

Investigation on the Research Trends and Analysis Technique using X-ray for Nuclear Forensics

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1. Introduction

According to the IAEA's Incidents and Illegal Transactions Database (ITDB), nuclear and radioactive materials that have consistently been reported stolen or lost since the collapse of the Soviet Union in 1991. [1]

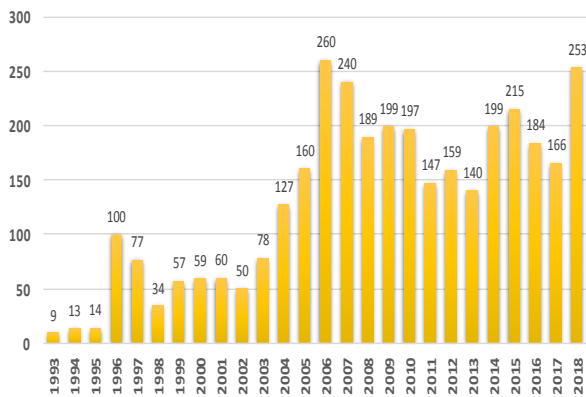


Chart 1. Incidents reported to the ITDB, 1993–2018

These materials pose a potential threat to the general public as well as to vulnerable national infrastructure. The international community has held several summit meetings to determine appropriate, active responses to nuclear terrorism exploiting these materials, and has emphasized the importance of nuclear recognition as one of the primary means for nuclear security.[2]

In response to such objective, KINAC has completed initial research to establish a national nuclear forensics system. Currently, further research is underway to advance sample analysis and measurement techniques applicable to nuclear forensics. In this study, we investigated research trends and analysis techniques that utilize x-rays as related to nuclear forensics.

2. Analytical techniques in nuclear forensics

When an unknown nuclear material is found, identifying its sources and histories through early field and laboratory analysis is critical to responding to potential nuclear security events. To this end, the IAEA and ITWG have developed a model action plan as shown in Figure 1. as the international standard for the overall process of nuclear forensics.

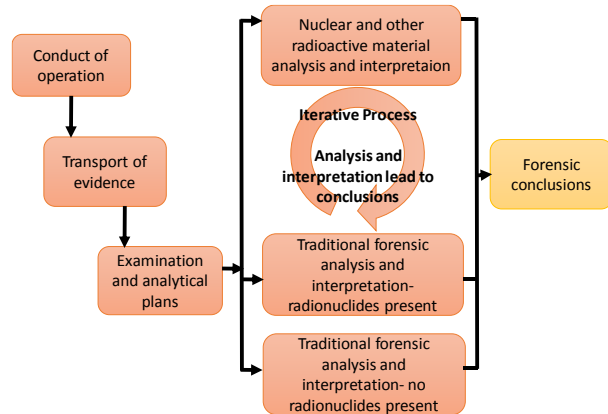


Figure 1. Nuclear forensics model action plan

The main purpose of nuclear forensics analysis is to identify the intended use of a given the material, its origin/source, process/production history, and age. In determining the source of material, chemical composition, isotopic composition of the constituent elements, morphology, impurities and residual organic solvents are all investigated.[3]

2.1 Physical characterization

The first step in assessing the physical characteristics of a nuclear material is usually to measure macroscopic information such as the color, size, mass, and density of the material.[4] The measurement of macroscopic information is characterized by good repeatability and reproducibility with low measurement uncertainty. The second step is to measure microscopic information such as chemical bonding and microstructures. Generally, microscopic measurement consistently improves with the advancement of scientific techniques.; the following are examples of analytical studies using XRD and SEM.

2.1.1 X-Ray Diffraction(XRD)

The X-Ray Diffraction(XRD) technique causes partial diffraction when an x-ray is incident on the sample, and since diffraction angle and intensity are inherent material properties, these characteristics are used to infer the crystal structure of the sample.

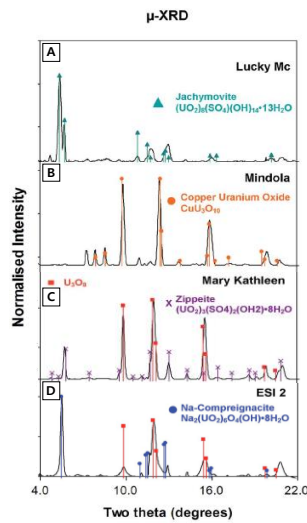


Figure 2. Synchrotron X-ray microanalysis data from A, B: UOC samples containing only hexavalent uranium species, and C, D: UOC samples containing a mixture of U₃O₈ and hexavalent uranium species. [Daniel E. Crean, *RSC Adv.*, 2015, 5, 87908–87918]

The plots in **Figure 2.** were identified by sampling UOCs from the uranium ore concentration(UOC) mines distributed around the world and analyzing them with XRD. A range of processing operations are used for UOC to extract and concentrate various uranium species from the nuclear fuel cycle, where the chemical and physical characteristics of the product, including signatures, are specific to the type of treatment and local geology.

