Application of Pseudocyclic INAA to Determine Se, Sc, and Dy in Ghanaian Fishes Using GHARR-1

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Pseudocyclic Instrumental Neutron Activation Analysis, INAA, was applied in the determination of Se, Sc, and Dy in *Selene* Dorsalis, *Pomadasys* peroteti, *Brachydenterus* aurita, *Selar* crumenophthalmus, *Sargocentron* hastatus, *Dactylopterus* volitans, *Hemiramphus* balao, *Auxis* thazard, *Pagellus* belloti, *Citharicthys* stampflii, *Neorossia* caroli, *Scomber* japonicus, *Calappa* pelii, and *Decapterus* rhonchus. All these marine fishes were selected from Biriwa, Cape Coast and Elmina in the Central region of Ghana. In this technique, thermal neutrons were employed. 94.7% accuracy was achieved by analyzing International Atomic Energy Agency (IAEA) Reference Materials (RM). The *Relative standardization* method was used in the quantification of all the elements. Dy, Se and Sc were significantly registered in *Pomadasys* peroteti, *Dactylopterus* volitans, *Hemiramphus* balao and *Scomber* japonicus. The daily intake of Se for seven out of the fourteen fishes, which represent 50%*; Selar* crumenophthalmus, *Hemiramphus* balao, *Pagallus* belloti, *Citharicthys* stampflii, *Decapterus* rhonchus, *Scomber* japonicas, and *Dactylopterus* volitans were found to be in agreement with the Recommended Dietary Allowance (RDA) for both males and females. Sc and Dy, which are not vital trace elements and also do not have RDAs, were also present in varying quantities in all the fourteen fishes. *Calappa* pelii registered the highest daily intake of Dy 997µg/d, whilst *Selene* dorsalis registered the least daily intake of Dy 39µg/d. The intake of Sc for *Pagellus* belloti (2.59µg/d) was the highest as even *Auxis* thazard registered the least daily intake of Dy with 0.06µg/d.

1. Introduction

Due to the high cost in raring small ruminant, "bush meat", poultry, pork, beef, milk, and egg, most Ghanaians prefer taking fish as their source of protein other than taking meat. It is also easier to get fish from the sea especially for people staying along the coast. Therefore, fish is the chief source of protein in Ghana [1]. The public awareness of foot-and-mouth disease, mad cow disease and the bird influenza has also influenced the dietary habit in favor of fish [2]. The consumption of fish in Ghana is higher, i.e., average consumption of fish is 22kg/capita/year [3], than that of meat, i.e., 1.08kg for beef, 0.70kg for small ruminants and poultry meat, 0.49kg for pork, 1.46 litres of milk, and 18.9 eggs per year by 2000, which represents about 6.7% of the average for Africa and only 2% of FAO recommendation [3].

Aside the protein obtained from fish, it is a good source of both trace and major elements. For example, [4] states that Selenium (Se) is a vital trace element and very important to good health:

- A powerful antioxidant, it keeps hemoglobin from being damaged by oxidation;
- Regenerates the liver, especially after cirrhosis;
- Protects the body from mercury, aluminum, lead, and cadmium poisoning;
- Prevents cancer, increases immune function and protects against cardiovascular diseases;
- Ensures proper fetal growth and development;
- Prevents sudden infant death syndrome;
- Improves male fertility;
- