60 - 100

*isotopic vector of plutonium 238:239:240:241:242 was 1.4:55:25.3:13.3:5.

3. Results

In Fig. 1a, the ten reactor-spent fuel combinations considered in Table 2, are clustered together on the basis of their similarities in their isotopic composition. Hence, they are clustered together according to the reactor type where the fuels were irradiated and their charge composition. The fuels are clearly resolved between them. In order to improve the resolution of the graph displayed, the MTR fuels are removed, revealing clearly the U and UGd fuels from the PWR, BWR, LMFBR and CANDU reactors (Fig. 1b).

Spent fuel compositions at EOI were simulated, using the code ORIGEN-2, for PWR and BWR uranium fuels with different charge compositions of ^{235}U (3% - 5%) and ^{236}U (0 or 0.6%). The purpose of these simulations was to assess if the inclusion of ^{236}U in the charge composition of the fresh fuels would affect the clustering of their corresponding spent fuels in the frame of isotopic fingerprinting. The 3D plots, on the basis of the U and Pu isotope ratios, are shown in Figs. 2a & 2b for the PWR and BWR cases given in Table 2 respectively. The inclusion of ^{236}U does not affect the clustering.

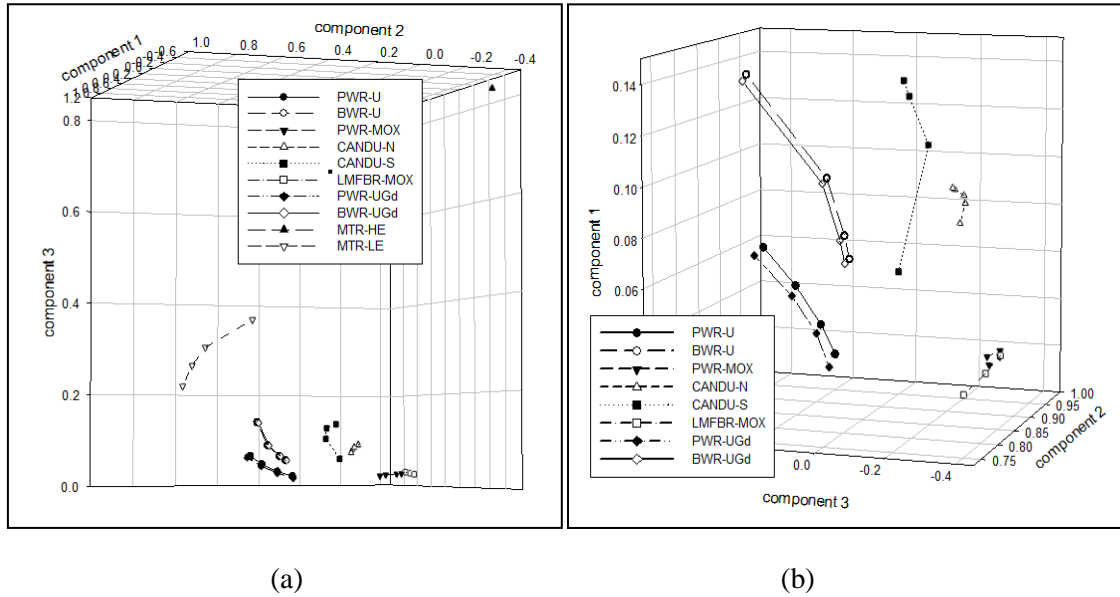


FIG. 1. (a) The ten simulated spent fuels clustered on the basis of their U and Pu isotopic composition; (b) enhanced resolution of (a) with the MTR reactor cases removed.

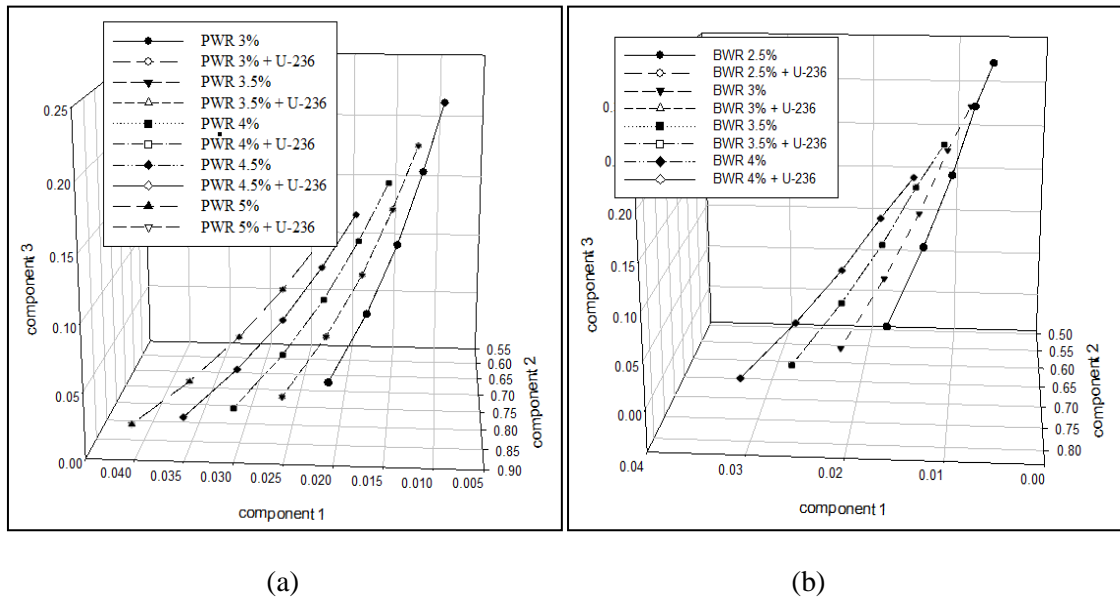


FIG. 2. Spent fuel PWR (a) and BWR (b) cases with and without ^{236}U at charge.

Sensitivity analysis has been carried out on the spent fuels from the SFCOMPO data bank given in Table 1, on the basis of their U and Pu isotopic compositions. The analysis has been carried out in the cases of PWR and BWR reactor/fuel combinations given in Table 1, differentiating well: (1) spent fuels from different reactor types (PWR and BWR), (2) spent fuels of different ^{235}U enrichments from the same reactor; and (3) spent fuels of similar ^{235}U enrichments from different reactors. Hence, the 3D plot on the mixing of PWR and BWR spent fuels from the SFCOMPO data bank shows a good discrimination between the fuels (Fig. 3a). Similarly, the sensitivity analysis carried out on the spent fuels from the SFCOMPO data bank (Table 1), on the basis of their Pu compositions has yielded a 3D plot on a mixing of the PWR and BWR spent fuels from the SFCOMPO data bank, showing a good discrimination between the fuels (Fig. 3b). The analysis again has differentiated well: (1) spent fuels from the different reactor types (PWR and BWR), (2) spent fuels of different ^{235}U enrichments from the same reactor; and (3) spent fuels of similar ^{235}U enrichments from different reactors.

