

Inductively Coupled Plasma Mass Spectrometry (ICP-MS): A Modern Analytical Technique for Nuclear Forensic Application

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Abstract

The inductively coupled plasma mass spectrometry (ICP-MS) as a modern analytical technique is a highly sensitive and precise type of mass spectrometry that can measure both metals and non-metals in a given material at very low concentrations of less than a part in trillion (part per trillion). It has very wide area of applications due to its ability to separate and detect ions with high precision and time saving. In nuclear forensic science, ICP-MS find significant place in the characterisation of nuclear and other radioactive materials for determination of unique signature. Uranium isotope concentration and ratio, trace elements and rare earth elements pattern among other parameters provide solid base information for provenance, in order to thwart illicit trafficking and smuggling of nuclear materials. ICP-MS was used to analysed four mined uranium ore rock samples from parts of northern Nigeria and the results showed the technique to be very sensitive with high ion signal intensity and low detection limit. The three elements lead, thorium and uranium studied presented a range of 3.2 to 4300 cps/ppb wide enough to cover elements of lower to higher mass. Results of trace elements has range of 4.0700 ppb to 7472.0250 ppb with mean 1774.1277 ppb for sample U001. Sample U002 has range of 2.0800 ppb to 674.1750 ppb with mean 213.0349 ppb. Sample U003 has range of 12.8200 ppb to 2810.3650 ppb with a mean of 858.4727 ppb and sample U004 has range of 12.4550 ppb to 2641.5900 ppb with a mean of 613.3938 ppb. The concentration values were comparable with those of related work using similar analytical technique applied to nuclear materials.

Keywords: ICP-MS, Nuclear Forensics, Signature, uranium ore

INTRODUCTION

The threat to global nuclear security, its devastating effects and consequences on human beings as well as the environmental impact of naturally occurring radioactive material (NORM) is a topic of international interest. It is still receiving global attention, especially by

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member states in the United Nation (Mayer *et al.*, 2005; Balboni *et al.*, 2016). This is informed by the fact that in recent years, criminal acts that involves nuclear materials (i.e. uranium or plutonium) and radioactive sources by way of illicit trafficking and smuggling have caused havoc thereby raising growing public concern (Mogenstern *et al.*, 2002; Stanley, 2012). From 1993 to the end of 2016, the IAEA's Incident and Trafficking Database (ITDB) compiled 3068 confirmed incidents of nuclear and other radioactive material out of regulatory control. Of heightened concern, recent incidents point to organized networks of sellers and buyers for this material (Kristo *et al.*, 2016; IAEA, 2017).

In the mid-1990s, the use of the term nuclear forensics first began, due to increasing number of seizures of nuclear material in support of law enforcement investigations, while many laboratories grappled with the analysis (Kristo *et al.*, 2016). "Nuclear forensics is the examination of nuclear or other radioactive material, or of evidence that is contaminated with radionuclides, in the context of legal proceedings under international or national law related to nuclear security. The analysis of nuclear or other radioactive material seeks to identify what the materials are, how, when, and where the materials were made, and what their intended uses were" (IAEA, 2015; Balboni *et al.*, 2016). The purpose is to thwart the plan of further use and illicit trafficking of such nuclear and radioactive.

The development of nuclear forensic capabilities has helped in identification of various viable analytical techniques for the task of characterising nuclear materials to obtain signature that are unique and point to the origin of the material (Krajko, *et al.*, 2014; Moody *et al.*, 2014). "Signature" is a term used to describe material characteristic that may be used to link samples to people, places and processes. It provides description of any characteristics or group of characteristics, which can be used to assist in differentiating materials from another or spot the process history of a given material (Hutcheon *et al.* 2013).

Given that some of the analytical tools used in radioactive material analysis are destructive (analysed sample cannot be reused), such as inductively coupled plasma mass spectrometry (ICP-MS), the proper selection and sequencing of analyses is critical. This sequencing will be determined by the ultimate goals of the investigation, leads in the case, the potential nuclear forensic signatures (physical, chemical, elemental, isotopic) (Mayer *et al.*, 2011) enabling precise interpretation, the amount of sample available for analysis, and analytical methods for measuring nuclear forensic signatures. It is important to emphasize that all sampling and analyses have to be performed with due regard for preservation of evidence and maintaining an evidentiary chain of custody (IAEA, 2014).

