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Using lead isotope ratios to distinguish between samples of diffrent uranium mines

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Abstract
In this work, a total of twenty samples selected for investigation originate from South Africa and Namibia uranium mines. The aim of this study was to determine whether the lead ratios measured in particular samples could be used to attribute the uranium sample to the production or reprocessing plant. Measurements were carried out using an inductively coupled plasma mass spectrometer PerkinElmer NexION 2000. The precision obtained for the $^{208}Pb/^{206}Pb$ ratio, the $^{207}Pb/^{206}Pb$ ratio and the $^{204}Pb/^{206}Pb$ ratio values was considerably lower than 0.02% demonstrating the applicability of the technique for Pb isotope ratio studies.

Keywords Lead isotopic ratio · Nuclear forensic signatures · ICP-MS

Introduction

Illicit trafficking of radioactive material and especially nuclear material (thorium, uranium, and plutonium) has been an issue of concern since the beginning of the 1990s, when the first seizures of nuclear material were reported to the International Atomic Energy Agency [1]. However throughout the world, nuclear and radioactive materials are used daily for beneficial purposes, in industry, medicine, agriculture and research. The use of nuclear and radioactive material generates some risk due to radiation being emitted, which is harmful to human health especially if they enter the human body even at low levels (i.e. microgram amounts) [2]. The main security concerns relating to their use, are perceived ease of access to them, the culture of personnel responsible for managing the material, and the potential for theft and construction of radiological dispersive devices (RDDs) also referred to as "dirty" bombs [3, 4].

The clear evidence of significant amount of nuclear material outside regulatory control has created international concern over the importance of maintaining global nuclear order [4]. This has resulted in the development of a new branch of science called "Nuclear Forensics" with the intent not only to identify and characterize illicit nuclear or radioactive material but also to learn more about the intended use of the seized material as well as its origin and about the potential trafficking route. [4, 5].

Applying Nuclear Forensics as a fingerprinting tool to compare with reference data allows the researcher to determine the origin, the intended use, the last legal owner and the smuggling route of the nuclear or radioactive material [6]. This makes Nuclear Forensics to be a key element of Nuclear Security.

In South Africa, the Nuclear Forensics efforts are still in a developing stage. In nuclear forensics, the isotopic composition of nuclear material aid as one of the parameters that contribute to "nuclear fingerprint" of the material and thereby provide a basis for drawing conclusions on the potential origin of the material. Nuclear fingerprinting refers to the determination of origin, mode of production from the composition of nuclear material [5]. In the context of this

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work, fingerprinting would refer to the process of identifying signatures in the nuclear fuel cycle.

Signatures are measurable attributes of nuclear fuel cycles [7]. Therefore nuclear forensic analysis is a key technical capability that utilizes signatures inherent to nuclear or other radioactive material to provide information on its source, production and history [8, 9]. This study investigates the application of lead isotopic ratios and lanthanides pattern in nuclear forensics.

Lead isotopic composition

In South Africa, the uranium is produced as a by-product of gold or copper mining [10, 11] while in Namibia uranium is directly mined from the uranium mine. The proportion of the lead isotopes is constant in nature regardless of the type of mineral or deposit in which the uranium is found [12]. Another parameter of main interest in uranium/gold mining, is the level of trace elements or impurities [13]. These trace elements are of great interest to nuclear forensics, because they can be used to attribute the uranium material to its geological source, i.e., to a uranium ore deposit type [14].

Measuring the stable isotope such as Lead (Pb) is an established technique in geolocation [6, 15]. Natural Pb is composed of four stable isotopes, and the International Union of Pure and Applied Chemistry (IUPAC) [16] reports small natural variations on the representative isotopic composition: ^{204}Pb—1.4%, ^{206}Pb—24.1%, ^{207}Pb—22.1% and ^{208}Pb—52.4%. Therefore the stable lead isotope composition gives information on the initial U/Th ratio in the ore deposits and on the age of the ore. Due to the fact that the variations in the composition for different mines are significant, investigating the stable lead isotopes can locate the original mine.