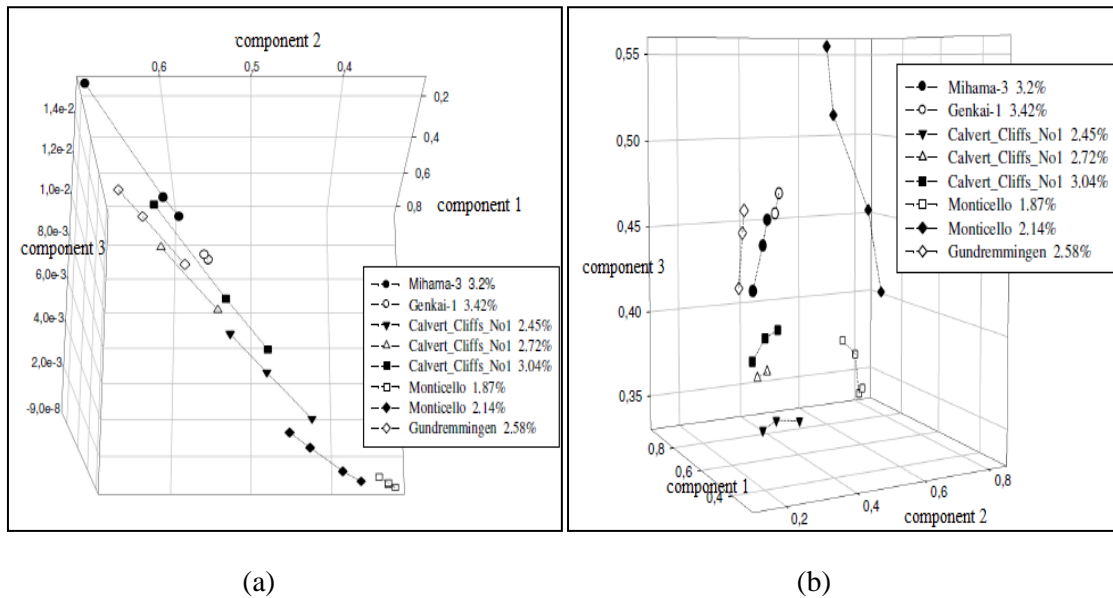


FIG. 3. Spent fuel PWR and BWR cases clustered on the basis of U and Pu (a) and Pu (b) isotopic compositions

4. Conclusions

The isotopic fingerprinting method was sensitive enough to resolve spent fuels from: different reactor types, the same reactor but with different charge composition and of the same charge composition but from different reactors. This is demonstrated for simulated isotopic compositions of conceptual fuels and also isotopic compositions from the Post-Irradiation Examination of real spent fuels. The simulation of spent fuel composition when ^{236}U is considered in fresh fuel has resulted in the conclusion that the inclusion of ^{236}U does not affect the clustering. Spent fuels have been resolved on the basis of U and Pu or only Pu isotopic composition.

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Analysis of a Uranium Ore Concentrate Sample Interdicted in Durban, South Africa (FSC 14-1-1)

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Abstract. We provide a concise summary of the analyses of a 1 kg uranium-rich sample seized in Durban, South Africa on 15 November 2013. Results are presented for compound identification, U assay, trace element abundances, Sr, Pb, U and Pu isotope compositions and model age. The sample is a fine-grained mixture of two common uranium compounds – ammonium uranyl fluoride and a hydrated uranium-ammonium oxide. The uranium isotope composition indicates the material is depleted in ²³⁵U relative to natural uranium, consistent with the initial NDA measurements performed by the Nuclear Energy Corporation of South Africa (NECSA). A comparison of the analytical results for this sample with data in the NNSA Uranium Sourcing Database failed to find a match, indicating the sample was not produced from a source or at a facility represented in the database. The presence of ²³⁶U and trace Pu point to the use of recycled (irradiated) uranium. Calculations of the performance of a graphite moderated reactor using natural uranium fuel suggest the characteristics of the Durban sample are consistent with the tails derived from fuel from a graphite moderated reactor irradiated to a burn-up of 1.6 GWD/MTU and used as the feedstock for an enrichment cascade producing uranium enriched in ²³⁵U to between 2 and 10%. The uranium isotope composition of the Durban sample is similar to that of commercial uranium-rich reagents.

1. Introduction

This report documents the analysis of a 1 kg uranium-rich sample seized by South African police in Durban, South Africa on 15 November 2013. The sample was initially analyzed by NECSA using non-destructive methods and determined to have an isotopic composition depleted in ²³⁵U with a ²³⁵U abundance of 0.32% compared to the value of 0.72% for natural uranium. In December 2013, the U.S. State Department and Department of Energy and the South African Department of International Relations and Co-operatives organized transportation of a ~10g aliquot of the sample to Lawrence Livermore National Laboratory (LLNL) on for a comprehensive nuclear forensic analysis. The results of these analyses are presented herein.

2. Analytical Methods

Shortly after the sample was received from Necsa, the entire sample was transferred to a plastic container and analyzed in the LLNL gamma-ray counting facility for 5 days. Following this analysis, ~1g was removed for analysis and split into aliquots. The analytical procedure began with XRD analyses, followed by analyses for compound identification, morphology, U concentration, trace element abundances, Sr, Pb U and Pu isotopes and age.

The phase composition was determined by X-ray diffraction (XRD). The samples were analyzed on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a LynxEye 1-dimensional linear Si strip detector; DIFFRACplus Evaluation package Release 2009 software was used for data analysis. Morphology was characterized with an FEI Inspect FE-SEM equipped with a Kevex EDS x-ray system. A visible/NIR spectrometer (Analytical Spectral Devices, Inc.) equipped with three detectors that spanned consecutive spectral regions: 350 – 1000 nm (Vis+), 1000 – 1800 nm (NIR1), and 1800 – 2500 nm (NIR2) was used for optical spectroscopy. Trace element abundances were measured with a ThermoFisher Trace 2000 and analysis were performed using the Unscrambler X ver. 10.1 (CAMO Software AS). Trace element abundances were determined using a ThermoScientific ICP-Q ICP-MS, while the U concentration was measured by Davies-Gray titration. Sr isotope compositions were measured following chemical separation by thermal ionization mass spectrometry (TIMS, ThermoScientific Triton), while Pb, U and Pu isotope composition were measured using mass spectrometry after dissolution in HNO₃/HF using high-resolution multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS, Nu Plasma). The time since the sample was last chemically reprocessed (model age) was determined using the ²³⁴U – ²³⁰Th chronometer.

3. Abundances of Radionuclides

Following the 5-day gamma-ray count, the abundances of radionuclides were determined using GAMANAL. Only the isotopes of uranium were detected and results are shown in table 1.

Table 1. Radionuclide abundances in the Durban uranium oxide.

Radionuclide	Concentration (at. %) ¹	Concentration (atoms)
⁹⁵ Zr		<1.23 x 10 ⁷
¹⁰⁶ Ru		<1.85 x 10 ⁹
¹²⁵ Sb		<3.69 x 10 ⁸
¹³⁷ Cs		<1.85 x 10 ⁹
¹⁴⁴ Ce		<3.69 x 10 ⁸
¹⁵⁵ Eu		<3.69 x 10 ⁸
²³⁴ U	(1.020 ± 0.20) x 10 ⁻³	
²³⁵ U	0.333 ± 0.001	
²³⁸ U	99.67 ± 0.20	

1. Uncertainties are 2 standard deviations

4. Phase Composition

The analytical results are shown in Table 2. The analyses demonstrate that the sample is a mixture of ammonium uranyl fluoride plus three hydrated uranium-ammonium oxide phases differing in the relative abundances of NH₃ and UO₃.

Table 2. Analytical x-ray diffraction results.

Ammonium Uranium Fluoride	(NH ₄) ₂ UF ₆
Uranium Oxide Ammonia Hydrate	2UO ₃ ·NH ₃ ·3H ₂ O
Ammonium Uranium Oxide Hydrate	UO ₃ ·NH ₃ ·H ₂ O
Ammonia Uranium Oxide Hydrate	UO ₃ ·zNH ₃ ·xH ₂ O

5. Optical Spectroscopy

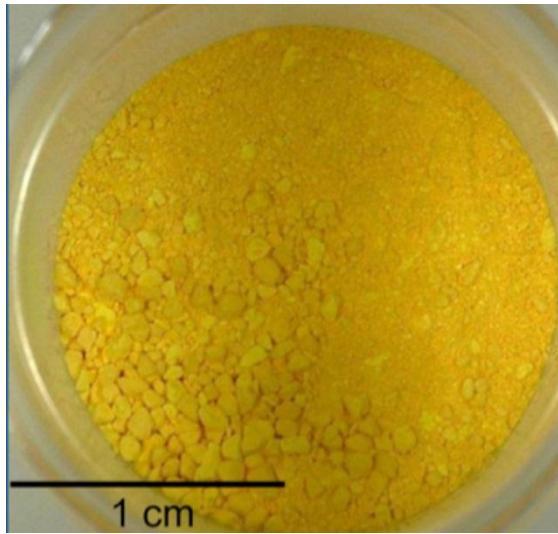


Figure 1. White light photograph of FSC 14-1-1.

The sample is a fine-grained powder as shown in the white light photo in Figure 1. Vis/NIR reflectance spectroscopy provided a rapid non-destructive evaluation of the phases present in the Durban sample. The inhomogeneity inferred from the visual appearance was confirmed with the spectral measurements. The sample appears to have been produced by the NH₃ process with a relative low drying temperature of between 85° and 150° C. Some lighter colored particles may have experienced a different temperature and/or may have come from a different location in the furnace or from a different batch but appear to have been produced by same process. Based on a comparison of the spectra for the Durban sample to other samples in the Uranium Sourcing Database, the material is primarily ammonium uranate with one of the following the general formulae: (NH₄)₂U₂O₇, UO₃·xH₂O·yNH₃, or UO₂(OH)₂·xH₂O·yNH₃ (Klunder et al., 2013).

6. Morphology

SEM/EDS reveals the sample is a fine-grained aggregate of tabular to anhedral grains ranging in size from <0.2 to $1 \mu\text{m}$; thin platelets are particularly abundant. No correlation between chemical composition and morphology was observed. A number of small aggregates $5\text{--}10 \mu\text{m}$ in size, composed of multiple fine grains are present (Figs. 2, 3).

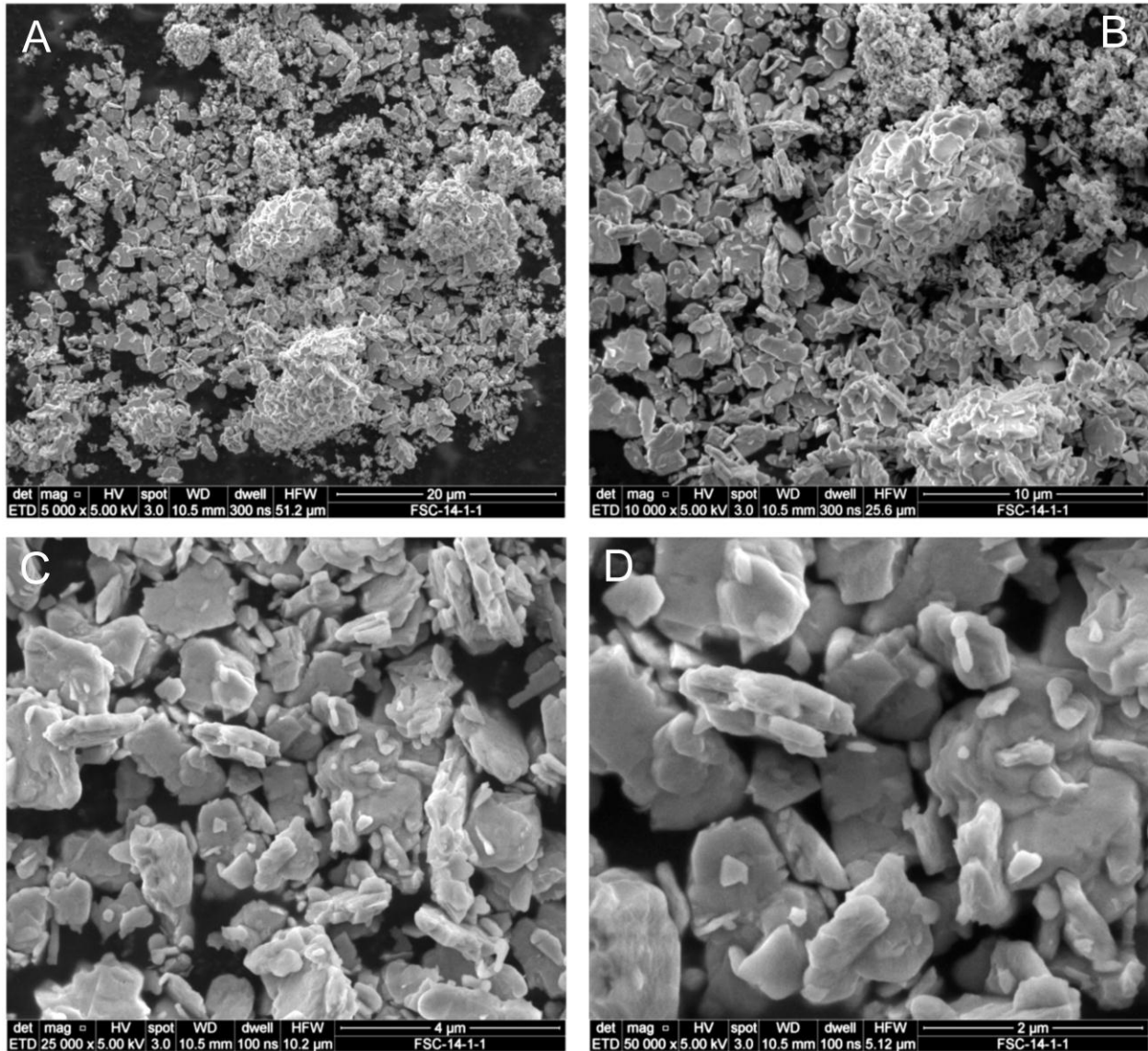


Fig. 2. SEM secondary electron photomicrographs showing characteristic morphologies of FSC 14-1-1. (A) Dispersed particles; scale bar is $20 \mu\text{m}$. (B) Close up of aggregate composed of dispersed individual grains and clumps of grains; scale bar is $10 \mu\text{m}$. (C, D); Close-up views of individual grains showing varied morphologies; scale bars are 4 and $2 \mu\text{m}$, respectively.

