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Instrumental neutron activation analysis in forensic science in Jamaica: The case of the Coral Springs beach theft

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ABSTRACT

Following the theft of sand from the Coral Springs beach in Jamaica, authorities approached the International Centre for Environmental and Nuclear Sciences to determine if geochemical analysis could add evidentiary value to collected sediment samples. Forty-three beach sediments comprising of scene and suspect samples were submitted for inorganic elemental investigation by neutron activation analysis. The samples were analyzed for thirty-five elements of which nine (Al, Ca, Ce, Cr, Dy, Fe, Mn, Sc and Sr) were used in statistical evaluation including agglomerative hierarchical clustering, of the dataset. Al, Fe and Sc were the elements with greatest discriminatory power. The methodology illustrated clear similarities in elemental profiles between the donor beach and some suspected receptor beaches while excluding other suspected receptor beaches and potential donor beaches. Interrogation of the dataset provided additional and important information for the authorities and indicated that neutron activation analysis with the use of multivariate statistics can contribute significantly to geoforensic investigations.

1. Introduction

The discovery of the theft of an estimated five-hundred truckloads of beach sand from the Coral Springs Beach, Trelawny in Jamaica garnered much local media attention in July of 2008 [1]. The estimated hundreds of tons of sand that were thought to have been moved spoke to a level of organization that was of note even in a country where illegal sand mining is a regular occurrence. Several months later the case started to gain international attention while still not resulting in any arrests locally [2]. It was reported that the authorities were employing various techniques to match samples of the beach in Coral Springs with several other resort areas on the north coast of Jamaica [3]. Presumably wishing to augment the discriminatory power of the methods used up to that point, the Forensics Science Laboratory, now merged with the Legal Medicine Unit to form the Institute of Forensic Science and Legal Medicine, approached the International Centre for Environmental and Nuclear Sciences (ICENS) to determine if instrumental neutron activation analysis (INAA) was an appropriate technique for the analysis of the beach samples.

Neutron activation analysis (NAA) featured quite prominently in forensics applications as early as the 1960 s when it was first used in court cases in the United States [4]. Research illustrated the many contributions this mature technique could make to forensic science [5–9]. As a chemically non-destructive, multi-element technique, with a wide linear range of measurement and that is largely matrix independent the technique had clear advantages. Furthermore, when practiced as INAA the sources of error are well understood and the case has been made that this technique should be considered a primary ratio method [10]. However as competing techniques with similar sensitivities became more available [11,12], including nuclear analytical techniques [13] that had several of the advantages of NAA but could offer additional parameters, were less expensive, more rapid and more available to forensics departments NAA was less frequently used by law enforcement.

It has been noted that INAA is well suited for the analysis of soils and sediments [14]. Several of the more sensitive techniques for geochemical analysis require digestion and those that require less or none in general do not have the requisite sensitivities [15]. With no need for chemical dissolution this technique has the added benefit of eliminating this source of error while still being very sensitive. NAA still features prominently in cases where its unique mix of analytical capabilities can aid conventional procedures to meet the needs of forensic science [16,17]. This work presents the methodology employed and the contribution made

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when INAA was used to generate geochemical data for the forensic community for the investigation of the Coral Springs beach theft.

2. Materials and methods

2.1. Sample preparation

Samples were received from the then Forensics Science Laboratory (FSL). Following obligatory chain of custody records, the samples were registered in the Sample Collection and Analysis Information System at ICENS which generates unique identification numbers for each sample as well as a sample preparation worksheet. Beach sand samples were dried at 60° C for two days in analytical ovens in the geological sample preparation laboratory at ICENS. These samples were then ground using a Fritsch Pulverisette automated agate pestle and mortar. Samples were then placed in acid-washed high density polyethylene jars and stored securely prior to irradiation.

2.2. Instrumental neutron activation analysis

Approximate masses of 0.20 g (short-lived radionuclides) and 0.25 g (intermediate and long-lived radionuclides) of soil sample were accurately weighed out in acid-washed polyethylene vials (Polyvials EP 338®) and then heat sealed. These vials were subsequently encapsulated in larger polyethylene vials (Polyvials EP 290LG®) which were also heat sealed. Samples were irradiated using the JM-1 SLOWPOKE-2 (Atomic Energy of Canada Limited, ON, Canada) at ICENS at a thermal neutron flux of $\Phi_{th} = 5 \times 10^{11}$ cm^{-2} s^{-1} for 2 min (for short-lived radionuclides) and of $\Phi_{th} = 1 \times 10^{12}$ cm^{-2} s^{-1} for 60 min (intermediate and long-lived radionuclides) [18]. The counting regime is outlined in Table 1. Samples were measured on Ortec High-Purity germanium (HPGe) coaxial gamma photon detector systems with efficiencies of 15% and 20% and resolutions of 1.8 keV and 1.9 keV at the ^{60}Co 1332 keV gamma line.