Methodology

Measurement of nuclear material is the backbone of the verification measurements in the nuclear forensics environment and thus provide clue for determination of sample origin. Measurements of nuclear material can provide information on the uranium content, as well as uranium isotopic composition in a given material. However, the measurements methods of nuclear material is an elaborate and time-consuming process. The measurements requires clean working environment to monitor the impurity levels that arise from any working procedure involved.

Samples

Samples selected for this study are water samples recovered from the mine tailings for reuse in the plant samples collected from the uranium mines areas. The water samples in this case was part of the reprocessing from the mine waste which is an intermediate step of the front end in nuclear fuel cycle. The origin for all samples used in this work cannot be revealed due to confidentiality agreements with the mines.

Samples preparation

A total of 20 water samples from two mines area were collected and used for analysis with inductively coupled plasma mass spectrometer (ICP-MS). A set of ten samples were collected from South African uranium mine area and another ten set of samples from Namibian mine area. A water sample of 5 mL each were mixed with 1 mL of 70% high purity nitric acid (HNO_3) (Sigma Aldrich, South Africa). All solutions were prepared with 18 MΩ Millipore Milli-Q system distilled water (Millipore, USA). For analysis of Pb isotope ratio, about 0.8 g of high-purity Pb metal (NIST SRM 981 standard) purchased from the National Institute of Standards and Technology (NIST) was used as a Pb isotope ratio standard. The Pb standard were dissolved in 1 M HNO_3 to prepare a stock solution.

During the analysis, quality control samples such as blanks and certified reference materials were included in the analyses. The ICP-MS were set to run a blank and a standard check at every ten samples for every set of measurement.

Instrumentation

All analyses were conducted at North-West University's Centre for Applied Radiation Science and Technology. The instrument used in this study is a NexION 2000 ICP-MS (PerkinElmer Inc., Connecticut, USA) which is equipped with a Quadrupole ion deflector that focuses the ion beam to the dual mode detector. In addition to being highly sensitive, the NexION 2000 ICP-MS uses a helium gas collision system that greatly reduces the spectral interference caused by argon and chlorine. The instrument were optimized using the automated SmartTune™ procedure. All the data acquired were processed using the Syngistix™ Nano Application Software Module (PerkinElmer Inc.). The instrumental operating conditions and signal measurement settings are summarized in Table 1.

Results

A major advantage of the ICP-MS is sensitivity and before the start of the analysis the instrument were allowed to run for 30 min following plasma ignition to reach thermal stability. For lead isotopic ratio measurement, a 20 ppb solution of NIST SRM 981 isotope ratio standard were measured for 5 replicates. The Pb NIST SRM 981 was used to

Table 1 Nexion 2000 ICP-MS instrumental operating conditions

RF frequencies	27.12 MHz
RF power	1.2 kW forward, < 10 W reflection
Outer	Argon plasma flow
Intermediate	Nebulizer flow
Central	AUX flow
Nebulizer	Meinhard type C
Spray chamber	Dual sychronic/double Scott glass chamber (ambient temperature)
Sample uptake	50 µL/min (free aspiration)
Number of sweeps	1000
Number of replicates	5
Ion energy	10,000 V
Extraction	2000 V
Typical transmission Pb	90,000 counts (cps/ppb)

MHz, Megahertz; W, watts; µL/min, microliters per minute; V, volt; cps, counts per second; ppb, parts per billion

correct the mass bias of the ICP-MS instrument used for the isotope ratio analysis. The instruments showed excellent precision as provided in Tables 2 and 3. The typical within-run precision of the isotope ratio measurement of NIST SRM 981 was less than 0.02% for ratio $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. All of the laboratory utensils used in the preparation of standard and digestion were properly washed, acid-soaked and finally rinsed with 18 MΩ Millipore Milli-Q system distilled water prior to use.