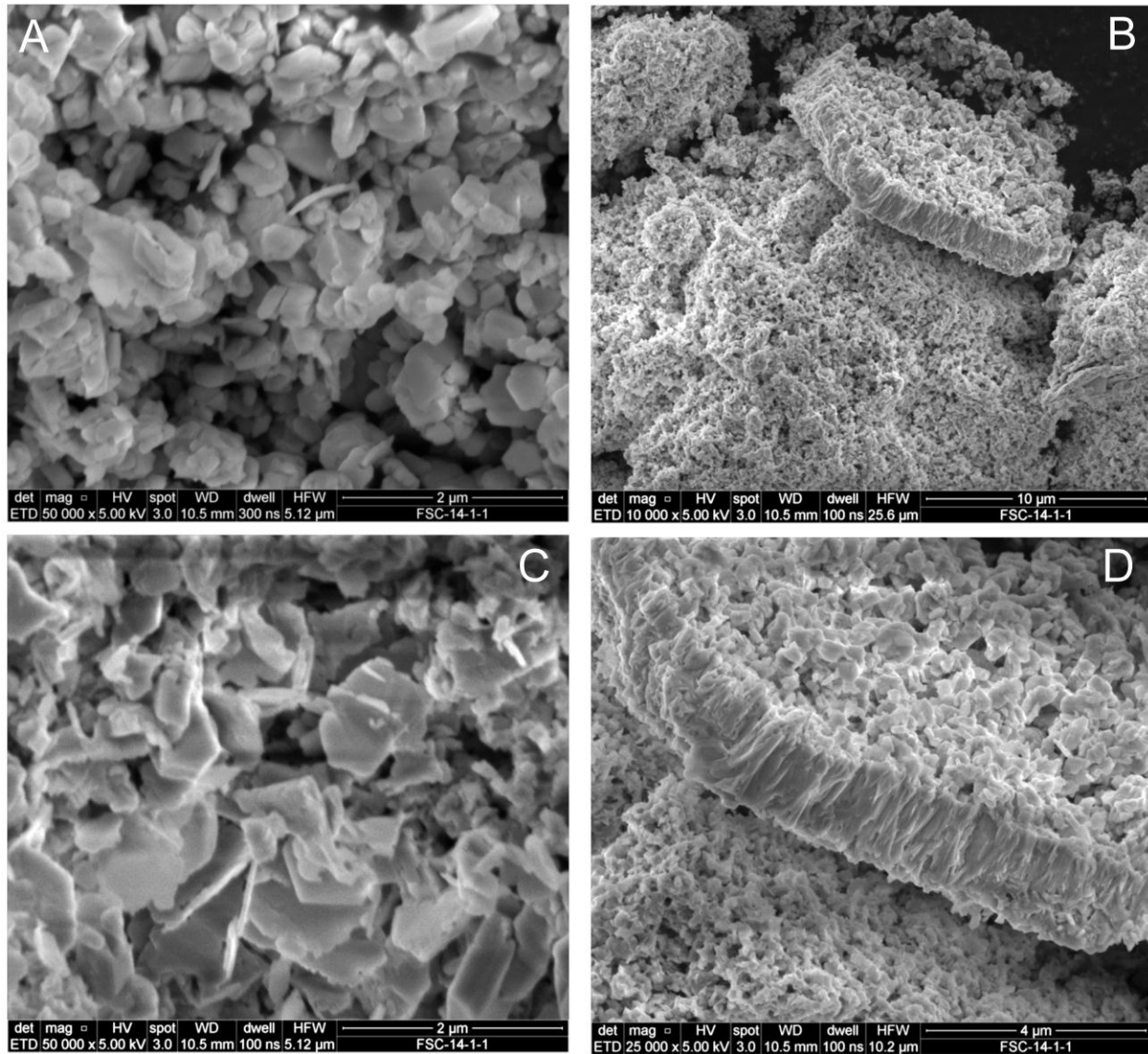


Fig. 3. SEM secondary electron photomicrographs showing characteristic morphologies of the Durban sample. (A) Dispersed particles; scale bar is 2 μm . (B, D) Views of platelets composed of particle aggregates; scale bars are 10 and 4 μm , respectively; (C) Close-up views of top surface of platelet shown in (B). Individual grains exhibiting varied morphologies are apparent; scale bar is 2 μm .

7. Trace Element Abundances and U Assay

Trace elements abundances and U content were determined on separate aliquots of the dissolved sample; results are summarized in table 3. The trace element abundances are unremarkable other than the unusually high abundance of Cs (156 $\mu\text{g/g}$). The total impurity content of $\sim 400 \mu\text{g/g}$ is low and more characteristic of a laboratory chemical rather than an industrial product (unless directly converted from UF_6).

Table 3. Trace elements abundances and U content.

Element	Technique	unit	Avg. (n=3)	uncertainty	L_c^{1,2}
Be	ICP-MS	μg/g	0.008	0.004	0.0025
B	ICP-MS	μg/g	3	8	0.42
Na	ICP-MS	μg/g	34.4	1.8	9
Mg	ICP-MS	μg/g	1.3	1.3	0.6
Al	ICP-MS	μg/g	8	2	1.2
Si	XRF	μg/g	<270		267
P	XRF	μg/g	<200		200
S	XRF	μg/g	<175		172
Cl	XRF	μg/g	<125		123
K	ICP-MS	μg/g	90	30	14
Ca	ICP-MS	μg/g	38	14	30
Sc	ICP-MS	μg/g	0.28	0.16	0.026
Ti	ICP-MS	μg/g	0.9	0.2	0.21
V	ICP-MS	μg/g	0.23	0.03	0.0022
Cr	ICP-MS	μg/g	8	3	0.2
Mn	ICP-MS	μg/g	0.8	0.2	0.019
Fe	ICP-MS	μg/g	100	30	3.3
Co	ICP-MS	μg/g	0.36	0.04	0.002
Ni	ICP-MS	μg/g	3	2	0.1
Cu	ICP-MS	μg/g	0.78	0.16	0.05
Zn	ICP-MS	μg/g	2.8	1.8	0.7
Ga	ICP-MS	μg/g	0.009	0.002	0.00061
Ge	ICP-MS	μg/g	0.023	0.02	0.005
As	ICP-MS	μg/g	0.55	0.04	0.0016
Se	ICP-MS	μg/g	12	0.5	0.4
Br	XRF	μg/g	<80		80
Rb	ICP-MS	μg/g	0.088	0.005	0.014
Sr	ICP-MS	μg/g	0.27	0.05	0.04
Y	ICP-MS	μg/g	0.0026	0.0005	0.00022
Zr	ICP-MS	μg/g	0.11	0.06	0.008
Nb	ICP-MS	μg/g	0.113	0.009	0.00029
Mo	ICP-MS	μg/g	18.8	0.9	0.01
Ru	ICP-MS	μg/g	0.0007	0.0009	0.00022
Rh	ICP-MS	μg/g	0.00028	0.00015	0.00011
Pd	ICP-MS	μg/g	0.0011	0.001	0.0003
Ag	ICP-MS	μg/g	0.23	0.03	0.006
Cd	ICP-MS	μg/g	3.08	0.19	0.0019
Sn	ICP-MS	μg/g	0.49	0.04	0.033
Sb	ICP-MS	μg/g	2.12	0.14	0.003
Te	ICP-MS	μg/g	0.86	0.13	0.006
Cs	ICP-MS	μg/g	156	12	0.0041
Ba	ICP-MS	μg/g	3	0.2	0.04
La	ICP-MS	μg/g	8.9	0.5	0.0028