Inductively coupled plasma mass spectrometry (ICP-MS) is an elemental analysis technology capable of detecting most of the periodic table of elements at milligram to nanogram levels per liter or grams. It is used in a variety of industries including, but not limited to, environmental monitoring, geochemical analysis, metallurgy, pharmaceutical analysis, and clinical research.

The ICP-MS technique has proved to be excellent over other analytical techniques such as XRF, alpha and gamma spectrometry due to its sensitivity, ability to measure small amount of sample with wide range of multielement analysis up to part per trillion levels within short period of time (Svedkauskaite-Le Gore, 2008; Batsala *et al.*, 2012). It is therefore able to measure with high degree of accuracy, the required parameters inherent to a nuclear or radioactive material for attribution.

This study focused on the ICP-MS analytical technique with a view to providing experimental evidence validating the ICP-MS device as it offers more robust measurement outcome applied to nuclear forensic science and characterisation of nuclear and other radioactive material,

whether of natural or processed source. The significance of the ICP-MS device is to provide and perform quantitative analyses and to serve as an excellent semi-quantitative instrument as well, being able to analyse up to 80 elements in short period of time.

Consequent upon this, four uranium ore samples from parts of northern Nigeria were analysed in order to validate the ICP-MS analytical method as well as to characterise the materials for nuclear forensics application. This study generated baseline data on uranium ore of African origin thereby partly closing the wide existing gap in data for reference, added up to the national nuclear forensic library (NNFL). In this, paper however, discussion centered on the ICP-MS technique and its robustness in being able to measure to as low as possible, concentration of samples with high level of sensitivity and accuracy, giving a wide coverage of the elements.

Methodology

Agilent 7700 Series ICP-MS Device

The Agilent 7700 series ICP-MS of Agilent Technologies, Inc. USA, at the Environmental Analytical Chemistry, School of Chemistry, University of the Witwatersrand, Johannesburg was used for the analysis of uranium ore samples in this work. The Agilent 7700 series ICP-MS equipment which is environment dependent, is installed in an enclosed coolest environment at an average temperature of 17°C. Connected to a chiller at 10000°C while running to cool the plasma and with water circulating at room temperature, depending on the season. A fume extraction component attached to the device assists to avoid corrosion of instrument and supports the cooling of the whole plasma component.

Also attached is sample delivery system, an integrated, covered auto-sampler with pumped rinsed station, ideal for ultra-trace analysis and small sample volumes (as low-as 0.5 ml). Three types of gas are used - Argon (Ar), Helium (He) and Hydrogen (H), in nebuliser to generate plasma and converts sample to ion form for mass spectra set-up. Other important components for the instrument as shown in Figure 1 include:

- Low flow sample introduction system, which increases operational stability and consistency.
- Patented High Matrix Introduction (HMI), which increases matrix tolerance and improves plasma robustness, virtually eliminating matrix suppressions.
- Plasma-RF generator - A fast, frequency-matching generator, which increases the tolerance of changing matrices. It includes shield Torch system as standard, providing the narrow ion energy spread required for effective interference removal in He mode.
- Electronic gas control - a proprietary active Mass Flow Controllers that delivers precise control of all plasma and cell gas.
- Interface and cones - A robust, standard Nickel or platinum tipped cones, Torch position automatically realigns with the interface following maintenance to the torch or cones.
- Electronic gas control - A proprietary active mass flow controller that deliver precise control of all plasma and cell gases.
- Off-axis ion lens - This provides for a continuously focused ion transmission and the lowest mass bias. It is located outside the high vacuum region making it easy to access for scheduled cleaning.
- Vacuum system - This comprise of a single high-performance split-flow turbo pump and a single external rotary pump, which ensures for fast pump-down and simple maintenance.

