Journal of Environmental Radioactivity 162-163 (2016) 172–181

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

# Applying multivariate statistics to discriminate uranium ore concentrate geolocations using (radio)chemical data in support of nuclear forensic investigations

David G. Reading [a, *], Ian W. Croudace [a], Phillip E. Warwick [a], Kassie A. Cigliana [b]

[a] GAU-Radioanalytical Laboratories, Ocean and Earth Science, University of Southampton, National Oceanography Centre, European Way, Southampton, Hampshire SO14 3ZH, UK
[b] Faculty of Humanities, University of Southampton, University Road, Highfield, Southampton, Hampshire, SO17 1BJ, UK

ARTICLE INFO

*Article history:*
Received 2 March 2016
Received in revised form
29 April 2016
Accepted 14 May 2016

ABSTRACT

The application of Principal Components Analysis (PCA) to U and Th series gamma spectrometry data provides a discriminatory tool to help determine the provenance of illicitly recovered uranium ore concentrates (UOCs). The PCA is applied to a database of radiometric signatures from 19 historic UOCs from Australia, Canada, and the USA representing many uranium geological deposits. In this study a key process to obtain accurate radiometric data (gamma and alpha) is to digest the U-ores and UOCs using a lithium tetraborate fusion. Six UOCs from the same sample set were analysed 'blind' and compared against the database to identify their geolocation. These UOCs were all accurately linked to their correct geolocations which can aid the forensic laboratory in determining which further analytical techniques should be used to improve the confidence of the particular location.



## 1. Introduction

One of the main objectives of nuclear forensic science is to investigate and determine the geographical origin (or geolocation) of illicitly recovered nuclear materials via specific characteristics that are unique to that particular specimen. The necessity and demand for such investigations is amply demonstrated by the existence of IAEA's Incident and Trafficking Database (ITDB) where 257 cases of recovered or discovered nuclear material were reported in 2014 (IAEA, 2015). Due to the confidentiality and security of the ITDB in protecting IAEA member states' declarations, it is not known how many of these incidents directly involved uranium ore concentrate (UOC). However, a limited number of studies and media reports suggest that in the last decade, several large scale trafficking incidents of UOC have been intercepted including the seizure of 324 kg of UOC in Namibia (NTI, 2012a), the seizure of 170 kg of UOC stolen from the Rossing Mine (Blake, 2011; NTI, 2012b) and the foiled attempt to sell and transfer 1000 metric tonnes of UOC to Iran (Mutua, 2015). The ability to confidently identify potential geolocations of such recovered samples rapidly and accurately is a key area of interest for nuclear forensic investigations.

This study explores the use of multivariate statistical analysis (Principal Components Analysis, PCA) using radiometric data obtained from uranium ore concentrates (UOC or "yellowcake"). Whilst PCA analysis has traditionally been applied to identify trends and groupings in data, it has rarely been employed as a discriminatory method where statistical comparisons are made between a database of signatures and the unknown to identify a single sample or family of samples (Ho Mer Lin et al., 2015; Keegan et al., 2008; Klunder et al., 2013; Lin et al., 2015; Robel et al., 2009; Švedkauskaitė-LeGore et al., 2008).

Gamma spectrometric data were selected as the investigative signature for the PCA as uranium ore milling causes radioactive disequilibrium in the uranium and thorium decay chains. Many of the associated radionuclides in these chains emit gamma photons on decay enabling observations on the extent of disequilibrium. The disequilibrium is due to the preferential leaching and precipitation of uranium from the ore feed resulting in absent or very low concentrations of other uranium and thorium progeny radionuclides in the final UOC which could be diagnostic of a particular uranium mill. This gamma spectrometric signature consists of data from $^{234}$Th, $^{234m}$Pa, $^{214}$Pb, $^{210}$Pb, $^{235}$U, $^{228}$Ac and $^{208}$Tl.

* Corresponding author.
*E-mail address:* d.reading@noc.soton.ac.uk (D.G. Reading).

http://dx.doi.org/10.1016/j.jenvrad.2016.05.013
0265-931X/

High-resolution gamma spectrometry (HRGS) is recommended by the nuclear forensics International Technical Working Group as one of the first experimental procedures that should be conducted on receipt of nuclear material for forensics investigations (Hanlen, 2011; Hutcheon et al., 2013; Kristo, 2012; Mayer et al., 2005; Wallenius et al., 2006, 2014). Therefore, the use of a statistical technique incorporating data from the first experimental procedure would enhance the investigation by providing the laboratory with an initial geolocation possibility. This information could guide the laboratory to narrow the field of geolocation options.

Gamma spectrometry is typically used in non-destructive mode and serves to preserve the sample. It can often be applied with few problems when studying homogenised samples, such as uranium fuel pellets since photon detection efficiencies can be adjusted to reflect the uniform sample density. This relationship becomes more difficult to estimate when a sample has a heterogeneous matrix such as uranium ore and UOC which typically consist of higher density uranium-bearing minerals (typically between 5 and 8.5 g $cm^{-3}$) of variable grain size dispersed within lower density mineral phases (e.g. quartz, feldspars, micas, carbonates and iron-oxides; Fig. 1).

The higher density grains in such heterogeneous matrices cause significant self-attenuation of low to medium energy (<200 keV) gamma photons ($^{210}$Pb, $^{234}$Th, $^{226}$Ra, $^{235}$U) with minor but still significant effects on high energy gamma photon such as $^{234m}$Pa (1001 keV) (Reading et al., 2015).