Ce	ICP-MS	µg/g	0.061	0.003	0.0004
Pr	ICP-MS	µg/g	0.0017	0.0006	0.00009
Nd	ICP-MS	µg/g	0.005	0.002	0.00023
Sm	ICP-MS	µg/g	0.0012	0.0007	0.00038
Eu	ICP-MS	µg/g	0.0005	0.00016	0.00008
Gd	ICP-MS	µg/g	0.0021	0.0006	0.00033
Tb	ICP-MS	µg/g	0.00006	0.00018	0.000034
Dy	ICP-MS	µg/g	0.0005	0.0007	0.0001
Ho	ICP-MS	µg/g	0.00014	0.00008	0.000038
Er	ICP-MS	µg/g	0.0005	0.0005	0.00016
Tm	ICP-MS	µg/g	0.00011	0.00006	0.000019
Yb	ICP-MS	µg/g	0.0005	0.0003	0.00013
Lu	ICP-MS	µg/g	0.00012	0.00006	0.000025
Hf	ICP-MS	µg/g	0.0017	0.0013	0.00054
Ta	ICP-MS	µg/g	0.0009	0.0005	0.00007
W	ICP-MS	µg/g	0.22	0.02	0.0015
Re	ICP-MS	µg/g	0.0005	0.0002	0.000208
Ir	ICP-MS	µg/g	0.0003	0.0005	0.0003
Pt	ICP-MS	µg/g	0.0004	0.0007	0.0003
Tl	ICP-MS	µg/g	0.298	0.015	0.00021
Pb	ICP-MS	µg/g	7.6	0.5	0.007
Bi	ICP-MS	µg/g	0.12	0.02	0.03
Th	MC-ICP-MS	µg/g	0.170	0.018	0.0006
U	D-G	g/g (%)	74.9	0.5	

¹Limit of detection

²The units of the L_c values correspond to column 2.

8. Sr, Pb, U and Pu Isotope compositions and Age

The Sr, Pb and U isotope compositions were determined by MC-ICP-MS on chemically purified aliquots of the sample. The data are shown in tables 3-6 and Fig. 4. The uranium isotope composition indicates the Durban material is depleted in ²³⁵U compared to natural uranium, while the elevated ²³⁶U content indicates the parent material was irradiated in a nuclear reactor. The U-isotope composition of the Durban material was compared to soil samples from LLNL Site 300, where the U.S. conducts high explosive tests of materials containing depleted uranium. The U-isotope composition of Site 300 soils reflects mixing between U.S. depleted uranium from the tests and natural uranium from soil (Esser et al., 2002); no match was found. The Sr and Pb isotope compositions of the Durban sample and a variety of UOC samples are depicted in an isotope correlation diagram (Fig. 4). The data confirm the absence of a match between the Durban sample and any of the UOC samples in the U-Sourcing Database. The time since the sample was last chemically processed (model age) was determined using the ²³⁴U – ²³⁰Th chronometer; the model age is 30.9 ± 0.4 years, corresponding to a production date of 30 April 1982 with an uncertainty of 130 days. The model age assumes complete separation of Th and U during chemical processing and represents an upper limit to the actual time of production.

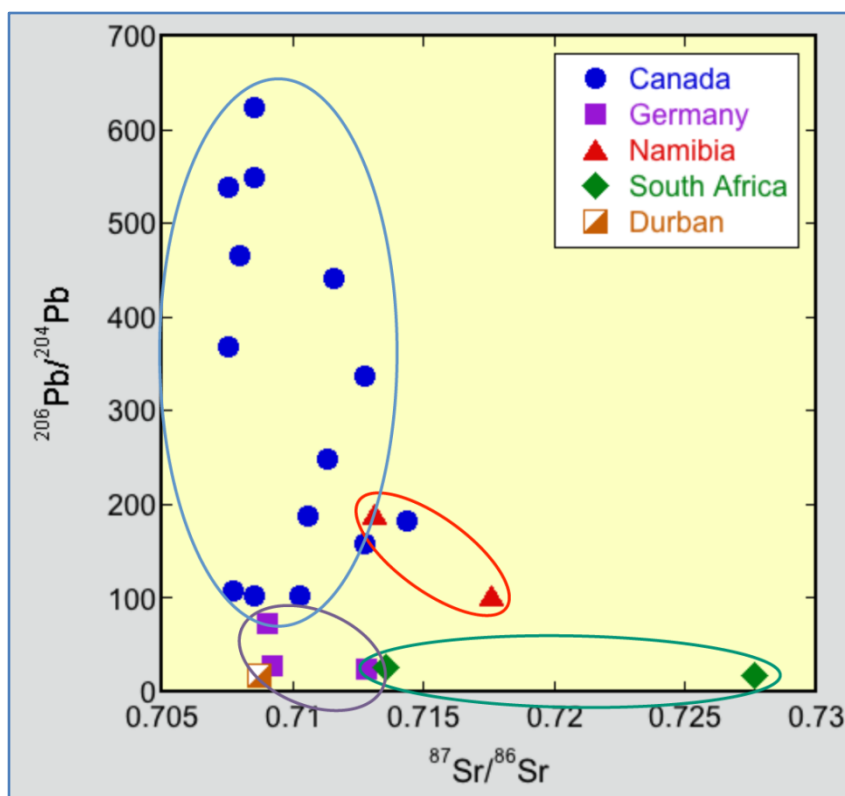


Fig. 4. Isotope correlation diagram showing Sr and Pb isotope compositions of the Durban sample compared to UOC from Germany, Namibia, South Africa and Canada; data for the UOC samples are taken from the Uranium Sourcing Database (Robel et al., 2011). The lack of a match for the Durban sample with UOC from the database is apparent.

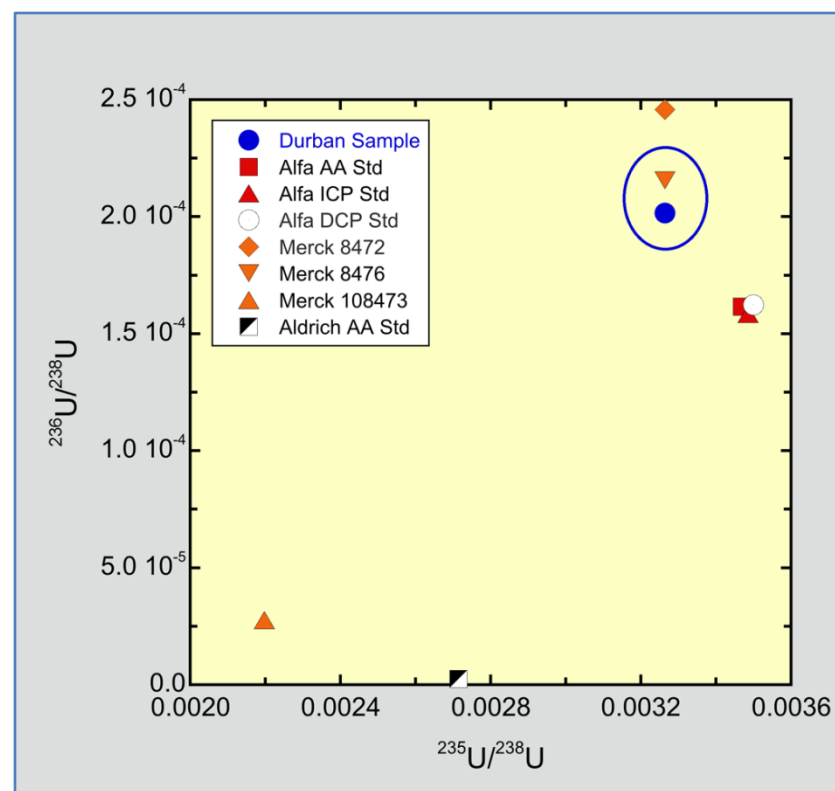


Fig. 5. Uranium 3-isotope plot showing $^{236}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios for the Durban sample compared to values of several commercial uranium reagents; data from Richter et al. (1999). The composition of the Durban sample is similar to that of Merck 8476, a uranyl nitrate solution. The common depletion in ^{235}U compared to natural uranium, suggests all of the samples are a by-product of enriched uranium produced for the nuclear power industry.

