Quantitative determination of uranium in U_3O_8 by ICP-MS for nuclear forensic investigation

Presenter: Kupi TG, PhD, Pr.Sci.Nat

Co-authors: Khumoetsile Jonas, Valid Seerane, Gabriel Monye, Ntaoleng Kunene and Samuel Odumu Ogana John

Centre for Applied Radiation Science and Technology (CARST)

North-West University

South Africa

#DiscoverNWU

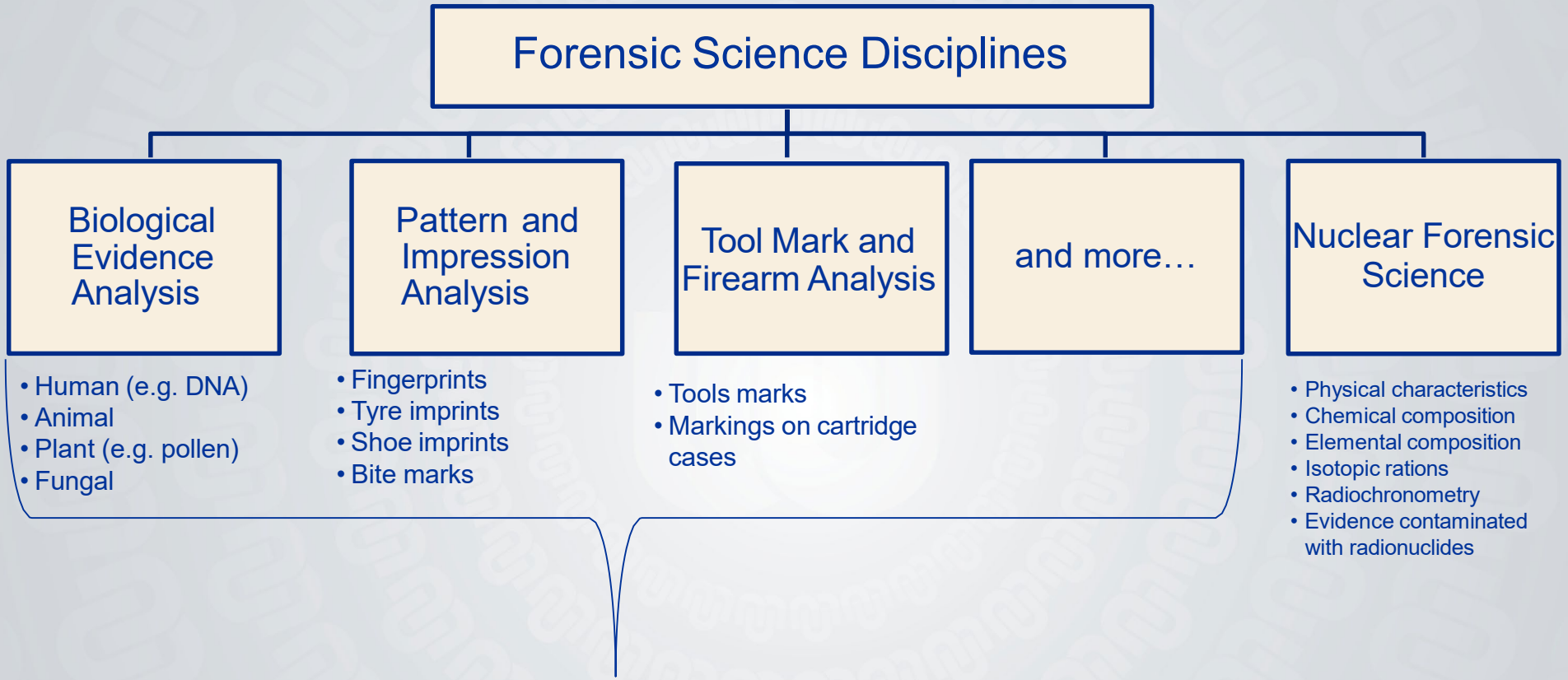
Content

What is Nuclear Forensics?

Nuclear forensic science, referred to as nuclear forensics, is a subset of forensic science.

Nuclear forensics is the **examination** of nuclear or other radioactive materials, or of **evidence contaminated** with radionuclides, in the context of legal proceedings under international or national law related to nuclear security.