- Octopole Reaction System (ORS) – A temperature-controlled collision/reaction cell, which has low internal volume, making it ideal for high cell pressures and rapid cell mode switching. It greatly discard compromised mixed gas condition.
- Octopole ion guide – This provides high ion transmission and superior focus, ensuring that there is minimal ion scattering at high cell pressures. A feature that makes it operate efficiently in He mode, delivering also, lower detection limits without reactive cell gases drawbacks.
- Hyperbolic quadrupole – Superior peak separation and abundance sensitivity is delivered by this component, without needing custom quad setting to separate adjacent peaks.
- Electron multiplier detector – This provides for a full 9 orders dynamic range with a standard hardware and operating conditions. In both pulse and analog mode, a short integration time of 100 μ s is obtainable.
- MassHunter Workstation – ICP-MS computer software which controls the operation of the set-up on the monitor. Functions such a preparing samples for analysis, igniting plasma, checking tuning running of the samples, analysing the samples and quantitative data analysis, are manipulated. The analysis results are displayed along with the calibration curves.

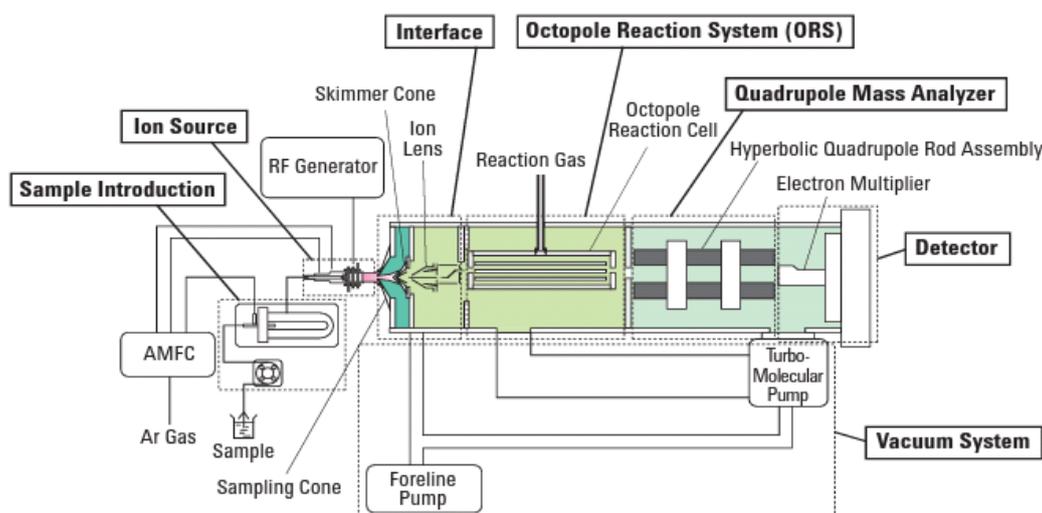


Figure 1: Schematic diagram showing the components of the Agilent 7700 series (Agilent, 2010)

Other materials used

Dickie and Stockler TS-250 Rock crusher and Milling machines, used to crush the uranium ore rock samples and then milled to very smooth texture for direct dissolution in the digestion process.

Anton Paar Multiwave, PerkinElmer Germany, digital Microwave Digestive System. A device used to perform the digestion process and complete dissolution of milled samples.

Teflon sample container, where samples were placed for both digestion and ICP-MS analysis process. Rhodium (^{103}Rh) as internal standard (ISTD).

Polyvinylidene difluoride (PVDF) 0.22 μm membrane filtering device, used to filter samples before placement in the ICP-MS sample loader for analysis.

Sample Preparation

Four open pit mined uranium ore rock samples were collected from Adamawa, Kano and Taraba with sample ID U001 (Riruwai), U002, U003 (both from Mika) and U004 (Michika). The Agilent 7700 series technology, USA ICP-MS device, offered high accuracy values with Anton Paar multiwave micro digestive system and high grade reagents such as aqua regia, hydrogen fluoride (HF). ^{103}Rh internal standard used, sample dilution of 10% and 50% and two set of quality control applied. The ICP-MS requires sample to be introduced in liquid or aerosol matrix. The rock samples were crushed milled before digestion and complete dissolution was achieved. The digested/dissolved samples were then measured in the ICP-MS.

RESULTS AND DISCUSSION

Calibration of ICP-MS device

Both the actual and measured concentration values for the prepared standards of ^{232}Th and ^{238}U isotopes were compared and the error in measurement determined as shown in Figure 1. The result for prepared blank samples indicated zero background interferences that would contribute to any error in the measurements. The spikes by level standard of 5 ppb to 1000 ppb presents values compatible with high sensitivity, stability, detection limits and background equivalent concentration measurement by the equipment. The calibration parameters, therefore, validates the ICP-MS device for the measurement of up to 50 isotopes concentrations for nuclear forensic application.

