A Deeper Look at Nuclear Forensic Chemistry

When it comes to solving crimes, there is an overarching genre used to describe the science that is used for each and every case: forensic science. Inside of that genre are multiple subgenres, reaching increasingly niche subjects that are not often turned to. One particularly niche subject is the study of nuclear forensic chemistry. While being niche, nuclear forensic chemistry is very highly turned to when needed as there is no other subgenre of chemistry that can cover as many bases as this particular genre does. Nuclear forensic chemistry is the practice of analyzing radioactive materials that have been used in a criminal setting,[1] such as uranium bombs. Multiple sciences have combined in order to shape and create this genre of forensics, including physics, engineering, and subgenres of chemistry like inorganic and analytical.[1] Other subjects are also equally important in the application and investigation sequences of nuclear forensic chemistry, such as political science and international law.[1]

Nuclear forensic chemistry is an imperative part of any criminal nuclear case. As stated before, it covers many large bases in terms of the forensics world, and criminal nuclear cases would most likely take much longer to process and analyze if it weren't for specialists that work in nuclear forensics. The primary idea behind nuclear forensic chemistry is to be able to offer significant and proper analysis of any seized nuclear materials.[1] It is important to have a niche subject such as this when working in the forensics field as the materials and equipment normally used in criminal cases will not be able to handle evidence of the radioactive kind.[2] Conversely, not all forensic scientists, chemists, or law enforcement officers are properly trained to deal with nuclear materials and evidence,[2] which makes nuclear forensic chemistry that much more important to the scientific community.

Nuclear forensics is an amalgamation of different sciences, but one of the biggest influences on this particular subject is analytical chemistry. Many of the analysis techniques used are credited to analytical chemistry over any other type of science.[2] These techniques help nuclear forensic scientists do a range of things, mainly falling under the material characteristic label. The heavy influence of analytical chemistry helps scientists determine isotopic abundances of a certain nuclear material, the physical and chemical formations of compounds, and some processes can even determine physical dimensions so law enforcement and nuclear technicians can link specific mixtures or elements to related ones from other linked cases.[2] The determination of certain characteristics can even end up being linked to specific locations or a niche creation process that is limited to certain jurisdictions.

With a wide array of sciences under the nuclear forensics umbrella, there is bound to be a sizeable selection of methods and equipment to choose from when investigating a case. Table 1 showcases a breakdown of the different classes of methods and what the equipment or technique may be used for.

Table 1. Methods Used in Nuclear Forensics.[2]

Class of Techniques	Examples	Applications
Bulk analysis	X-ray fluorescence (XRF) and X-ray diffraction (XRD)	Characterize the elemental and isotopic composition of the bulk material
	Inductively coupled plasma mass spectrometry (ICPMS)	Detect and quantify trace constituents
	Gamma spectrometry	
Imaging	Optical microscopy	Determine sample homogeneity or heterogeneity
	Scanning electron microscopy	Assess material morphology and microstructure
Microanalysis	Secondary ion mass spectrometry (SIMS)	Quantitatively or semiquantitatively characterize the individual constituents of the bulk material
	X-ray microanalysis	Particle analysis
		Analyze thin layers or coatings

The examples shown cover a very minimal area of total processes and equipment used. Though there are only three very broad classes, each given example has a different use and can cover various types of analyses. The microanalysis section is a good example, where the applications of each technique are noticeably different from the others while still fitting inside the same category. There are many commonly used techniques and instruments that did not make it onto Table 1, and some commonly referred-to topics within nuclear forensics that have not yet been covered.

One popular technique used in nuclear forensics is alpha spectrometry (AS). This technique is specifically used for pieces of evidence that are time-sensitive or contain certain amounts of actinides.[1] The alpha particle emissions help decay the actinides found in the sample, which can then open the gateway to isotopic fingerprinting.[1] Isotopic fingerprinting is often used for plutonium and uranium, two of the most common elements left behind in nuclear forensics cases. In order to obtain an isotopic fingerprint and be able to trace these elements back to a source or suspect, many investigators will rely on alpha spectrometry. Not only is alpha spectrometry specialized for further insight into isotopic fingerprinting, the highly sensitive and accurate technology is needed in order to be able to detect small variations in isotopic ratios.[4]

Alpha spectrometry is a highly valued technique when it comes to nuclear forensics due to its extreme sensitivity, accuracy, and quick analysis rate. Unlike most other techniques, alpha spectrometry takes significantly less time to prepare samples, and is comparably less expensive.[1,5] In many forensic cases, especially ones involving chemicals of a radioactive nature, time is key. Taking too long analyzing evidence may cause damage in the long run if suspects are unable to be caught. Alpha spectrometry spectra results are quick while also being detailed enough to offer extremely important pieces of information that other processes take many longer steps to reveal.