Table 4. Sr Isotope Composition

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	2σ	k	$^{84}\text{Sr}/^{88}\text{Sr}$	2σ	k
FSC-14-1-1-B	0.708699	0.000040	2	0.056536	0.000026	2

Table 5. Pb Isotope Composition

Sample	Pb (ng/g)	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ	k	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	k	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	k
1-B	552	37.849	0.023	2	15.6088	0.0076	2	18.0630	0.0086	2
1-B ¹	676	37.848	0.022	2	15.6090	0.0076	2	18.0633	0.0086	2

¹Duplicate analysis.**Table 6. U Isotope Composition**

Isotope	Abundance (atom %)	Uncertainty
^{234}U	0.0021107	0.0000072
^{235}U	0.31963	0.00024
^{236}U	0.018592	0.000070
^{238}U	99.6597	0.0020

Table 7. Pu Abundance and Isotope Composition

Sample	Pu (pg/g)	2σ	k	$^{240}\text{Pu}/^{239}\text{Pu}$	2σ	k
1-B	9.69	0.67	2	0.0719	0.0037	2

9. Reactor Models

To explore potential sources of the Durban sample, we modeled the performance of a graphite moderated, natural uranium (NU) fueled reactor using the MAGNOX reactor model included in the Origen-ARP component of SCALE 6.1 (Bowman and Cook, 2000). NU fuel irradiated for ~100 days to a burnup of 1.6 GWD/MTU would have a ^{240}Pu content of ~14% at discharge. Assuming this fuel was then used as feedstock for an enrichment cascade producing ^{235}U enriched to 2%, we used the ORNL MSTAR program to calculate the U isotopic composition of tails from the cascade. The calculated values, $^{234}\text{U}/^{235}\text{U} = 0.009$ and $^{236}\text{U}/^{235}\text{U} = 0.04$, agree reasonably well with the measured U-isotope composition of the Durban sample. Increasing the enrichment in ^{235}U in the calculation to 10% also yields a $^{236}\text{U}/^{235}\text{U}$ ratio similar to the observed value but predicts a ^{235}U abundance that is ~5% too low.

10. Summary

A U-rich sample interdicted in Durban, South Africa is a fine-grained mixture of two common uranium compounds – ammonium uranyl fluoride and a hydrated uranium-ammonium oxide. The presence of ^{236}U and trace Pu point to the use of recycled (irradiated) uranium and the low trace element abundances and depletion in ^{235}U relative to natural uranium suggest the material originated as a by-product of enriched uranium produced for the nuclear power industry. A comparison of the properties of the Durban sample with samples contained in the Uranium Sourcing Database using principal components analysis, partial least squares discriminant analysis and the *iDAVE* search engine failed to produce a match, suggesting the material was produced from a source and at a facility not represented in the database. Natural uranium fuel irradiated in a graphite moderated reactor for ~100 days and then used as feed for an enrichment cascade to produce low enriched uranium would generate tails having ^{234}U and ^{236}U contents in reasonable agreement with values measured in the Durban sample. Legitimate commerce in depleted uranium is worldwide and depleted UF_6 can be converted to any uranium compound, depending on the end use, making it difficult to identify the source of the Durban sample.

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Informativeness of Microparticle Analysis for Nuclear Forensics

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Abstract. Different nuclear security events, investigation of which can require microparticle analysis, are considered. Capabilities of analytical techniques are reviewed. There is demonstrated that analysis of microparticles with sizes down to 0.5 μm provides investigation with information about nuclear materials detained out of regulatory control, route of this material transfer, people, which were involved to illicit trafficking.

1. Introduction

Investigation of microparticles can be useful for nuclear forensics goals in several cases. First of all these are the cases, when some unknown material is out of regulatory control, but it is not seized. Nevertheless trace amounts of this material can be found on the surfaces of different objects, which contacted with material, and these trace amounts may be the only source of information about material. Such objects can be empty container, wrapping material, worktop, special instruments, etc. In such cases completeness and accuracy of information about material depends on the number and sizes of microparticles had been detected as well as on the involved analytical capabilities. But in any case any information is better than nothing.

If material is seized, but the route of material transfer and involved persons are not established, analysis of environmental samples from suspicious areas, analysis of clothing and other belongings of suspicious people can clarify both: areas, on which some operations with material were processed, and people, who were involved.

The objectives of this paper are indication of such kinds of incidents and demonstration of the possibilities of corresponding analytical methods.

2. Nuclear forensics tasks, which need microparticles analysis

Analysis of individual microparticles can provide the prosecution with following useful information concerning the investigation of incident:

- Determination of characteristics of nuclear or other radioactive material out of regulatory control, when material is not seized, but some trace amounts of material are found anywhere, including crime scene. Such determination is relevant during investigation of incidents with deliberate or accidental dispersion of such unknown material as well as incidents with disappearance of material;
- Determination of the transfer route of material, which is found out of regulatory control, as well as possible sites of processing, people and items, which could be involved in illicit trafficking and hidden activity;

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- Indicating real manufacturer of the seized material, if the same materials could be produced by different manufacturers. Trace amounts of other materials inherent to real manufacturer can indicate it in such cases;
- Determination of characteristics of nuclear and other radioactive materials found out of regulatory control in the form of mixture of powders of different materials.

Despite of some diversity of these tasks from the prosecution point of view, all of them are decided on the base of determining of not so many characteristics of particles. Morphological characteristics: shapes, sizes and surface structures, elemental composition (including impurities), isotopic composition of uranium and plutonium in particles and content of specific isotopes (for example, isotopes-chronographs) – these are the characteristics, which can be determined in the result of particle analysis. But determination of these characteristics allows to characterize materials with some accuracy.

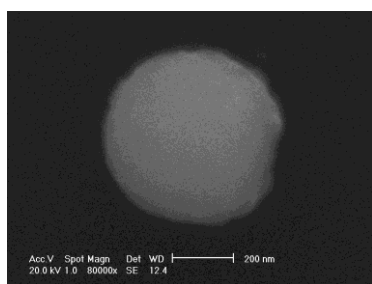
3. Determination of the material characteristics

The results of microparticles analyses allow to determine the composition of materials as well as to decide some tasks, which are connected with determination of the age of materials.

3.1. Determination of isotopic compositions of uranium and plutonium

Isotopic compositions of uranium and plutonium determine designation and, in some cases, manufacturer of nuclear material. Thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry, using large geometry mass spectrometer Cameca IMS-1280 (LG-SIMS), provide most accurate isotopic analysis of uranium and plutonium in particles. Accuracy of measurements by means of these two methods is approximately the same [1]. Of course it depends on the amount of uranium and/or plutonium in particle that is on the size of particle and on real density of uranium and/or plutonium in particle.