What is Nuclear Forensics? *cont…*

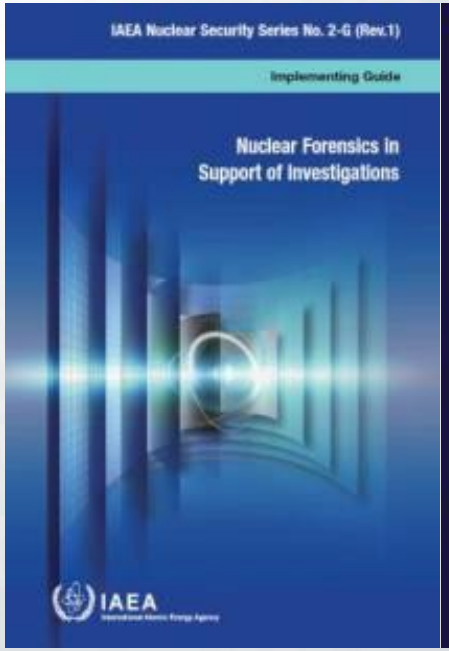


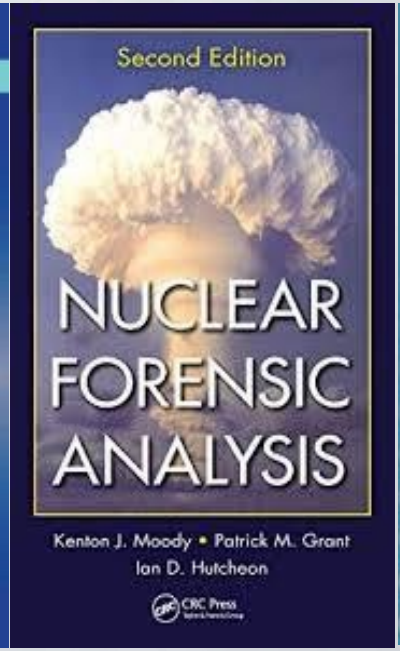
Traditional forensic science disciplines, the majority have considerable history, are scientifically established and findings are admissible in court.

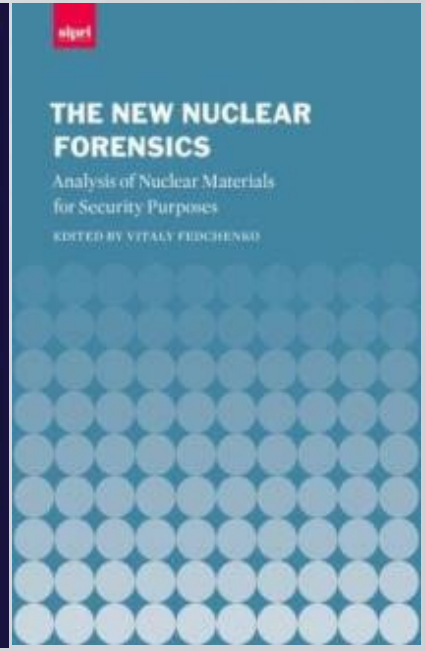
What is Nuclear Forensics? *Cont…*

Nuclear Forensics Science

- Physical characteristics
- Chemical composition
- Elemental composition
- Isotopic ratios
- Radiochronometry
- Evidence contaminated with radionuclides







Types of Nuclear Forensic Samples

Sample Type	Potential Forensic Value	Laboratory Requirements
Bulk nuclear or other radioactive material	• Inform determination of violation of possession statutes • Identify possible material origin or process history • Connect cases	• Capability and infrastructure for handling and characterising bulk amounts of nuclear or other radioactive material • Expertise in nuclear fuel cycle technology
Items contaminated with radionuclides	• Identify places where materials have been handled or processed • Link people to material	• Capability and infrastructure for handling radioactively contaminated items • Trace analysis capabilities • Ability to perform (selected) traditional forensic examinations
Environmental or geologic samples associated with nuclear or other radioactive material	Provide information on possible smuggling routes or pathways over which the nuclear or other radioactive material may have been transported	Expertise with environmental, biological etc. analysis (minerals, dust, pollens, etc.) and interpretation of geological and geochemical data

International Atomic Energy Agency, Nuclear Forensics in Support of Investigations, IAEA Nuclear Security Series No. 2-G (Rev.1) IAEA, Vienna (2015)

Two Degrees of Analysis

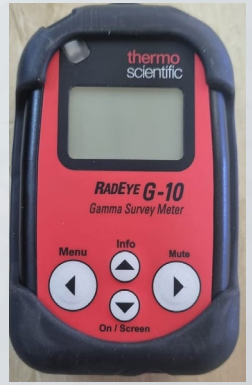
Categorization	Characterization
▪ Assessment of material by making preliminary determinations of relevant radionuclides present and the associated levels of radiation. Generally occurs at the scene of the event and confirmed at laboratory ▪ Helps to determine if statutes covering the unauthorised use or possession of radioactive material have been broken	▪ Determination of the nature of the material through physical, chemical, elemental and isotopic analysis, including major, minor and trace constituents, as necessary ▪ Does not typically include analysis using traditional forensic disciplines, nor does it comprise interpretative steps

