

HIGH RESOLUTION ICP-OES: A POWERFUL DIAGNOSTIC TOOL FOR NUCLEAR FORENSIC STUDIES

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Introduction

Knowledge of the elemental and isotopic composition of a seized radioactive sample is a key parameter in nuclear forensics. While mass spectrometry is used in most instances for obtaining such data, recent developments in high resolution inductively coupled plasma – optical emission spectrometry (HR-ICP-OES) allow for fast and reliable comparative analysis (Krachler et al., 2015; Krachler & Alvarez Sarandes, 2015; Krachler & Alvarez Sarandes, 2016) Employing two instrumental techniques (mass spectrometry and optical emission) based on different physical detection principles, the accuracy of analytical data can be ascertained (Krachler et al., 2015).

The high optical resolution of HR-ICP-OES of <5 pm enables the detection of emission lines of individual isotopes of plutonium (Pu) and uranium (U), for example (Figure 1). As such, valuable isotopic information is also accessible with HR-ICP-OES (Krachler & Carbol, 2011; Krachler & Wegen, 2012).

In this context the current study highlights two selected domains of isotopic analysis using HR-ICP-OES and compares the ICP-OES results with mass spectrometry data: (a) the assessment of depleted, natural and enriched uranium, and (b) Pu age-dating using the $^{234}\text{U}/^{238}\text{Pu}$ chronometer.

Methods

All measurements were carried out with a commercial high resolution (HR-) ICP-OES instrument (Ultima2, HORIBA Jobin Yvon, Longjumeau, France). The entire sample introduction system including the autosampler (AS500, HORIBA) of this sequentially working optical spectrometer has been installed in a glove box enabling the analysis of the radioactive samples. This demanding adaptation of original ICP-OES set-up protected the analyst from α and β radiation of the sample solutions to be analysed. A PolyPro ST nebuliser (Elemental Scientific, Inc., Omaha, NE, USA) was attached to a high efficiency sample introduction system enhancing ICP-OES performance. Detailed operating and data acquisition parameters of the HR-ICP-OES were reported earlier (Krachler & Carbol, 2011; Krachler & Alvarez Sarandes, 2016).

Similarly, sector field ICP-MS (Element2, Thermo Fisher Scientific, Bremen, Germany), MC-ICP-MS or TIMS, all operated at routine settings in-house, were employed for comparative mass spectrometric measurements.

Results

HR-ICP-OES provides fit for purpose U isotopic information with reasonable accuracy (typically 1.5%) and precision (~1%) within a couple of minutes. As such, HR-ICP-OES can be employed as a reliable, fast screening tool to identify the U isotopic composition and as such, complements the more laborious mass spectrometric analysis routinely employed for this purpose.

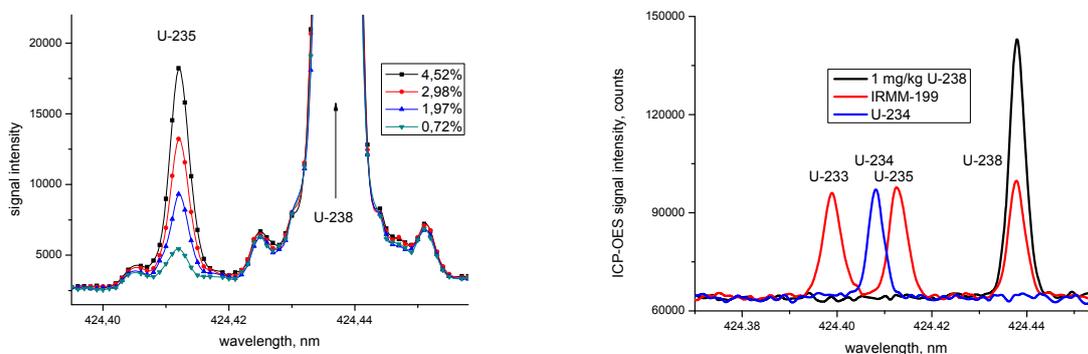


Figure 1. Left: Optical emission spectra of samples containing natural (0.72% ²³⁵U) or slightly enriched uranium (Krachler & Carbol, 2011). Right: Spectroscopic identification of the decay product ²³⁴U in a ²³⁸Pu sample. The emission spectra of the certified reference material IRMM-199, containing ~1/3 of each ²³³U, ²³⁵U, and ²³⁸U as well as of a conventional ICP standard solution are given for comparison.

While mass spectrometry may utilize various parent/daughter pairs (²³⁴U/²³⁸Pu, ²³⁵U/²³⁹Pu, ²³⁶U/²⁴⁰Pu, ²⁴¹Am/²⁴¹Pu) to ascertain the accuracy of Pu age-dating, the employment of various Pu and U emission wavelengths confirms the "correct" date derived from HR-ICP-OES measurements. Preliminary data show a high degree of agreement between both instrumental approaches, effectively complementing each other.

Conclusion

HR-ICP-OES is a powerful screening tool for the quick assessment of depleted, natural and enriched U as well as for age-dating of ²³⁸Pu materials with reasonable accuracy and precision. Such direct optical emission analysis is straightforward and does not require a chromatographic separation prior to the quantification step as mandatory for most mass spectrometric measurements.

References

- Krachler, M.; Alvarez Sarandes, R. (2016). Capabilities of High Resolution ICP-OES for Plutonium Isotopic Analysis. *Microchem. J.*, 125, 196-202.
- Krachler, M.; Alvarez Sarandes, R. (2015). Improved Plutonium Concentration Analysis in Specimens Originating from the Nuclear Fuel Cycle Using High Resolution ICP-OES. *J. Anal. At. Spectrom.*, 30, 1655-1662.
- Krachler, M.; Alvarez Sarandes, R.; Van Winckel, S. (2015). Challenges in the Quality Assurance of Elemental and Isotopic Analyses in Nuclear Domain Benefitting from High Resolution ICP-OES and Sector Field ICP-MS. *J. Radioanal. Nucl. Chem.*, 304, 1201-1209.
- Krachler, M.; Wegen, D.H. (2012). Promises and Pitfalls in the Reliable Determination of ²³³U Using High Resolution ICP-OES. *J. Anal. At. Spectrom.*, 27, 335-339.
- Krachler, M.; Carbol, P. (2011). Validation of Isotopic Analysis of Depleted, Natural, and Enriched Uranium Using High Resolution ICP-OES. *J. Anal. At. Spectrom.*, 26, 293-299.