The Lucky Mc sample in **Figure 2.** A) contained the sulfate mineral jachymovite ((UO₂)₃ (SO₄)₂ (OH)₂ · 8H₂O), which appeared as a trace from the extraction process through ion-exchange by dissolution in sulfuric acid. The Mindola site is located within a copper belt, so that a reaction between uranyl nitrate and copper oxide occurs during the calcination process, that result in the copper uranium oxide(CuU₃O₁₀) in **Figure 2.** B). The data in **Figure 2.** C), D) was analyzed from a mixture of uranium species samples, including U₃O₈. The presence of uranium sulfate in the Mary Kathleen sample indicates a high concentration of sulfate in the precipitation solution, indicating the possibility that ammonium sulfate was used in the extraction process. The presence of sodium compreignacite in the ESI2 sample is suggestive of sodium hydroxide precipitation from a low sulfate liquor, leading to the formation of sodium-uranium-hydroxide species.[5]

2.1.2 Scanning Electron Microscope(SEM)

As employed in nano-analysis, Scanning Electron Microscope(SEM)s allow for observation of the topology and atomic composition of samples by

detecting secondary electrons, back-scattered electrons, and X-rays that occur as a result of collisions between high-energy electrons and the sample.

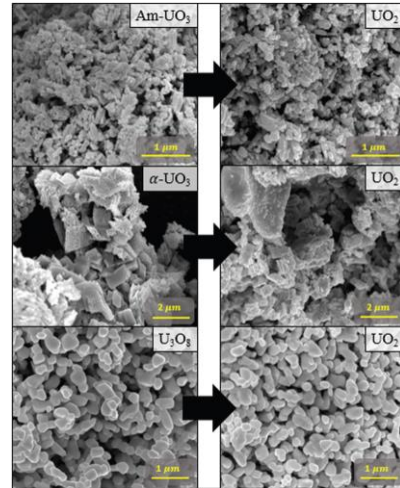


Figure 3. SEM images of the surface structures of UO₂ and intermediates. [E. C. Abbott., *Radiochim. Acta.*, 2019]

Figure 3. is a series of SEM images of UO₂ synthesis from amorphous-UO₃, α-UO₃ and U₃O₈ to observe morphological changes. The morphology of Am-UO₂ is relatively small in size and has rounded edges. The α-UO₃ sample contains both large and small particles, with a relatively low sphericity and irregular shapes. The UO₂ derived from U₃O₈ takes the form of relatively regular, independent spheres. What these three UO₂ sample images have in common is that the form of the starting materials is mainly retained, thereby showing the potential for SEM results to be used as signatures in nuclear forensics.[6]

2.2. Elemental/Chemical composition

The chemical properties of nuclear material can also provide important information about the manufacturing process of the material. The following are examples of analytical studies using XPS and XRF.

2.2.1 X-ray Photoelectron Spectroscopy(XPS)

X-ray Photoelectron Spectroscopy (XPS) binding energies are measured through the kinetic energy of photoelectrons emitted by irradiating a sample with x-rays under high vacuum. As binding energy is an inherent element property, XPS allows for elemental analysis of the sample as well as analysis of its chemical bonds.

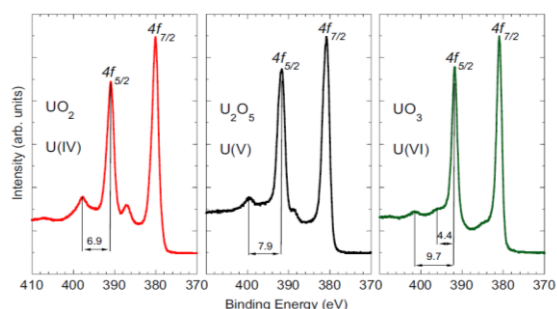


Figure 4. Uranium 4f core level X-ray Photoemission Spectra recorded for U(IV) in UO₂ (left), U(V) in U₂O₅ (center), and U(VI) in UO₃ (right). [T. Gouder., *Nature Scientific REPORTS*, 2018, 8, 8306]