Discussion and conclusion

The aim of this study was to determine whether the lead ratios measured in particular samples could be used to attribute the uranium sample to the production or reprocessing plant. As a means of looking for variations or similarities in the measurements of South African and Namibia water samples recovered from the mine tailings for reuse in the plant, the ratios $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ were determined. In both Tables 2 and 3 the measured NIST SRM 981 and certified NIST SRM 981 [17] results are different as a results of the mass bias effect. The mass bias effect is used as a correction factor for mass bias correction. Tables 2 and 3 illustrates the data from the analyses of both South African and Namibia mine taillings and shows very interesting results. For example, the isotopic ratios $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ measurements results for South African mine are 1% less than the measured NIST SRM 981 isotope ratio standard while the Namibia mine results are 1% more than the measured NIST SRM 981 isotope ratio standard.

These results confirm that, lead isotopic ratio used for origin location do reflect significant variation within mine and thus provide valuable information about the geochemical formation and origin. The difference of both results is distinct and shows that it is possible to distinguish between South Africa and Namibia uranium samples from different sources.

The South African results are similar to those obtained by Khumalo and Mathuthu [18]. These results support and strengthen national nuclear security in deterring theft of nuclear material by nuclear terrorist for non-peaceful purposes within the country, as South Africa seek to develop and establish a national nuclear forensic library.

It is recommended that comprehensive sampling be undertaken to give the full view of the forensics signatures in different stage of the nuclear fuel cycle (cradle to grave and mining to waste characterization). However, this study has clearly demonstrated that the nuclear forensics signatures from the gold/uranium mine can be distinguished

Table 2 Results of Pb isotope ratio measurements of South African mine tailing samples

Sample ID	$^{204}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
C5W-1	0.0482	0.8159	2.0108
C5W-2	0.0484	0.8115	1.9457
C5W-3	0.0498	0.8221	2.0326
C5W-4	0.0507	0.8269	2.0349
C5W-5	0.0488	0.8144	2.0434
C5W-6	0.0488	0.8221	2.0217
C5W-7	0.0496	0.8193	1.9589
C5W-8	0.0495	0.8192	2.0331
C5W-9	0.0510	0.8304	2.0427
C5W-10	0.0487	0.8187	2.0481
Mean	0.04935 ± 0.0017	0.82005 ± 0.0194	2.01719 ± 0.0606
Measured NIST SRM 981 (this work)	0.05888 ± 0.0001	0.91441 ± 0.0036	2.17061 ± 0.0013
Certified NIST SRM 981 [17]	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

Table 3 Results of Pb isotope ratio measurements of Namibia mine tailing samples

Sample ID	$^{204}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
TSF2-1	0.0589	0.9672	2.3113
TSF2-2	0.0612	1.0153	2.4330
TSF2-3	0.0584	0.9658	2.3160
TSF2-4	0.0614	1.0148	2.4278
TSF2-5	0.0610	1.0111	2.4209
TSF2-6	0.0606	0.9993	2.4004
TSF2-7	0.0605	1.0059	2.4007
TSF2-8	0.0605	1.0045	2.4075
TSF2-9	0.0606	1.0065	2.4037
TSF2-10	0.0606	1.0020	2.3969
Mean	0.0604 ± 0.00091	0.9992 ± 0.01708	2.3918 ± 0.04078
Measured NIST SRM 981 (this work)	0.05888 ± 0.0001	0.91441 ± 0.0036	2.17061 ± 0.0013
Certified NIST SRM 981 [17]	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

using isotopic profiles and the ICP-MS PerkinElmer NexION 2000 is a good choice for isotope ratio analysis since it has very good nebulization efficiency and stability. Further improvements in precision of results may be carried out by slightly modifying the method used in this study. For example, Tl may be added to the sample as an internal standard [19].

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