The process of alpha spectrometry uses two main instruments: a form of vacuum, and electrodeposition. The vacuum procedure begins alpha spectrometry, involving a thin layer of the sample being placed within the vacuum. This is to prevent possible interactions with other particles or debris and to help return a clear reading.[1,6] After the vacuum procedure is completed, more information is usually needed with help from a destructive sample analysis, which is where the electrodeposition process enters. Electrodeposition requires a solution made from sample and a solvent of best fit, which is then spread on a platinum plate.[1] Once the plate is prepared, the analyst may calculate how many actinides the sample contains – this is called counting.

While alpha spectrometry is used for isotopic fingerprinting, it can also be used for nuclear fuel analysis. More specifically, if the isotopes ^{232}U and ^{238}Pu are present in fuel, alpha spectrometry can pick up on the usually miniscule amount of those isotopes in the mixture which is helpful as those particular isotopes are relatively short-lived.[5] Alpha spectrometry is also used to further determine the ratio of ^{232}U in a ^{233}U sample, which can hint at production history of the uranium and reveal its potential to be used in a nuclear explosive.[5] A spectrum created by alpha spectrometry is shown in Figure 1, displaying the typical energies of different isotopes found in a radioactive sample containing only uranium.

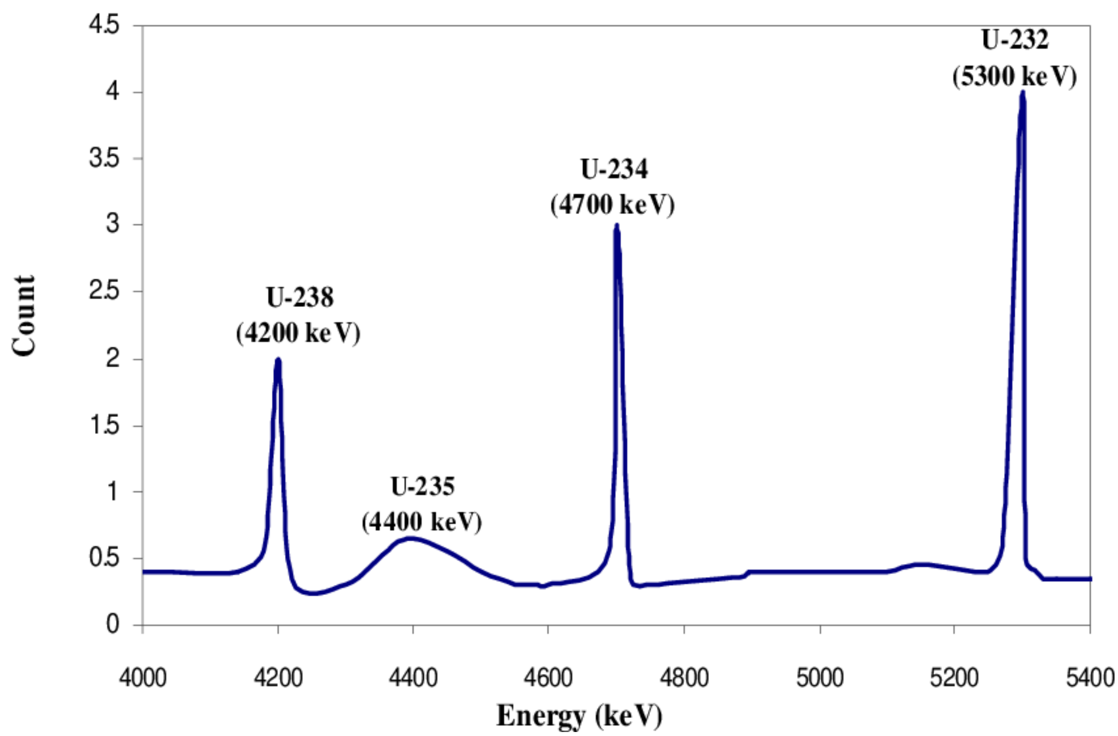

Figure 1. Typical spectrum of uranium isotopes created by AS.[7]