Figure 4. shows the results of an analysis of the oxidation states of uranium oxide through XPS. Although the main peaks do not present much difference, the oxidation states can be analyzed through the satellite peaks. When electrons are released, electrons in the orbital functions are excited. The satellite peaks demonstrate energy loss equal to the difference between the ground state and the excited state, and have higher binding energies than the main peaks. The characteristics of the satellite peaks differ depending on the oxidation state of uranium.; XPS studies of uranium oxide therefore offer more possibilities for precision analysis in nuclear forensics.[7]

2.2.2 X-Ray Fluorescence(XRF)

The X-Ray Fluorescence(XRF) spectrometer provides the means to analyzes the resulting spectra from x-rays incident to a sample and reflected after reaction. Useful signatures can be determined by detecting various impurities as well as uranium at ppm levels. Additional advantages of XRF include being non-destructive as compared to ICP-ms, and more sensitive and deeper probing than SEM-EDS.

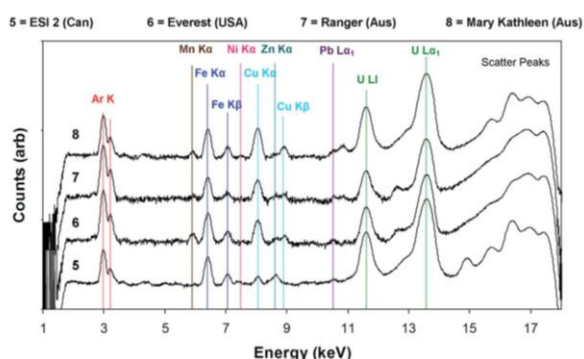


Figure 5. Synchrotron X-ray fluorescence elemental profiles of UOC samples. Variable levels of transition metals and lead can be detected in different samples. Argon K X-rays are due to the excitation of air in the beam path. [Daniel E. Crean, *RSC Adv.*, 2015, 5, 87908–87918]

Figure 5. shows an analysis of semi-quantitative overall impurity profiling of uranium particles via XRF spectrometer. The composition and amount of impurities vary according to the UOC sample, and it can be seen that the concentration of iron and copper impurities is high.

3. Trends Analysis

Nuclear forensics research using x-rays has mainly focused on the identification of nuclear forensic signatures for UOCs, on account of UOCs being the most internationally mobile material in the nuclear fuel cycle.

Table 1. lists each x-ray sourced analytical technique available to investigate an unknown nuclear material and the related information that can be obtained.

Table 1. Analytical utilizing x-rays tools applicable to nuclear forensics

| Technique | Information obtained | Approximate analysis time |
|----------------------------------|---|---------------------------|
| X-Ray Diffraction | Chemical form, morphology | 1-2 days |
| Scanning Electron Microscope | Particle size; elemental distribution(with EDS), grain size, porosity | 1-3 days |
| X-ray Photoelectron Spectroscopy | Elemental composition, chemical state, binding energy | 1-3 days |
| X-Ray Fluorescence | Elemental composition (major and minor), distribution | <24 hours |

The table indicates that the simpler the pretreatment process, the shorter the analysis time. Among the analytical instruments for determining the origin and source of a material, the chemical form and oxidation state can be analyzed through XRD, particle size can be determined with SEM, and element distribution can be determined from SEM with EDS. In addition, the chemical state and binding energy can be known through XPS, and multi-element composition is analyzed through XRF. In order to obtain accurate information on nuclear materials, analysis results from the above techniques are combined to increase reliability.[5]

4. Conclusion

In this paper, the current status of KINAC's nuclear forensics research, the international standard model of nuclear forensics and sample analysis/measurement techniques were investigated. The main research subjects covered were XRD, SEM, XPS, and XRF using x-rays as a source. Most of the research has been

conducted in the form of table tops for the characterization of nuclear material. This focuses on achieving high accuracy and precision under tight environmental control. To date, most existing analytical methods have been found to have sufficient performance, and future studies will be conducted to satisfy sufficient performance levels and short analysis times in external environments such as nuclear security events.

We note that XRF with portable equipment has already been developed, and is frequently used in industrial sites. Future studies will determine whether such equipment has sufficient capabilities to measure nuclear material and be employed to identify nuclear forensic signatures.

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