To accurately characterise U-ore and UOC via HRGS without the requirement for attenuation correction factors as used in environmental samples (Cutshall et al., 1983; Długosz-Lisiecka and Bem, 2013; Pilleyre et al., 2006; Sima and Dovlete, 1997), an effective and rapid preparative procedure was applied using a lithium tetraborate fusion that readily dissolves all components of the sample matrix (Croudace et al., 1998; Reading et al., 2015). The subsequent quenched glass is quickly dissolved in nitric acid resulting in a homogeneous, aqueous sample with significantly reduced self-attenuation effects with a density closer to aqueous calibration standards.

In this study a comparison between the pre- and post-dissolution gamma spectrometric data for a set of UOCs is made. This demonstrates the benefits of using lithium borate fusion to remove particle/density effects in UOCs and uranium ores. The procedure enables trends and anomalies from the uranium ore feed and milling process to be identified which might otherwise would be missed in the traditional HRGS screening of illicitly recovered UOCs.

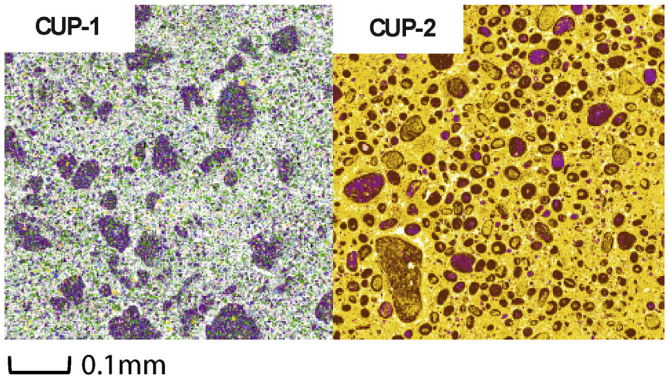


**Fig. 1.** QEMSCAN false-colour images for CCRMP certified reference materials CUP-1 (U-ore) and CUP-2 (UOC). CUP-1 agglomerations (purple) are composed of muscovite and biotite mica with silicates. The gangue is composed of feldspars, pyrite, ankerite, apatite and calcite. CUP-2 agglomerations are composed of U-carbonates (pink and brown). The surrounding matrix (yellow) is composed of other U-phases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 1.1. Uranium ore concentrates

A set of 19 UOCs were supplied by research partners at the Atomic Weapons Establishment (AWE) that represent part of a large, diverse and historical UK collection of samples originally derived from the former BNFL Springfields site (now managed and operated by Westinghouse Electric UK Ltd on the NDA's behalf). This valuable archive was catalogued, rationalised and made available to selected members of the international nuclear forensics community for R&D purposes. The names of the UOCs (derived from sources in Australia, Canada and the USA; Fig. 2) are given based on the mine site, mill site, or the company responsible for the sample production. Therefore, some similarities could be observed between UOCs as mine/mill sites were sold between companies (for example Faraday and Madawaska – see Tables 1a and b). The ore feeds for each UOC are from a variety of localities and geological settings (Table 1a and Fig. 2) and processing techniques (Table 1b).

## 2. Methodology

### 2.1. Instrumentation

Gamma emitting radionuclide activity concentrations were determined using Canberra 50% N-type HPGe well-type spectrometers. The spectra were collected using Genie 2000 acquisition software (Canberra Industries, Harwell, UK) and were analysed using Fitzpeaks spectral deconvolving software (JF-Computing, Stanford in the Vale, UK). The spectrometers were calibrated using spiked radionuclide standards throughout several geometries of varying density and composition (matrices of cellulose, water, sand, steel and boron, and a tin-tungsten ore). A mixed nuclide source (NPL, Teddington, UK) and a $^{210}$Pb solution standard (PTB, Braunshweig, Germany) were used. All samples were counted for 1 h as low detection limits and low counting uncertainty (<6% relative $^{234}$Th fused matrix and <16% relative $^{234}$Th solid matrix) were achievable with this count time.

The $^{210}$Pb activity concentrations were determined via the alpha emitting grand-daughter radionuclide $^{210}$Po that had been plated onto silver discs (Flynn, 1968) and counted using an Ortec PC alpha spectrometer system fitted with 450 $mm^2$ Ultra detectors. All measurements were made *in vacuo* for 36 h. Spectra were acquired using Maestro 7 and analysed by WinPlots 7 (AMETEK, Wokingham, UK).

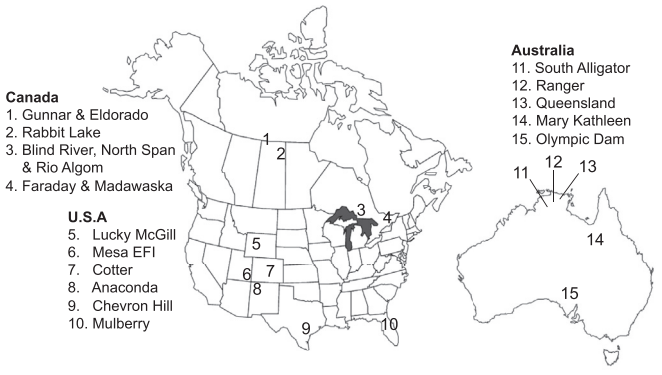


**Fig. 2.** Geographical locations of U mines and milling facilities used to manufacture the UOCs in this study.