2.3. Quality control

NIST (National Institute of Standards and Technology, MD, USA) 2709 San Joaquin Soil and NIST 2711 Montana Soil were used for quality control. Reference materials were irradiated and analysed under the same conditions mentioned in Section 2.2 and in batches with the unknown samples. In the case of elements with certified reference values zeta-scores were calculated. The zeta-scores fell within the satisfactory range of ±2 (see Table 2). For non-certified elements, having no uncertainty scores, z-scores were estimated using the Horwitz function to determine the standard deviation as stated below:

$$\sigma_H = 0.02C^{0.8495} \quad (1)$$

where C is the dimensionless mass fraction of the measurand and σ_H is the standard deviation as estimated by the Horwitz function. The z-scores fell within the acceptable range of ±2 (see Table 2).

The standardization of the HPGe detectors is achieved by irradiating and counting single element standards with identical geometry as that used for samples. Sensitivity constants are generated for specific elements at a given geometry. Because of the stability of the neutron flux of the SLOWPOKE reactor and stability of the HPGe photon detector's intrinsic efficiency the sensitivity constants generated allow this version of the comparative method of INAA to be used for extended periods without the need for co-irradiation of primary standards [19].

Table 1
Irradiation and measurements conditions for the analysis of beach soil samples [18]

Irradiation flux	Irradiation time	Decay time	Acquisition time
5×10^{11} cm^{-2}s^{-1}	2 mins	10 mins	300 s
		60 mins	600 s
10×10^{11} cm^{-2}s^{-1}	60 mins	4 days	7200 s
		21 days	10,800 s

3. Results and discussion

A total of forty-three beach samples were analysed for thirty-five elements using INAA. These included Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Dy, Eu, Fe, Ga, Hf, Hg, K, La, Lu, Mn, Na, Nd, Sb, Sc, Sm, Sr, Tb, Th, Ti, U, V, Yb and Zn. Of the samples analysed twenty elements had significant percentages of results below the limit of detection of the technique and were therefore excluded from consideration for statistical analysis of the dataset. These elements included Ag, Au, Ba, Cd, Co, Cs, Eu, Ga, Hf, Hg, K, Lu, Nd, Sb, Tb, Th, Ti, V, Yb and Zn. There are several methodologies proposed for the use of values obtained below the limit of detection, also known as censored values [20,21]. Several of these substitutions methodologies can introduce significant bias and the best methodologies, those involving extrapolation, still require some assumptions of the data such as normal or log-normal distribution [22]. Substitution techniques were deemed unsuitable in this case because of the forensic and potential legal implications of the data generated. These exclusions reduced the number of identified elements to fifteen, of which nine were consistently above the limit of detection of the method and showed most discriminatory power. These were the elements considered in statistical analysis of the data and are presented in Table 3.

The sediments submitted to ICENS by the FSL were an unknown mixture of samples collected from Coral Springs beach, other potential donor beaches or alibi samples and samples that were taken from suspected receptor beaches. The original sample serial

Table 2
Quality control data for NIST 2709 San Joaquin soil and NIST 2711 Montana soil (results in μg/g unless stated).

Element	Reference value	Observed value	Zeta-score	Z-score
Al%	7.50 ± 0.06	7.51 ± 0.05	0.1	–
Ca%[1]	2.88 ± 0.08	2.78 ± 0.3	−0.3	–
Ce[2]	42	41.8 ± 0.8	–	−0.1
Cr	130 ± 4	126 ± 0.8	−1.0	–
Dy[1,2]	5.6	5.1 ± 0.4	–	-0.7
Fe%	3.50 ± 0.11	3.40 ± 0.02	−0.9	–
Mn[1]	638 ± 28	610 ± 4	−1.0	–
Sc[2]	12	11.5 ± 0.02	–	-0.4
Sr	231 ± 2	245 ± 24	0.6	–

[1] NIST 2711.
[2] Non-certified values.

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