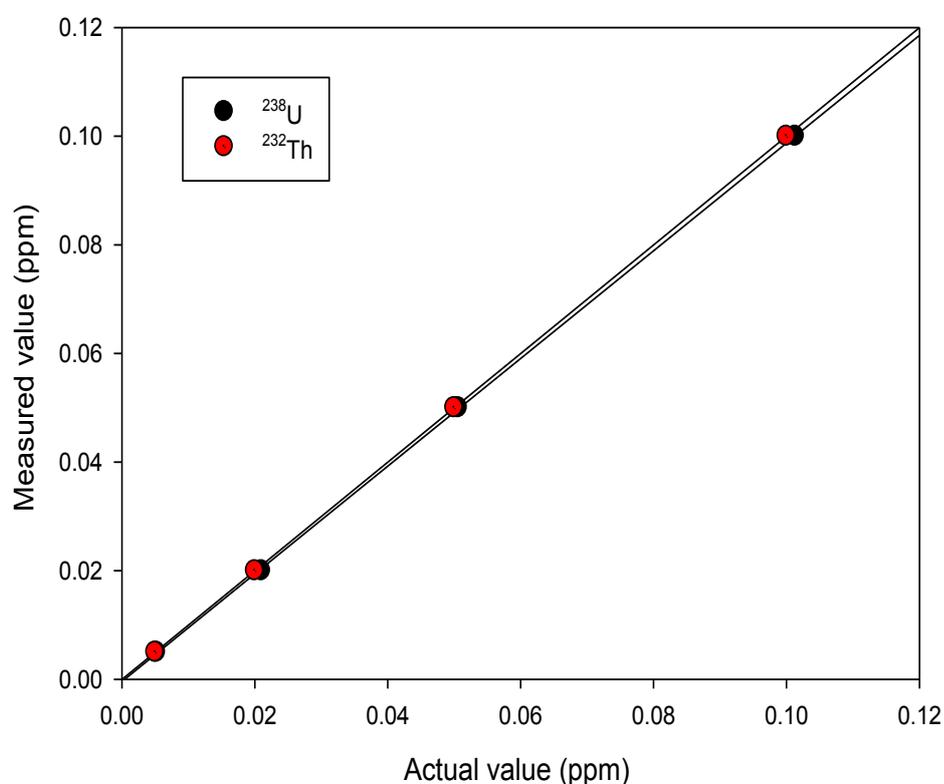


Figure 1: ICP-MS device calibration curve for ^{232}Th and ^{238}U

Ion signal intensity and concentration

The results showed that ICP-MS is capable of measuring elements with atomic mass of ranges 7 to 250, including lithium to uranium. Both lower and higher masses elements were hereby considered in this study. Higher values of ion signal intensities were recorded and the higher the signal the better masses are recorded with greater sensitivity in the mass spectrometer for accurate counting. For the four samples, a range of 233347.70 cps (from sample U003) to 241249.00 (from sample U004) was recorded, which correlated significantly with the output atomic spectra which yielded the high precision values comparable with the available standard as provided by the IAEA, 2017 and other related works, Batsala et al. (2012).

Table 1: Mean values of the ion signal intensity (cps) compared with concentration (ppb)

Sample ID	cps value	Pb cps/ppb	Th cps/ppb	U cps/ppb
U001	235080.30	52.8569	43.4496	178.3113
U002	237522.50	619.8072	4300.6070	2820.5970
U003	233347.70	112.3079	1465.7520	3.1548
U004	241249.00	1682.5850	3983.6360	30.7149

From table 1, the analysed elements with respect to the ion signal intensity to the concentration in part per billion showed a wide range of the order 52.8569 to 1682.5850 for Pb, 43.4496 to 4300.6070 for Th and 3.1548 to 2820.5970 for U accordingly. These results are consistent with the modern analytical technique requirements for the elemental analysis in the area of nuclear forensics as well as other relevant applications (IAEA, 2017; Moody et al. 2014).