Properties of Nuclear and Other Radioactive Material

- **Physical characteristics**
  - Dimensions
  - Mass
  - Density
  - Colour
  - Particle size
  - Morphology
- **Chemical and elemental characteristics**
  - Elemental ratios
  - Chemical form
  - Trace elements
  - Main constituents
  - Anionic impurities
  - Crystal structure/Phase composition
- **Isotopic characteristics**
  - Radioisotopes
  - Stable isotopes
  - Decay products

Uranium has three naturally occurring isotopes

Isotope	%
^{234}U	0.0054
^{235}U	0.7204
^{238}U	99.2742



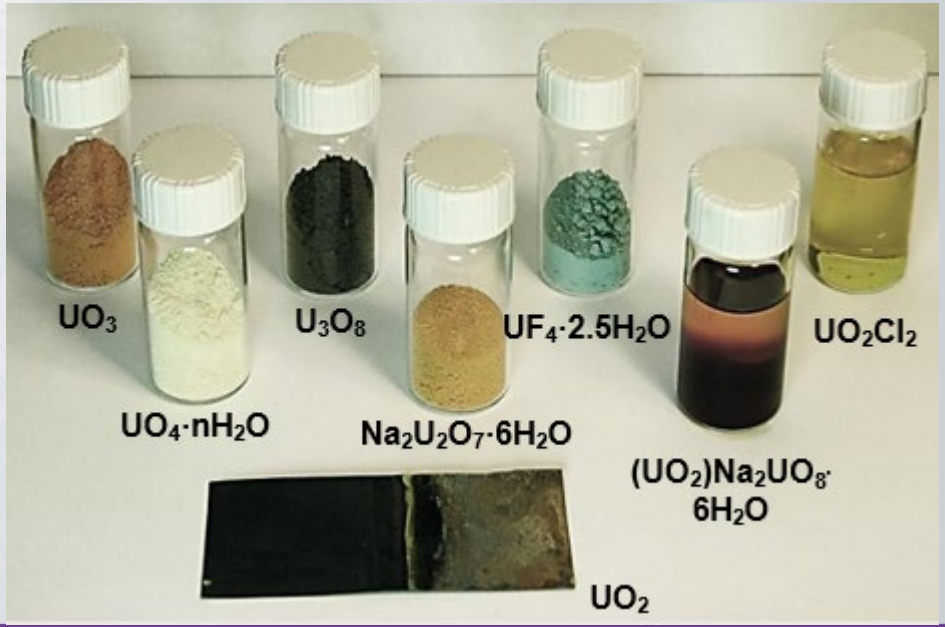
Application of Nuclear Forensics

- Utilizes physical, chemical, elemental and isotopic "**signatures**" inherent to nuclear and other radioactive material to **provide insight to its origin and history**
- Provides findings that may support court proceedings
- Can be used for strengthening **nuclear security** systems and methods

Nuclear Forensic Signatures

Nuclear forensic signatures are a characteristic, or set of characteristics, that can enable a sample to be distinguished, by exclusion or individualization

- Ideally, a signature, or set of signatures, points to a certain class of materials, processes or geolocations
- Signatures may also exclude a family of materials, processes or geolocations
- Signatures are **created** and **modified** throughout the **lifecycle** of nuclear and other radioactive materials