Another, more widespread, analysis technique is mass spectrometry (MS). This process is used more often in general forensic science, paired with usage in multiple subgenres of chemistry as well. Mass spectrometry is generally used in analytical chemistry to record the charge-to-mass ratio of a compound and its daughter ions, which is helpful in understanding how a compound may fracture when met with charge. Mass spectrometry did not begin its venture into the nuclear scene until approximately 1939, when Alfred Nier and Enrico Fermi paired together to begin separating ^{235}U isotopes in small samples in order to find out which isotope caused slow neutron fission.[3] With confirmation that mass spectrometry was able to determine the characteristics of specific isotopes, the usage of mass spectrometry within the nuclear science region began. Due to the importance of MS within the nuclear forensic genre, chemists who have experience with these procedures are highly sought after within law enforcement and forensics labs.[1,9]

Mass spectrometry offers extremely sensitive technology comparable to alpha spectrometry, also used for isotopic detection. This isotopic detection is comparable to fingerprinting, as mass spectrometry isotope detection reveals the age, origin, and history of the left behind sample.[1] This process can also reveal the isotopic composition of spent nuclear fuel and further reveal from which exact reactor the fuel may have originated.[1] Mass spectrometry also gives insight to an element's production date. The method – called chronometry - is originally used to determine the substance's age, and by also analyzing the decay of isotopes compared to the ratio at time of analysis, the production date can be found.[1]

An equally-important type of mass spectrometry is known as thermal ionization mass spectrometry (TIMS), which is more sensitive than general MS and is studied much more for use within the nuclear forensic chemistry region.[1] If alpha spectrometry is not available to a lab, they will be able to steadily rely on TIMS to get equally detailed isotopic fingerprinting data (especially for elements with low ionization).[1] Another plus for the use of TIMS is that results can be gathered from a very small amount of sample, so if a particular case doesn't have much to work with, TIMS tends to be the most effective option. The only glaring issue with TIMS is the fact that sample preparation is complex, due to the process's extremely sensitive nature.[1]

Thermal ionization mass spectrometry was the first type of mass spectrometry to be utilized in a nuclear forensics case, as nuclear forensics had only just been established a year prior.[9] This case offered a seized nuclear sample simply named "Find-1".[1,9] This sample consisted of seventy-two uranium pellets found in Augsburg, Germany.[9] TIMS was not the only method used in this case, however, it helped discover the composition and parameters of the pellets. Despite having the instrumentation to find in-depth info on this evidence, the young age of nuclear forensics cast a shadow over the details as most interpretation was left up to the researchers and scientists put in charge of the new subgenre of science. However, scientists broke through with the data from TIMS and potentiometric titration in order to calculate the data showcased in Table 2.

Table 2. Results of Find-1 Sample.[9]

Parameter	Dimension	U-isotope (wt.%)	U-concentration (wt.%)
Ø (mm)	11.45 ± 0.01	U-232 ($8.27E-8 \pm 6.5E-9$)	87.98 ± 0.03
Height (mm)	14.42 ± 0.24	U-234 (0.034 ± 0.002)	
Weight (g)	15.454 ± 0.315	U-235 (2.507 ± 0.014)	
		U-236 (0.449 ± 0.051)	
		U-238 (97.011 ± 0.067)	

Another popular type of MS within nuclear forensics is inductively-coupled plasma mass spectrometry (ICP-MS). Issues experienced by technicians using TIMS for sample analysis can easily be dismissed by using ICP-MS instead. Comparing the two subgenres of MS, ICP-MS has multiple advantages over TIMS, most notably the fact that ICP-MS can analyze elements that have a high ionization rate.[1] ICP-MS can also detect most of the elements on the periodic table, not just those with high ionization rates or with radioactive properties.[1] These details are imperative to tracing where a compound may have originated, as some trace elements are more prominent in certain places. Due to its multiple advantages and simpler sample preparation, the popularity of ICP-MS within the nuclear forensic community has been rising.[1] Not to mention, inductively-coupled plasma mass spectrometry has its own subgenre which incorporates laser ablation into the process.[1] The addition of laser ablation into the technique makes it less destructive than its other mass spectrometry siblings, as samples are able to be analyzed completely in the solid state.[1] This also means that no additional chemicals need to be added to the sample that can possibly destroy or otherwise contaminate the evidence. The introduction of a non-destructive type of MS is somewhat fresh to the nuclear forensic subject, partially causing its soar in popularity. A typical ICP-MS spectrum does not stray far from the visuals of an MS spectrum, as demonstrated in Figure 2. The pulse count of ICP-MS replaces the charge-to-mass ratio usually present on an MS spectrum.