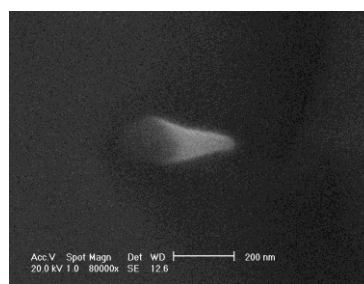
Most reliable results of TIMS analyses are provided by AFTAC laboratory [2]. LG-SIMS analyses are provided by several laboratories – members of IAEA network of analytical laboratories [3]. On the fig. 1 image of spherical UO_2 particle before LG-SIMS analysis and image of the residue of that particle after analysis are shown.



Reference values:

$$n(^{235}\text{U})/n(^{238}\text{U}) = 0,007\,043\,9 \\ \pm 0,000\,003\,5$$

$$n(^{234}\text{U})/n(^{238}\text{U}) = 0,000\,049\,817 \\ \pm 0,000\,000\,048$$



Measurements results:

$$n(^{235}\text{U})/n(^{238}\text{U}) = 0,007\,04 \\ \pm 0,000\,05$$

$$n(^{234}\text{U})/n(^{238}\text{U}) = 0,000\,053\,0 \\ \pm 0,000\,004\,2$$

FIG. 1. Uranium particle before (left) and residue of particle after (right) LG-SIMS analysis. Reference and measured values of isotope ratios are presented under pictures.

Diameter of initial particle is about 0.6 μm . Reference and measured isotope ratios presented on this figure also, they characterize the accuracy of measurement. Comparison of reference and measured values of uranium isotopes ratios allows to conclude, that approximately 7 fg of uranium-235 in that particle was measured with relative error less than 1%, and approximately 0.05 fg of uranium-234 – with relative error less than 10%. Analyses of other similar particles confirmed that relative errors less than 1% for uranium-235 and less than 10% for uranium-234 are typical for particles with diameters down to 0.5 μm .

Approximately the same results are obtained for analysis of plutonium particles. Unlike the almost regular spherical uranium particle, which is shown on the fig. 1, investigated plutonium particles had not so regular shape. Therefore the sputtered amounts of plutonium in particles are estimated more roughly, than in uranium particle on fig. 1. But several plutonium particles were analyzed, and the trend has been determined. The dependence of uncertainties of measured content of plutonium isotopes on the value of the content is illustrated on fig. 2.

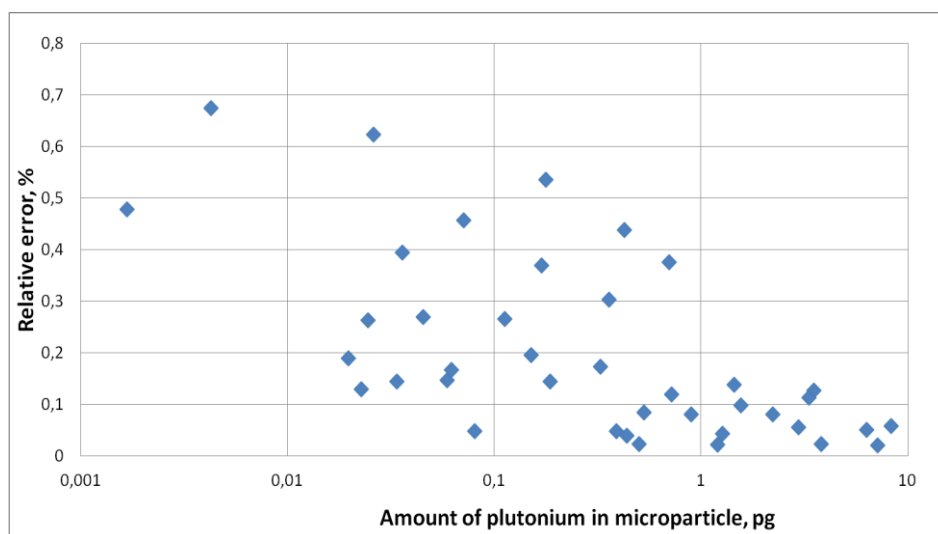


FIG. 2. Uncertainties of the results of measurement of the amount of plutonium in microparticles.

Deviations of relative errors for the same indicated amounts of plutonium in particles can be explained by complex shape, by different and not dense inner structure and accordingly by difficulty of estimation of sputtered amount of plutonium. Nevertheless the results for uranium and for plutonium particles are consistent with each other.

3.2. Determination of elemental composition of materials

Elemental composition (including impurities) of nuclear and other radioactive materials can carry information about its designation. Some impurities can also disclose information about raw materials and processing technologies. If the particles are the fragments of some material, elemental composition of particles and material are the same. In this case elemental composition of particles provides useful information for prosecution.

Elemental composition of the particles can be determined by using energy dispersive or wavelength dispersive X-rays detectors practically together with morphology investigation by means of scanning electron microscope. Detection limits of weight concentration are (0.2 ... 0.5)% for different chemical elements and for measurements by using more productive energy dispersive detectors [4]. Using wavelength dispersive X-rays detectors can decrease detection limits approximately on the order of magnitude [5].

Accuracy of measurements of elemental concentrations depends first of all on concentration value for particles with sizes more than (2 ... 3) μm . If the analyzed particle is smaller than volume of X-ray excitation, accuracy depends also on the size and density of particle. As a rule the measuring by using energy dispersive detectors provide relative errors of element concentrations in particles with irregular surface about 100% if concentration is smaller than 1%, and up to 10% for concentrations about 50%.

But last time the using of modern electron microscopes, equipped by productive EDX detector and inbuilt ion beam, allow to use more effective low energy electron beams and preparation of the particle surface for more accurate X-ray analysis. Cutting of some part of particle and smoothing of the analyzed surface in combination with using of low energy electron beam decrease the relative errors of measurement several times. Illustration of this fact can be found in papers [6, 7]. Fig. 3 shows UO_2 typical particle with rough surface (left) and similar UO_2 particle after preparation of the surface for more accurate analysis (right).

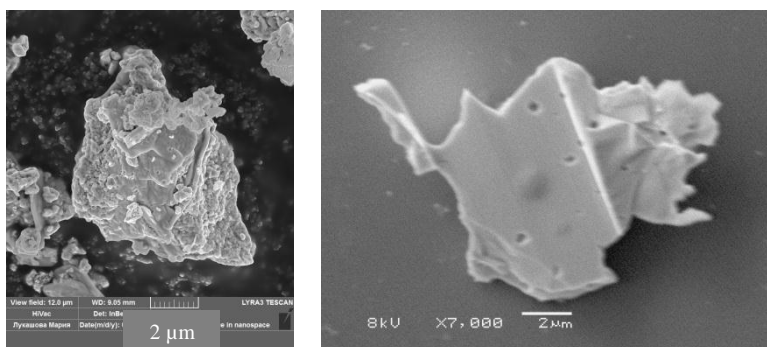


FIG. 3. Particle without influence of ion beam (left) and particle with truncated top (right).

Four successive measurements of concentration of uranium were implemented for each particle. These four analyses of each particle differed by the orientation of particle relative EDX detector – after each measurement the planchet with particle was rotated onto 90° . X-rays were collected from the same part of surface for each particle. Relative deviation of measured concentration for left particle was about 6%, for right particle with prepared surface – 3 times smaller.

3.3. Deciding of some tasks for age determination

It is known, that the age of uranium materials can be determined undoubtedly by using ICP MS techniques [8]. But such determination will be correct only if one nuclear or one other radioactive material is presented in analyzed sample and no isotope-chronograph presents in background particles of sample in significant quantities.

