Utilisation of the Jamaican SLOWPOKE reactor in environmental and health studies

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***Abstract*—Neutron activation analysis, using the SLOWPOKE research reactor at the International Centre for Environmental and Nuclear Sciences (ICENS), has been employed for a diverse number of applications from archaeology to forensic science. The SLOWPOKE reactor is known for its highly reproducible flux and neutron activation analysis has several inherent advantages including being chemically non-destructive, having a wide linear range of measurement and being less matrix dependent than comparable techniques. These properties have made this method of analysis appropriate for several studies including food composition analysis, dietary intake of trace elements by the Jamaican population, geochemical investigations of the coastal and marine environment and analysis of various human tissues to determine potential overexposure to toxic elements as well as deficiencies of beneficial elements. Results of these investigations have implications for human health, agriculture, trade and industry. The ability of SLOWPOKE to measure a wide range of elements in very different matrices is a distinct advantage in the environmental, food and health programmes conducted by ICENS**

***Index Terms*—Neutron activation analysis, SLOWPOKE, research reactor, food, health, Jamaica**

I. Introduction

Neutron activation analysis (NAA) is a mature technique that has made significant contributions to endeavours in inorganic chemical analysis. Even with great improvements in other analytical methods, the detection limits obtained with isotope dilution or radiochemical separation NAA are still outstanding. These separation techniques are not feasible for routine measurements but rather for verifying the accuracy of other techniques. Notwithstanding, instrumental NAA still remains a formidable analytical technique [1]. The principles are well understood and it is unlikely that there will be fundamental technological breakthroughs that will change its role dramatically. Nevertheless, improved detectors, faster electronics, automatic sample changers, and improved computer programmes for data analysis will likely contribute to incremental improvements in accuracy, detection limits, speed and convenience. INAA has the particular advantage that the method is not greatly matrix dependent and requires little sample preparation when compared to other methods of analysis. The development of very small safe low power nuclear reactors of very high flux stability to serve as the neutron source, such as the SLOWPOKE research reactor has made it possible for smaller institutions that possess neither large budgets nor large numbers of suitably qualified staff to utilize research reactors.

The SLOWPOKE-2 research reactor at the International Centre for Environmental and Nuclear Sciences (ICENS) is a light water moderated open swimming pool type reactor with a beryllium reflector. The first criticality was achieved in March 1984. In its over thirty-three years the reactor has been integral to research programs and projects in environmental geochemistry, human health and toxicological studies, food composition and land use studies. Our laboratory has taken advantage of the ability of SLOWPOKE-2 to measure a wide range of elements in very different matrices to determine the distribution and fate of both essential and potentially toxic elements in the soil-food chain. Here we present some salient aspects of INAA using the SLOWPOKE-2 reactor at ICENS that make it appropriate for various environmental and human health studies.

II. Methodology

A. Neutron Activation Analysis

The uniformity, stability and reproducibility of the neutron spectrum within the SLOWPOKE-2 core facilitates the use of activation constants (k) according to equation (1) in which m is the mass of a particular element in grams, R is the peak area, t_i, t_d, t_c, are the times of irradiation, decay, and counting respectively, and λ is the decay constant, i.e.

$$m = R \Big/ k \cdot e^{-\lambda t_d} \cdot (1 - e^{-\lambda t_i}) \cdot (1 - e^{-\lambda t_c}) \quad (1)$$

Where

$$k = \varepsilon \cdot \theta \cdot N_A \cdot \sigma \cdot \varphi \Big/ A_w \quad (2)$$

with ε = detector efficiency; θ = abundance of the activated nuclide; N_A = Avogadro's number = 6.023×10^{23}; σ = effective

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isotopic activation cross-section; φ = neutron flux in $ncm^{-2}s^{-1}$; A_w = atomic weight of the irradiated element. The irradiation regime and counting geometries for elements are standardized by irradiation of single elements standards. The sensitivity constants are recorded in tables that are used for extended periods and without the need for the co-irradiation of flux monitors or standards. This convenient standardization method has been called the improved relative (IR) method [2]. The activation constants once accurately measured on a primary spectroscopy system can be readily transferred to other spectroscopy systems using empirical measured efficiencies functions, thus reducing calibration time [3]. Optimised irradiation and measurement regimes are illustrated in Tables I and II.