Nuclear Security

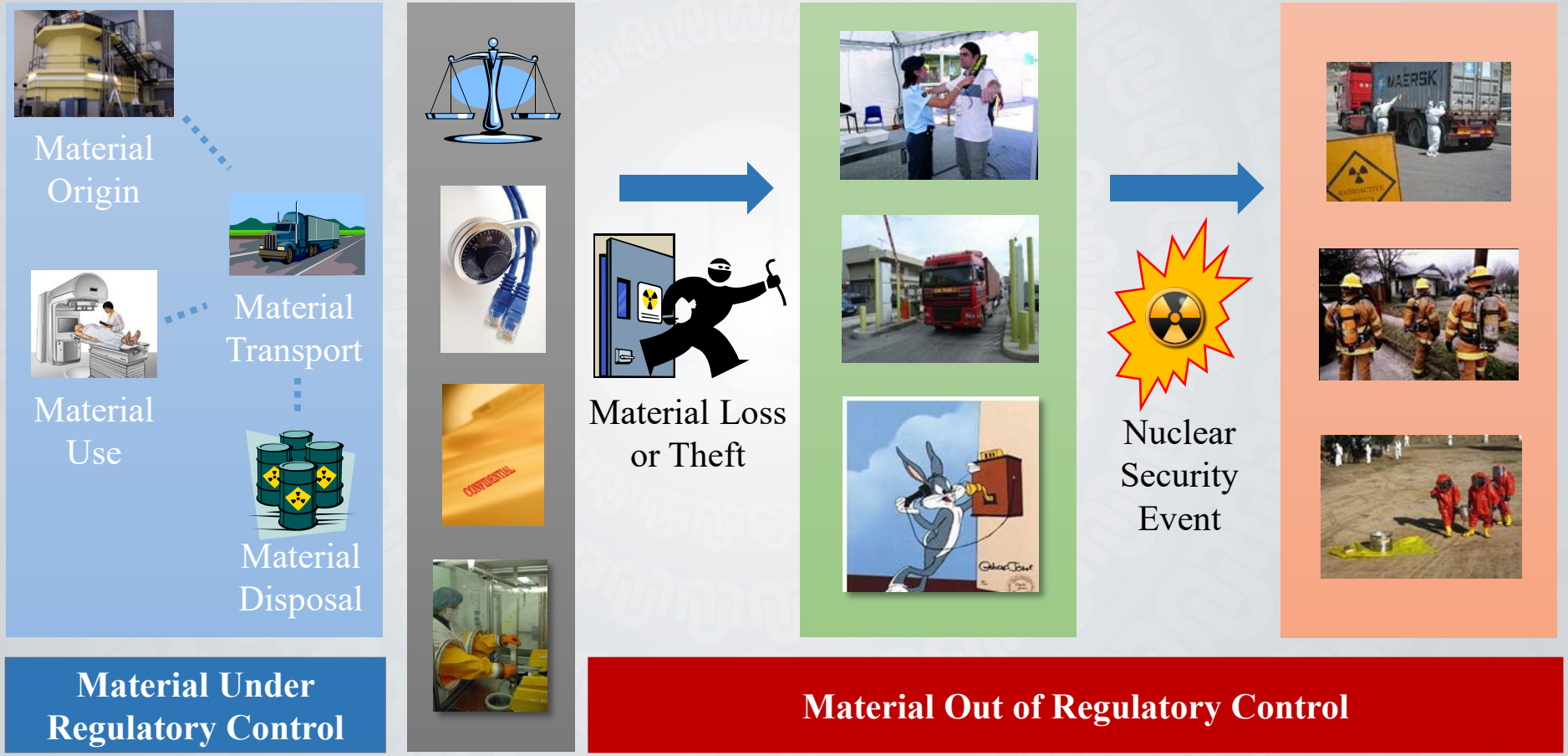
Prevention

Detection

Response

… theft, sabotage, unauthorized access, illegal transfer or other malicious acts involving nuclear material, other radioactive substances or their associated facilities.