In a June 2003 case, the Institute for Transuranium Elements received nuclear evidence from a seizure in Lithuania. A total of four uranium dioxide pellets were collected and all four were identical in appearance. Gamma spectrometry confirmed that all of the pellets were the same, therefore only one pellet was dissolved and destroyed for use in mass spectrometry.[10] The MS process was used for further insight on the isotopic composition of the pellets, especially to determine if ^{234}U and ^{236}U were in the sample.[10] Inductively-coupled plasma mass spectrometry was also utilized in this case along with a multi-collector detection system to compare both accuracy and precision between regular mass spectrometry and thermal ionization mass spectrometry.[10]

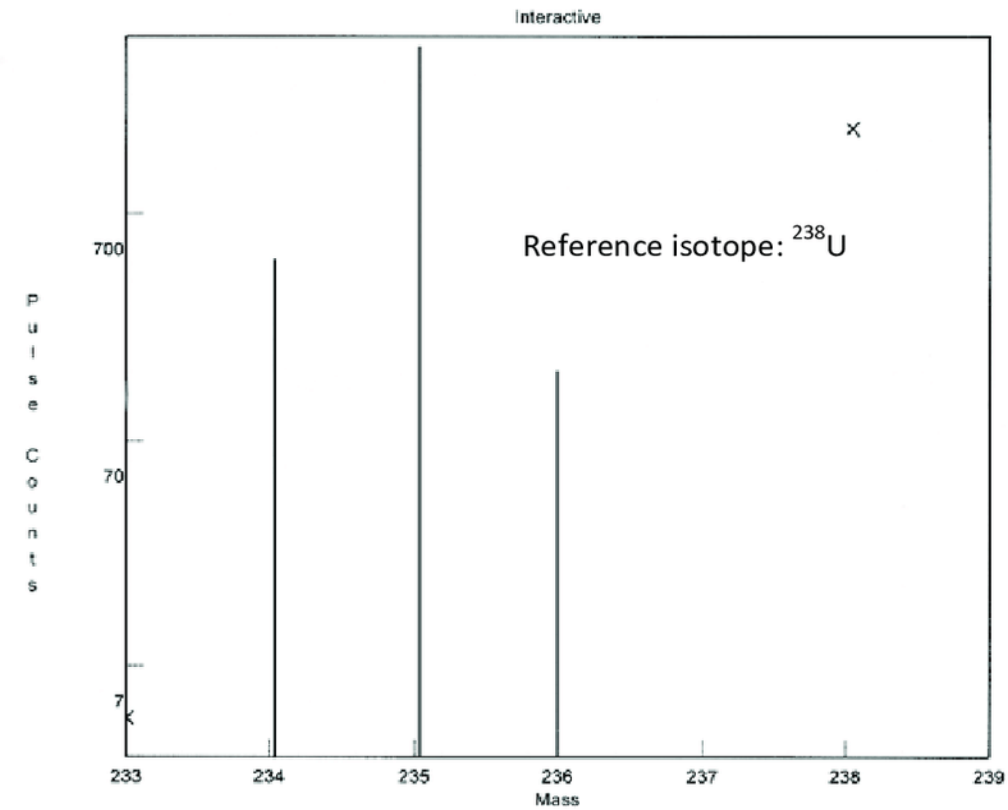

Figure 2. Isotopic abundance of uranium in a sample.[8]

An important topic within nuclear forensics covers microanalytical techniques. This class of technique is a large part of the techniques utilized within cases and evidence analysis. Without many of these methods, nuclear forensic chemistry would not be a sought-after subject. Microanalytical techniques have done the most to develop nuclear forensic chemistry into the subject that it is currently, using practices from nanoscience and subsequent advances in material chemistry to propel nuclear forensics further.[1] Though many of the techniques are well known in the general chemical world, the recent improvements made by influences from other sciences have made an impact on how these methods work in the nuclear forensic chemistry world.[1]

Microanalytical techniques such as secondary ion mass spectrometry (SIMS), electron microscopy, x-ray microscopy, and small-area microscopy have had a particularly large impact on nuclear forensics compared to other lesser-known techniques.[1] These methods are popular due to their ability to retrieve essential information such as chemical and physical properties from samples that can barely be seen.[1] The collaboration of material chemistry and nanoscience has created nanomaterials, which further allows microanalytical techniques to map out and identify structures.[1]

Secondary ion mass spectrometry is able to perform many of the same tasks as its MS relatives, such as isotopic ratio determination and identifying trace elements for source tracking. In addition, SIMS can perform basic surface imaging, which provides the shape and composition of an element.[1] SIMS works by overlapping (LA) ICP-MS and other certain forms of MS, which results in the surface of any evidence being captured by an ion beam projection.[1] The sample preparation for SIMS imaging is quick and minimal, making it a reliable and effective option for sample imaging.[1]