B. Detection Limits

The sensitivity of NAA for a nuclide is a function of the nuclear reaction cross-section and half-life of the produced nuclide, both of which are related to the fine structure of the nucleus; the detection limit is similarly dependent upon this nuclear constant but is also dependent upon reactor and detector properties, i.e. the neutron spectrum and fluence, detector efficiency as well as the matrix. The detection limits are also a function of matrix as this largely determines the analytical peak to background ratios. The detection limits were calculated using the standard Currie definition [4] for detection limit modified for neutron activation analysis and is defined in equation (3)

$$Limit_{detection} = \left(2.71 + 3.29 \cdot \sqrt{B}\right) \cdot k \cdot \left[\left(1 - e^{-\lambda t_i}\right) \cdot \left(e^{-\lambda t_d}\right) \cdot \left(1 - e^{-\lambda t_c}\right)\right] \quad (3)$$

Where B is the background count rate under analytical peak, k is the standardization factor, ti, td, tc are the irradiation, decay and counting times respectively and λ is the analyte decay constant.

Table I Optimised irradiation conditions

Schemes	*Sample mass(g)*	*Flux x 10^{11} $ncm^{-2}s^{-1}$*	*Irradiation time*
Geological Short	0.20	2.5	2
Geological Long	0.25	10.0	60
Biological short	0.7	5.0	3
Biological long	1.0	10.	240

Table II Optimised Measurement conditions

Schemes	*First Decay*	*First count*	*Second Decay*	*Second count*
Geological Short	10 min	5 min	60 min	10 min
Geological Long	4-5 d	2 hr	21 d	5 hr
Biological short	3 min	5 min	40 min	10 min
Biological long	2-3(5*) d	3 hr	14 d	6 hr

*human and animal tissue

III. RESULTS AND DISCUSSION

Table III gives an overview of elemental concentrations obtained from the analysis of several sample types by NAA. All batches of samples irradiated are irradiated along with certified reference materials. As part of the quality control, selected reference materials wherever possible, were matrix matched to sample types. These reference materials were purchased either from NIST or IAEA and were generally within ± 20% or better of certified values [5-7].

Table IV highlights selected projects that NAA using the SLOWPOKE research reactor has been integral in generating impactful data. The island soil survey and subsequent analysis found that some soils especially those in the interior of the island associated with cretaceous inliers were elevated in elements of toxicological concern [8]. This led to further research that sought to look at the soil to plant uptake of some of these elements and to determine transfer factors [9]. This research had implications for agriculture, health and trade. Following the food chain, the bovine kidney and liver research reiterated that the presence of elevated levels of potentially toxic elements could be geographically linked to the areas that had higher soil levels of these elements especially Cd [10]. The trace element content of Jamaican as well as imported tobacco products were investigated as cigarettes are an important source of exposure to Cd as well as other potentially toxic elements [6]. Trace element research was conducted in collaboration with the medical fraternity to determine the heavy metal exposure of pregnant women especially to Hg [11]. Food intake studies were next to determine the dietary intake of beneficial and potentially toxic elements by the Jamaican population. Rice being one of the most popular foods was selected. The data generated was robust enough to discretely identify the type of rice and the location in which the crop was grown [12] (see Table IV).

Table III Concentration Ranges and detection limits for selected elements in various matrices

Element	Geological		Plants				Animal				Human			
	Soil (N = 900)_		Root Crops (N = 600)		Leafy Vegetables (N = 40)		Bovine Liver Kidney (N = 200)		Fish (N = 20)		Placenta (N = 100)		Blood (N = 80)	
	Range	D.L	Range	D.L	Range	D.L	Range	D.L	Range	D.L	Range	D.L	Range	D.L
Al	1.9 – 24 *	0.05	<0.5 - 459	0.5	353 – 3718	6	1.5 - 272	1	-	-	-	13	-	-
As	3 - 380	0.2	-	0.01	0.02 – 0.97	0.02	0.1 – 1.4	0.07	-	-	-	0.1	-	-
Au (ppb)	<5 - 64	5	0.5 – 2.0	0.01	0.4 – 40	0.1	-	0.4	-	-	-	1	-	-
Br	4 - 148	0.4	0.28 - 19	0.03	0.1 – 450	0.06	3 - 356	0.15	-	-	15.4 - 80	0.2	-	-
Ca	0.2 – 28*	0.3	<40 - 3980	40	1.3 - 3.75	44	<12 - 2360	12	-	-	1126 - 32480	450	-	-
Cd	0.3 - 1000	2	0.06 - 4	0.05	<0.1 – 151	0.1	<0.4 - 449	0.4	-	-	<0.4	0.4	-	-
Co	1 - 105	0.3	-	0.04	0.14 - 2.51	0.01	0.08 – 0.9	0.01	0.06 – 0.16	0.02	0.06 - 0.2	0.015	-	-
Cr	31 - 1100	7	<0.1 - 3	0.1	0.16 – 12	0.1	0.3 - 4	0.1	0.1 – 2.9	0.15	0.2 - 96	0.2	<0.01 – 0.14	0.01
Cs		0.4	<0.004 - 0.2	0.004	<0.01 - 0.6	0.01	0.003 - 1.8	0.001	0.01 – 0.35	0.001	0.002 - 0.075	0.002	-	-
Eu	0.4 - 12	0.1	-	0.002	0.01	0.01	-	0.001	-	0.001	<0.002	0.002	-	-
Fe	1.3 – 22*	0.04	7 - 59	4	14 - 300	10	116 - 1250	6	16 - 98	5	494 - 3166	7	520 - 1080	15
Hg	-	1	-	0.05	-	1	<0.02 - 0.18	0.02	0.1 - 24	0.02	0.02 – 0.3	0.02	-	-
K (%)	0.01 - 3	0.002	0.47 - 2.3	0.01	0.1 – 15	0.01	0.7 - 1.3	0.04	-	-	0.8 - 1.3	0.05	-	-
La	4 - 302	0.3	-	0.01	0.1 – 7	0.03	0.009 - 0.4	0.005	-	-	<0.07	0.007	-	-
Mg	<0.5 – 3.7*	0.1	200 - 900	150	4470 – 9997	110	745 - 2410	450	-	-	-	750	-	-
Mn	10 – 7500	3	1 - 15	0.3	76 – 678	0.4	2.9 - 4480	1.5	0.1 - 4	-	<0.3 - 8	0.3	-	-
Na	0.02- 2.8*	0.0004	6.9 - 630	1	13 – 4242	1	6160 - 11233	2	-	-	0.9 - 1.4	4	-	-
Rb	<50 -	50	0.9 - 312	0.2	0.5 – 81	0.5	3 - 98	0.3	1 - 16	-	11 - 22	1.4	-	-
Sc	5 – 64	0.04	-	0.01	0.001 - 0.9	0.01	-	0.02	-	0.02	<0.001	0.001	-	-
Se	-	7	<0.04 - 0.13	0.04	<0.05 - 0.7	0.05	0.2 - 10	0.1	1 - 10	0.1	0.9 - 1.4	0.2	0.16 – 0.3	0.1
Sm	0.85 – 49	0.01	-	0.01	0 - 0.7	0.01	-	0.01	-	0.1	<0.002	0.002	-	-
Sr	80 – 700	50	<2 - 7	2	<6 – 616	6	<4 - 11	<4	7 - 80	3	<2.8	2.8	-	-
Th	1.9 – 39	1	-	0.004	0.06 - 0.9	0.01	-	0.05	-	0.02	<0.009	0.009	-	-
Ti	0.13 – 2.0*	0.1	-	10	76 – 199	30	-	0.1	-	0.1	-	0.1	-	-
U	1.6 – 25	0.3	-	0.02	<0.02 - 0.5	0.02	<0.05 - 0.6	0.05	-	0.05	<0.05	0.05	-	-
V	29 – 793	15	-	0.5	0.8 – 6	0.1	-	0.5	-	0.5	-	0.5	-	-
Zn	75 - 936	45	5 - 23	0.4	9 – 222	1.5	10 - 254	0.7	11 - 290	0.5	49 - 87	1.8	10 - 22	1.9

Table IV Selected environmental and human health Projects and associated remarks

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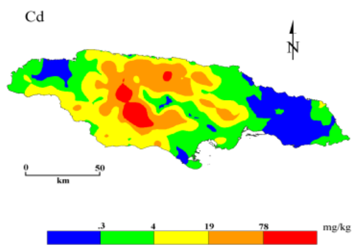
<td>
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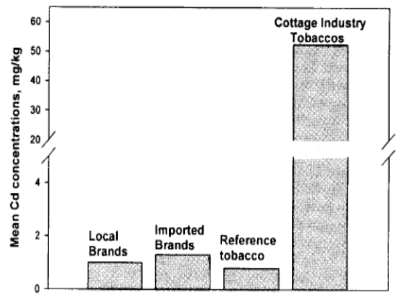
<td>Soil