Relationship between Prevention, Detection, and Response Measures

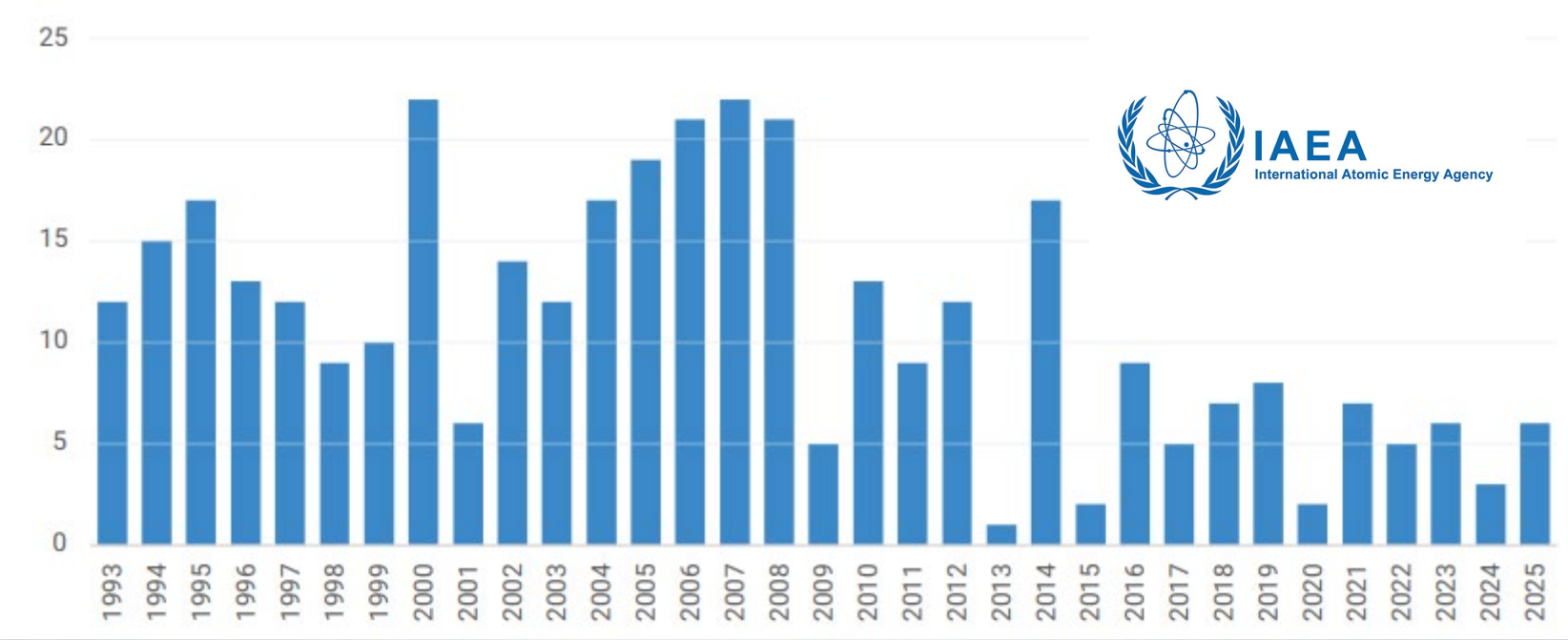


Illicit trafficking of nuclear and radioactive materials

- Illicit trafficking of nuclear and radioactive materials has been an issue of concern since the beginning of 1990s when the first case was reported to the International Atomic Energy Agency (IAEA, 2022).
- The use of nuclear or radioactive material generates some risk due to radiation being emitted even if they enter the human body at low levels (Aggarwal 2016).
- The main security concerns relating to nuclear and radioactive material use are the potential for theft and construction of radiological dispersive devices (RDDs) (Hutcheon, Kristo et al. 2013).

IAEA Incident and Trafficking Database (ITDB)

Confirmed incidents



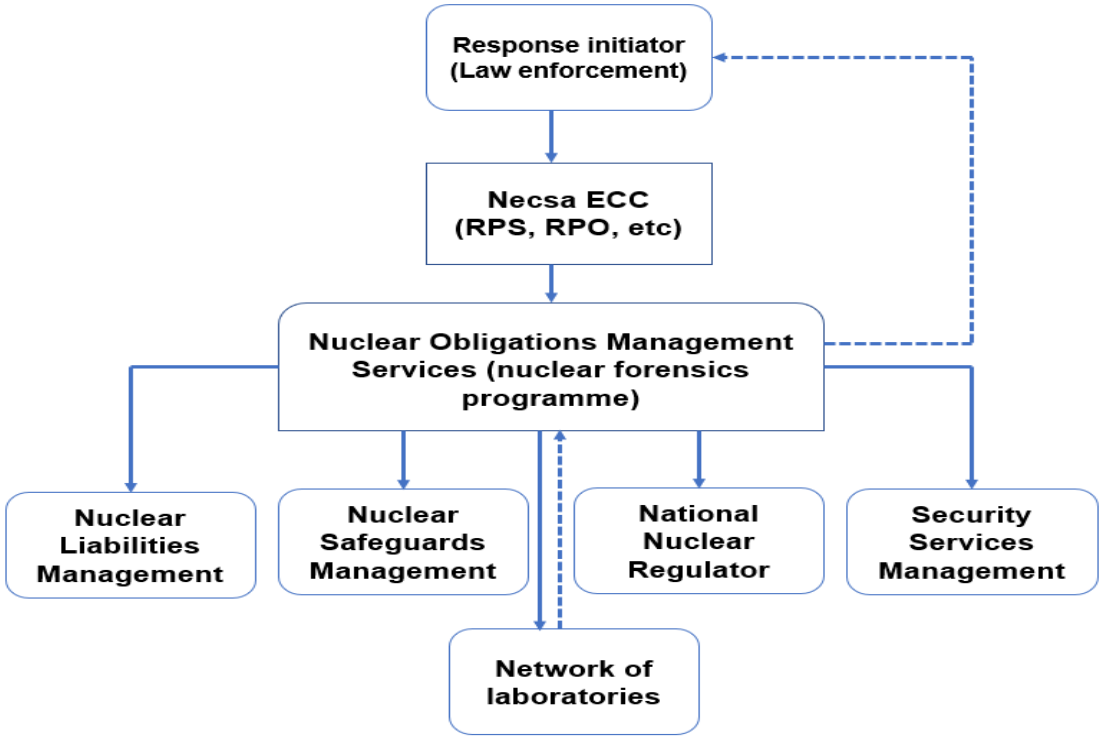
Incidents reported to the ITDB that are confirmed, or likely, to be connected with trafficking or malicious use, 1993 – 2025.

- The majority of incidents reported to the IAEA over the years have been due to theft and poor management.

Illicit trafficking of nuclear and radioactive materials

- In South Africa, cases of illegal trafficking of nuclear materials has been reported to the South African Police Services (SAPS) custody (Mogafe *et al*., 2015):
  - **Two containers of uranium materials (weighing 1.2 kg and 0.5 kg) reported on 10th January 2012 in Sandton area, Johannesburg,**
  - **One container containing uranium was (weighing 0,8 kg) seized on 13th January 2012 in Sandton area,**
  - **Two men arrested on 14th November 2013 on suspicion of having uranium and some pills stored in a plastic bag.**

National Response Plan



(Mogafe *et al.*, 2015)

- **LAW ENFORCEMENT AGENCY** - South African Police Services (SAPS), Bomb Disposal Explosive Section or any law enforcement,

- **NECSA EMERGENCY CONTROL CENTRE (ECC)** - the first contact point on all incidents involving illicit radioactive and nuclear materials brought into Necsa site,

- **NUCLEAR OBLIGATIONS MANAGEMENT SERVICES (NOMS)** - responsible for communicating nuclear forensics incident to Necsa Security Services Department,

- **NUCLEAR LIABILITIES MANAGEMENT (NLM)** - Necsa's main temporary storage facilities department for nuclear forensics material or samples,

- **NUCLEAR SAFEGUARDS MANAGEMENT** - responsible for reporting incident to the IAEA (on the IAEA's ITDB),

- **NATIONAL NUCLEAR REGULATOR (NNR)** - monitor and enforce regulatory safety standards for prevention of nuclear accidents or mitigation of nuclear accident consequences,

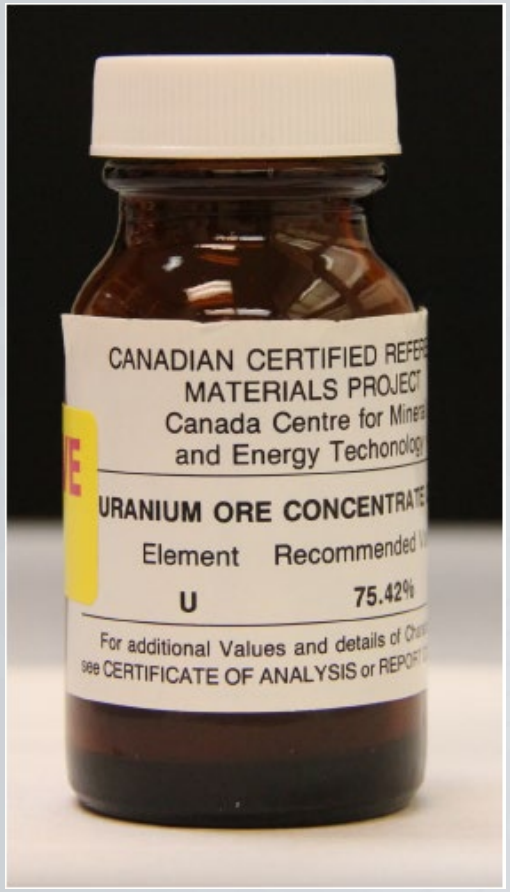
- **SECURITY SERVICES MANAGEMENT** - assist with the escort services in cases where SAPS officials are transporting the material on site.

- **NETWORK OF LABORATORIES** – e.g. Center for Applied Radiation Science and Technology (CARST) at North-West University.