Scanning electron microscopy (SEM) is also useful for surface imaging, though more powerful than the SIMS counterpart, and notably, SEM has been consistently researched and developed for nanomaterials which gives it a broad range of uses.[1] Though SEM initially had no particular specific uses in nuclear forensic chemistry, it did help material chemistry progress to the point where it could lend a hand in developing nuclear forensics to the point it is at currently.[1] Now, SEM is used for surface imaging much like SIMS, while also providing morphological analysis of the sample. Also comparable to SIMS and other types of MS is the fact that SEM does not require destruction of the sample in order to prepare and image it.[1]

In an April 2003 case, the Institute for Transuranium Elements acquired four powdered uranium samples, seized from the Czech Republic. During initial observation, the powder was found to be subsamples from larger batches that had been seized at various points during 1994-1995.[10] After multiple tests including ICP-MS, gamma spectrometry, and TIMS, the powder samples were prepped for use with SEM. This was done by placing a small amount of sample on an aluminum specimen stub and coating with carbon to promote conductivity.[10] The SEM process found that the internal structure of the grains matched with the external structure, showcasing that these powders were made up of finely grained materials. SEM also collected data pertaining to the irregular grain sizes, and average sizes of particles within the powders.[10]

With such a wide array of techniques and sciences combined, nuclear forensic chemistry is undoubtedly one of science's greatest creations. Nuclear forensic chemistry holds the ability to solve crimes and save lives, while further developing each science within as years pass. The popularity of nuclear forensics is still somewhat low, as not many people know the greater details of criminal nuclear cases. However, the sheer amount of work and development nuclear forensic chemistry has put out into the sciences and its methods in the past years says one thing: the world would not be where it is if it was not for nuclear forensic science.

References

1) Straub, M. D.; Arnold, J.; Fessenden, J.; Kiplinger, J. L. Recent Advances in Nuclear Forensic Chemistry. *Analytical Chemistry* **2020**, *93* (1), 3–22. (Accessed Apr 21, 2021).

2) Keegan, E., Kristo, M., Toole, K., Kips, R. and Young, E., 2016. Nuclear Forensics: Scientific Analysis Supporting Law Enforcement and Nuclear Security Investigations. *Analytical Chemistry*, 88 (3), pp. 1496-1505. (Accessed Apr. 5, 2021).

3) Griffiths, J. A Brief History of Mass Spectrometry. *Analytical Chemistry* **2008**, *80* (15), 5678–5683. (Accessed Apr 5, 2021).

4) Mayer, K.; Rasmussen, G.; Hild, M.; Zuleger, E.; Ottmar, H.; Abousahl, S.; Hrnecek, E. Application of Isotopic Fingerprinting in Nuclear Forensic Investigations. https://www.osti.gov/etdeweb/servlets/purl/20296989 (Accessed Apr. 5, 2021).

5) Aggarwal, S. K. Alpha-Particle Spectrometry for the Determination of Alpha Emitting Isotopes in Nuclear, Environmental and Biological Samples: Past, Present and Future. *Analytical Methods* **2016**, *8* (27), 5353–5371. (Accessed Apr 5, 2021).

6) Knoll, G. Radiation Detection and Measurement. https://phyusdb.files.wordpress.com/2013/03/radiationdetectionandmeasurementbyknoll.pdf (accessed Apr 15, 2021).

7) Abbasisiar, F.; Hosseini, T.; Fathivand, A.; Heravi, G. Determination of Uranium Isotopes and Natural Uranium in Water Samples by Alpha Spectrometry. Iranian Journal of Radiation Research 2004, 2 (1), 1–6 (Accessed Apr 5, 2021).

8) Chajduk, E.; Kalbarczyk, P.; Dudek, J.; Polkowska-Motrenko, H. Isotope Ratio Measurements for Uranium by Quadrupole-Based Inductively Coupled Plasma Mass Spectrometry. Application in Thorium Fuel Research. Procedia Chemistry 2012, 7, 660–665 (Accessed Apr 5, 2021)

9) Stanley, F.E., Stalcup, A.M. & Spitz, H.B. A brief introduction to analytical methods in nuclear forensics. *J Radioanal Nucl Chem* 295, 1385–1393 (2013). https://doi.org/10.1007/s10967-012-1927-3 (Accessed Apr 15, 2021)

10) Wallenius, M.; Mayer, K.; Ray, I. Nuclear Forensic Investigations: Two Case Studies. *Forensic Science International* 2006, *156* (1), 55-62. (Accessed Apr 21, 2021).