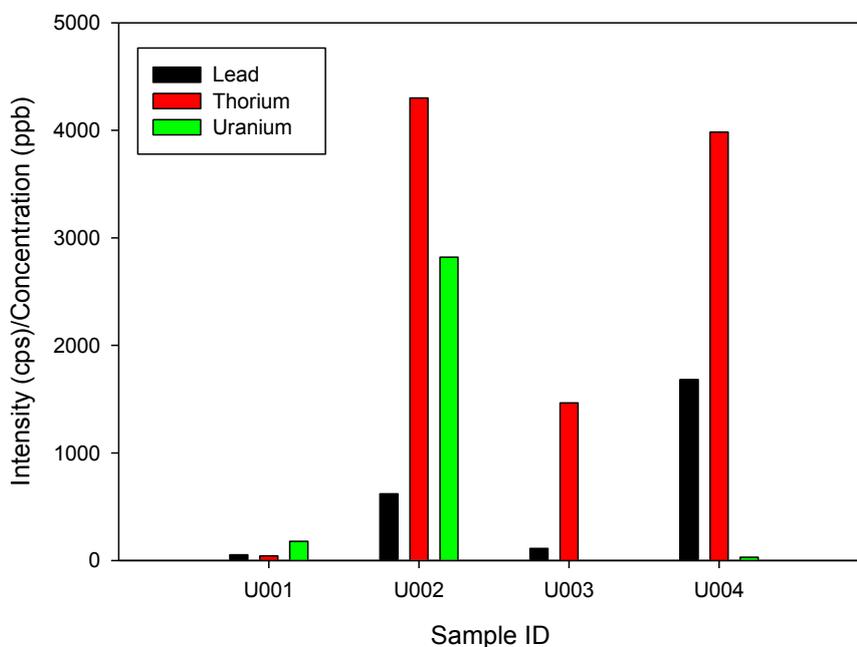


Figure 2: Graph of the ratio of ion signal intensity to concentration of the elements

From Figure 2, it can be seen that the ratio of the ion signal intensity to isotope concentration ranges between 3.2 to 4300 cps/ppb according to the calibration settings of the device and

sample preparation. An indication of low detection limit and background equivalent concentrations offered by the ICP-MS. The range is considered significantly effective to provide robust measurement of the samples. Also, sample U002 and the element thorium of mass 232 recorded the highest value then sample U003 from the element uranium with mass of 238. Implying higher mass elements are determined, which find high application in the characterisation of nuclear material in order to obtain forensic signatures for attribution. In addition, it can be seen that lower values are presented by sample U001 for the lead, thorium and uranium elements determined. The lowest value in the figure 1 can be seen as from uranium, in sample U003, which is a unique characteristic of the sample geochemical properties.

3.2 Trace elemental concentration

The result of some of the measured trace elements concentration in ppb from the uranium ore samples is presented and discussed in this section.

Table 2: Measured trace elements concentration (ppb) of the uranium ore samples

Element/ Sample ID	U001 (ppb)	U002 (ppb)	U003 (ppb)	U004 (ppb)
Be	39.1700	8.5250	41.9400	73.5450
Mg	3379.2850	674.1750	975.5100	2641.5900
Ti	2399.1000	38.5500	1393.6100	873.4900
Mn	1512.4650	327.1900	243.1050	500.5850
Co	4.0700	5.6390	12.8200	78.9800
Cu	94.2650	130.2750	255.7400	428.0900
Zn	3521.2050	365.9850	1437.4500	1665.4650
As	34.5400	2.0800	75.4400	12.4550
Rb	2147.6550	522.6250	166.0500	47.0850
Sr	186.4550	60.2150	1605.9300	484.5300
Y	1981.1750	24.9700	154.0800	64.2950
Zr	7472.0250	90.7650	1988.1050	223.9800
Ba	292.2500	518.4600	2810.3650	880.0300