OBJECTIVE

Develop a method to determine the weight percent of elemental uranium (U) and U_3O_8 in a solid sample using ICP-MS after acid digestion and dilution

Certified Uranium Ore Concentrate CUP-2



CCRMP
Canadian Certified Reference Materials Project
CANMET Mining and Mineral Sciences Laboratories
555 Booth Street, Ottawa, Canada K1A 0G1
Tel.: (613) 995-4738, Fax: (613) 943-0573
E-mail: ccrmp@nrcan.gc.ca
www.ccrmp.ca

PCMRC
Projet canadien de matériaux de référence certifiés
Laboratoires des mines et sciences minérales de CANMET
555, rue Booth, Ottawa, Canada K1A 0G1
Tél. : (613) 995-4738, Téléc. : (613) 943-0573
Courriel : pcmr@nrcan.gc.ca
www.ccrmp.ca

Certificate of Analysis

Certified Uranium Ore Concentrate CUP-2

Certified Value

U, mass %	75.42
95% Confidence limits	
Low	75.25
High	75.59

Description

CUP-2 is a uranium ore concentrate reference material produced as joint effort between CCRMP and the Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee.

The material was received from the Blind River refinery of Eldorado Resources Ltd. in the summer of 1986. It was blended, checked for homogeneity by X-ray fluorescence analysis, bottled in 25-g units and distributed for analysis.

Certification Project

CUP-2 was characterized by an interlaboratory analysis program. Eight member laboratories of the Analytical Subcommittee, six commercial laboratories, and three additional volunteer laboratories participated in the project by providing five replicate results on up to 17 analytes. Uranium was reported on a dry basis; all others were determined on an "as received" basis.

Recommended Values For Impurity Constituents

Moisture	2.94	B	0.0051*
S	0.80	Fe	0.311
Si	0.17*	Ni	0.0029
Ti	0.019	Na	0.459
Ca	0.62	Mo	0.069
V	0.066*	Mg	0.229
As	0.035	K	0.11*
Zr	0.044*	P	0.030*

* provisionally recommended

Legal Notice

The Canadian Certified Reference Materials Project (CCRMP) has prepared this reference material and evaluated the analytical data of the interlaboratory certification program to the

Methodology

Parameter	Value
Sample type	UO_2 solid
Sample mass used	0.200 g
Digestant	10 M HNO_3
Digest volume	5.0 mL

Methodology

Parameter	Value
Sample type	UO_2 solid
Sample mass used	0.200 g
Digestant	10 M HNO_3
Digest volume	5.0 mL
Aliquot taken for dilution	100 µL (0.100 mL)
Final dilution volume	1000 mL (1.000 L)

ICP-MS Measurement

ICP-MS Result

Analyte	Reported Concentration	Units
Uranium (U)	3061.92	ppb (µg/L)

La	0.06	5049
Ce	0.11	9833
Pr	0.02	1502
Nd	0.06	5409
Sm	0.03	2546
Eu	0.00	251
Gd	0.05	4146
Tb	0.01	894
Dy	0.09	5238
Ho	0.02	954
Er	0.04	2447
Tm	0.01	308
Yb	0.04	1936
Lu	0.00	224
Hf	0.00	32
Ta	0.00	5
W	0.06	1959
Re	0.00	3
Os	0.00	0
Ir	0.00	0
Pt	0.00	0
Au	0.00	1
Hg	0.00	0
Tl	0.01	547
Pb	0.48	24637
Bi	0.00	0
Th	0.64	19805
U	3061.92	121467829

TotalQuant Equations

Analyte	Equation
S	23.31*mass34
Ca	47.93864*mass 44
Ti	13.44*mass 47
Se	11.455*mass 82
Fe	47.17*mass 57
U	1.00731*mass238

Calculations

Equation 1: Uranium Concentration in the Solid Sample

$$C_{\text{sample}} = \frac{C_{\text{ICP-MS}} \times V_{\text{final}} \times V_{\text{digest}}}{V_{\text{aliquot}} \times m_{\text{sample}}}$$

Where:

- C_{sample} = uranium concentration in the solid sample (mg/g)
- $C_{\text{ICP-MS}}$ = measured uranium concentration (mg/L)
- V_{final} = final dilution volume (L)
- V_{digest} = digestion volume (L)
- V_{aliquot} = aliquot volume (L)
- m_{sample} = mass of the solid sample (g)

Calculations cont…

Equation 2: Weight Percent of Uranium

$$\%U = \frac{m_U}{m_{\text{sample}}} \times 100$$

Where:

- $\%U$ = weight percent of uranium (%)
- m_U = mass of uranium in the sample (mg or g)
- m_{sample} = mass of the solid sample (mg or g)

> *Note:* The mass of uranium (m_U) is obtained from Eq. 1 after applying all dilution corrections.