For particle analysis, which can be implemented by using SIMS, these restrictions are not valid. Practically the particle always characterizes only one material and does not contain background isotopes-chronographs. But determination of the age based on the result of measuring of the ratio of the contents of thorium-230 and uranium-234 – isotopes of different chemical elements. Difference of coefficients of ionization of uranium and thorium and dependence of these coefficients on composition of particle does not allow to use this method directly for determination of the age.

Nevertheless SIMS is very useful for dating of uranium materials, especially if the sample can contain small amounts of materials. In this case analysis of different fragments of materials by SIMS (particles) can confirm or not confirm the result, had been obtained by ICP MS. SIMS possibilities for the solution of the age task can be estimated with help of the fig. 4, which shows the particle of uranyl-nitrate before analysis and residue of this particle after sputtering.

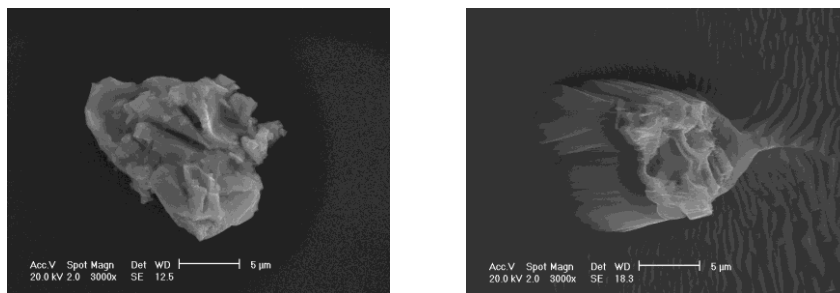


FIG. 4. Uranium particle before (left) and residue of particle after (right) LG-SIMS analysis. Ages, measured by ICP MS and LG-SIMS are presented under pictures.

The ratio of ion currents of thorium-230 and uranium-234, measured in the result of analysis is $(1.72 \pm 0.37) \times 10^{-5}$. The particle contained approximately 300 pg of uranium before sputtering. Age of material during analysis was (1.66 ± 0.05) years, uranium was enriched up to 4% on uranium-235. It means that if the age of uranium, which is enriched up to 4% on uranium-235, is approximately one and half years, analysis of uranium particle with effective diameter about 8 μm can provide uncertainty of measurements about 20%.

If all detected and analyzed particles will have the same ratio of ion currents of isotopes of thorium-230 and uranium-234 within the errors, the result of ICP MS is correct. Moreover, SIMS analysis of some relatively large particles can provide smaller uncertainties than uncertainty had been provided by ICP MS. In this case SIMS will improve the ICP MS result.

If particles will be characterized by different ratios of ion currents, the ages of materials of these particles are different also and the result of ICP MS can not be related to any of presented materials. But in this case the ages of different materials can be still estimated if the different particles have the same elemental composition. The “age”, which had been determined by ICP MS, can be correlated with the average ratio of ion currents of thorium-230 and uranium-234, which had been determined by SIMS for all analyzed particles. This correlation determines the ratio of coefficients of ionization of uranium and thorium, which should be the same for all particles with same elemental composition. Of course additional investigation of particles should be implemented in this case for confirmation of sameness of elemental composition of particles. Such investigation for example can be implemented by SEM-EPMA.

If different particles are characterized by different ages and different elemental compositions, ICP MS result is senseless. In spite of this fact some age estimations can be implemented for different particles in this case also. But information about the ratios of ionization coefficients for thorium and uranium should be provided from anywhere. It can be provided by the previous investigations as well as by the results of special measurements, which can be organized especially for the purpose of concrete crime investigation. Particles with elemental compositions identical to elemental compositions of particles in sample, which have to be investigated, should be manufactured from the material with known age. Results of the analysis of these particles allow to calculate the ionization coefficient ratios, like it was done in the work [9].

4. Determination of morphology characteristics

Morphological characteristics of nuclear materials particles are intensively investigating from 1990th seeing IAEA Safeguards goals. Corresponding tasks practically look like forensics tasks but without a court of law. Main purpose of the development of morphology investigation was determination of correspondence between the kind of operations with nuclear materials and sizes, shapes and surface structure of industrial dust particles, and accordingly determination of industrial dust features, which could facilitate identifying of the kind of nuclear activity. Industrial dusts of different enterprises were investigated, and particles with specific morphology characteristics were determined for each kind of enterprise.

Scanning electron microscopy is used for morphology analysis. The determination of morphology details with sizes down to 0.1 μm on the surface and on the perimeter of microparticles is possible. The paper [10] shows that the results of particle morphology investigation allow to distinguish industrial dust of enrichment plants, fuel fabrication facilities and reprocessing plants. Fig. 5 presents three particles; each of them is typical only for one of these enterprises.

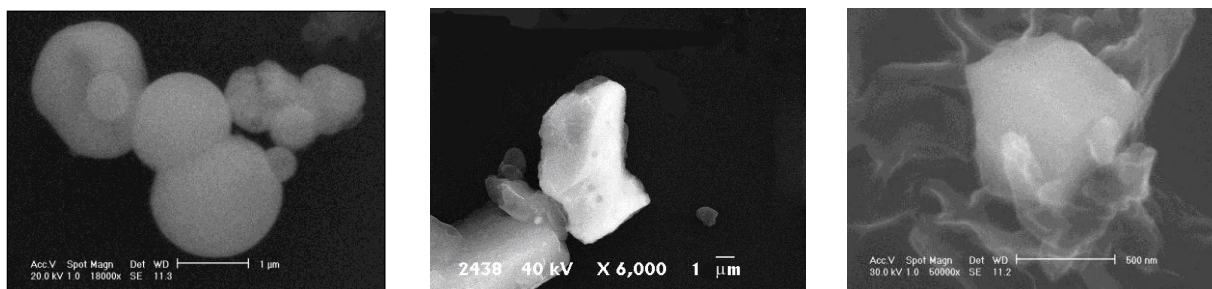


FIG. 5. Particles typical for enrichment plants (a), fuel fabrication facilities (b) and reprocessing plants (c).

Accordingly detection of any of these particles indicates the presence of industrial dust of corresponding enterprise. Signatures, which can distinguish industrial dust of different kinds of enrichment plants: centrifuge plants and diffusion plants, are considered in the paper [11]. Detection of particles with typical morphology allows to characterize the kind of facility, which can be concerned to the illicit trafficking of nuclear material, or kind of operations with stolen unknown material.

It is necessary to highlight, that differences of morphology characteristics are caused by different mechanisms of particle formation. Therefore the study of morphology characteristics of particles, detected on the site of deliberate or accidental dispersion of nuclear or other radioactive material can provide the prosecution with information about the method of dispersion and accordingly possible consequences of the incident.

5. Conclusions

- 5.1. Individual microparticles of nuclear or another radioactive materials can be only source of information about such material out of regulatory control, when material is not seized, but its trace amounts are found on the surfaces of some objects.
- 5.2. The particles of material, which is seized, but was out of regulatory control, can be source of information about the route of illicit trafficking and involved persons.
- 5.3. Analyses of particles with sizes at least down to 0.5 μm can provide the prosecution with useful information.
- 5.4. The advanced equipment and corresponding techniques are extremely important for obtaining of maximum useful information from analysis of microparticles.

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