Table 2 presents the concentration in ppb of some trace elements measured (using dilution factor 10%), which can be found both in the natural nuclear material as well as in nuclear fuel cycle. From the results, sample U001 has concentration range of 4.0700 ppb to 7472.0250 ppb with mean 1774.1277 ppb and standard deviation of 2065.1736. Sample U002 has range of 2.0800 ppb to 674.1750 ppb with mean 213.0349 ppb and standard deviation of 228.4583. Sample U003 has range of 12.8200 ppb to 2810.3650 ppb with a mean of 858.4727 ppb and standard deviation of 876.7293. While sample U004 has range of 12.4550 ppb to 2641.5900 ppb with a mean of 613.3938 ppb and standard deviation of 740.8347. Sample U001 can be seen to have a wider range of the concentration while sample U002 had less, of the 13 trace elements presented in table 2. These concentration values are a distinct reflection of the geochemical characteristics of the samples analysed. The range values also reflects a good and dynamic range and sensibility, which is compatible with ICP-MS analytical technique. They also present mean values that are reproducible with good accuracy, in spite of the possible effects of analyte signal suppression and spectral interferences. The concentration values determined are comparable to those from the works of Oliveira and Sarkis, (2002), who used similar technique in the analysis of uranium bearing materials.

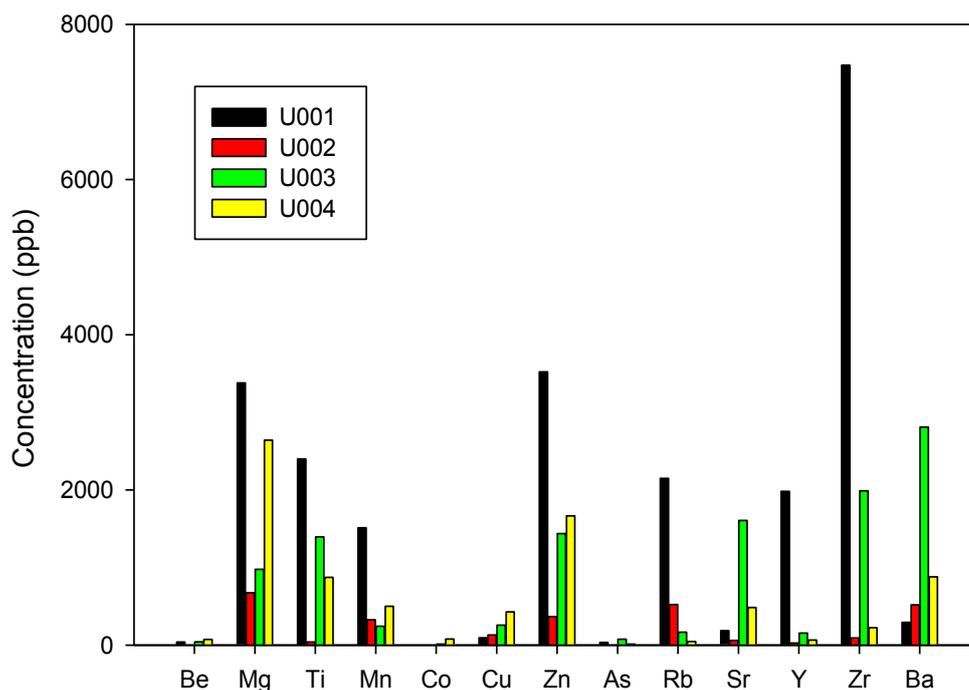


Figure 3: Graph of the concentration (ppb) of trace elements in the uranium ore samples

Figure 3 present the concentration of trace elements measured in the uranium ore samples using the ICP-MS analytical technique. It can be seen that distinct variable trace elemental concentrations are presented owing to the proficiency of the analytical technique. Sample U001 has highest concentration values of the trace elements, with Zr showing highest peak followed by Zn and Mg. least concentration values indicated by lower peaks are generally observed in sample U002 while trace elements Be, Co, As and Cu had low concentrations. Samples U003 and U004 however presented concentration peaks that lie between the first two samples and all are distinctively unique indicative of the characteristics of the sample location.

CONCLUSION

Based on the analytical procedure the determination of ion to concentration ratio as well as concentration of trace elements from uranium ore samples was achieved. The preparation of the samples was straightforward, simple and fast due to the good dynamic range and sensibility of the ICP-MS. It can be concluded that, due to the high sensitivity, low detection limit and background equivalent concentration of the ICP-MS device and technique, it has greater capability in the characterisation of nuclear and other radioactive materials for nuclear forensic application. Its availability and wide use would immensely support the enhancement of nuclear security as signature of nuclear and other radioactive materials would be obtained and included in the database.

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