Calculations *cont…*

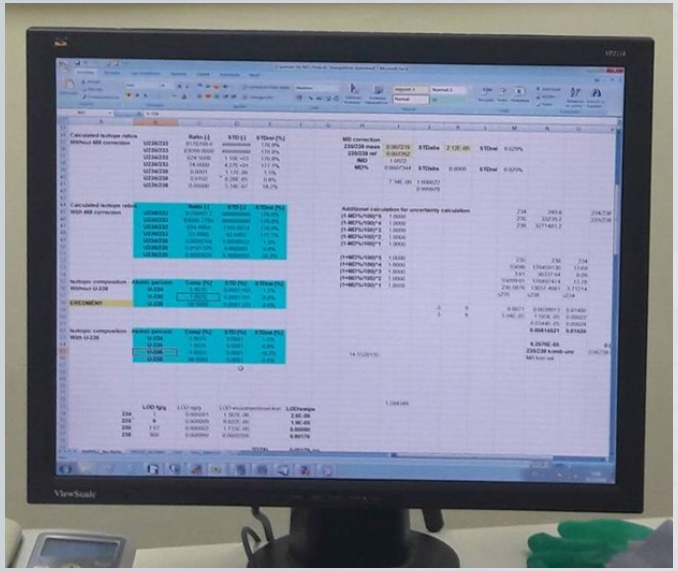
Equation 3: Conversion to U_3O_8

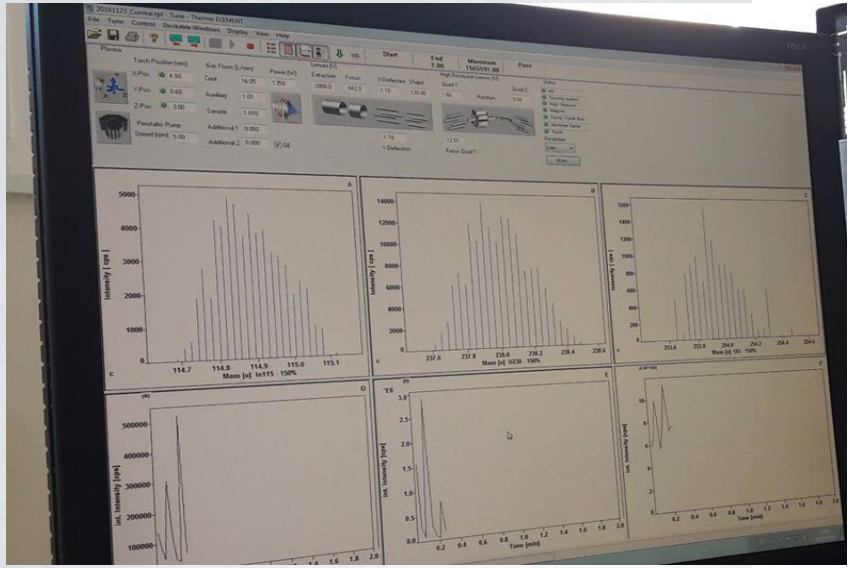
$$\%U_3O_8 = \%U \times \frac{M_{U_3O_8}}{3M_U}$$

Where:

- $\%U_3O_8$ = weight percent of uranium oxide (%)
- $\%U$ = weight percent of uranium (%)
- $M_{U_3O_8}$ = molar mass of U_3O_8 (842 g/mol)
- M_U = atomic mass of uranium (238 g/mol)

Results





Result	Value
Elemental U (wt%)	76.55 %
U_3O_8 equivalent (wt%)	90.27 %

Lawrence Livermore National Laboratory
Nuclear Forensics Group

Prepared July 2016 - LLNL-TR-701561

Conclusion

- The ICP-MS analysis of the acid-digested U_3O_8 sample indicates that the material contains 76.55 wt% uranium, corresponding to 90.27 wt% U_3O_8.
- These values fall within the expected purity range for high-grade U_3O_8.

- This study underscore the importance of nuclear forensics in the nuclear security and safeguard, giving the current move towards nuclear power mix.

- It also showcases the capability of our laboratory to generate its own nuclear forensics library-database for non-proliferation and check of illicit trafficking in nuclear and radioactive materials.

Acknowledgements

- International Atomic Energy Agency (IAEA) for sponsoring this project under CRP J02020 (Research Contract No. 28065).

- North-West University Centre for Applied Radiation Science and Technology (CARST) for financial support to attend and present part of this work at Advanced Nuclear Science and Technology Techniques Workshop (ANSTT 6), Cape Town, South Africa.

- National Research Foundation (NRF) for funding the purchase of the NexION 2000 ICP-MS at CARST.

THANK YOU

North-West University
Private Bag X 2046, Mmabatho, 2735
North West Province
South Africa
www.nwu.ac.za