An island wide soil survey found that some Jamaican soils, especially the bauxitic soils that overlie White Limestone geological group, are enriched in several heavy metals compared with world levels [8]. The soil cadmium levels in particular are up to a thousand times higher than the world averages.</td>
<td>
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<td>Tobacco
Fresh samples of Jamaican tobacco, artisanal cigarettes as well as locally and imported cigarettes and cigars were analysed by NAA for several trace elements. Samples from Manchester had average elemental results higher than other tobaccos including Cd but also Al, Ce, Cr, Cs, Fe, Th, U, V and Zn [6].</td>
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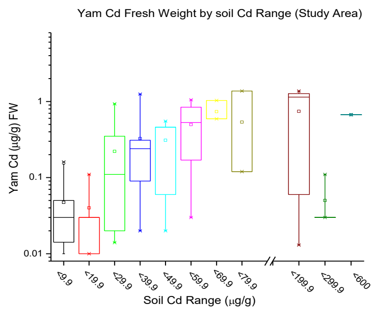
<td>
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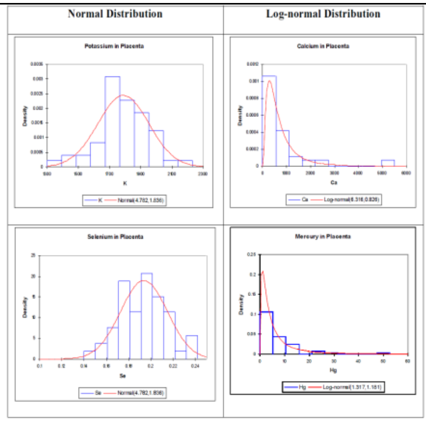
<td>Yam
Analysis of over 600 paired soil and food samples found significant soil/plant Cd correlations (R^2 >0.5); typically with soil Cd levels greater than 10 mg kg^{-1} the yams exceed the 0.1 mg kg^{-1} limit set by the EU. The precise plotting of maps showing Cd in soils and foods stratified by soil Cd concentrations. These data confirm the significant uptake of Cd by some foods and show that low-Cd products can be produced by judicious land use selection; a technically simple solution to meeting food standards. [9]</td>
<td>
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<td>Human Placenta

Placental Samples were analysed by neutron activation analysis for elements including Br, Ca, Cl, Fe, Hg, K, Na, Rb, Se and Zn. Apgar 2 scores were correlated with some elements. Consumption patterns were documented to determine mercury exposure [11].</td>
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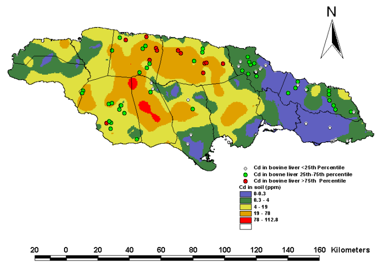
<td>
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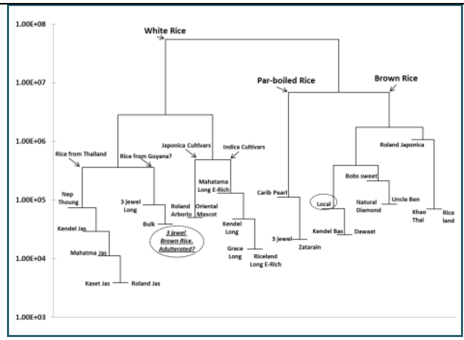
<td>Bovine Liver and Kidney
Paired liver and kidney samples from 100 free-range cattle in different parts of Jamaica were analyzed for the essential and non-essential trace elements. The map shows that the Cd levels found in cattle kidney closely followed that of the soil on which they reared. The intake of Cd from bovine liver and kidney was estimated to be 5.2µg/day based on an Island wide survey or 7% of the Provisional tolerable daily intake. [10]</td>
<td>
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<td>Rice Cluster Analysis
Market surveys of twenty rice samples were conducted. All samples were analysed by NAA for several major and trace elements. The use of cluster analysis proved to be a rapid method for the analysis of the dataset, correctly clustering rice by process, that is, polished, parboiled and brown, with sub-clusters that further identified location [12].</td>
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IV. Conclusions

The data presented here illustrates how NAA can be used to provide valuable data applicable across a wide spectrum of programmes, particularly in the earth and environmental sciences. While complementary techniques exist at ICENS that have properties that make them more suitable for particular elements or sample types than NAA, this technique has contributed greatly to almost every significant environment, food and health project that has been conducted at ICENS. The reliability and stability of the SLOWPOKE-2 reactor and breadth of elements and sample types that can be analysed using this technique means that NAA will continue to be an important tool in research activities at ICENS.

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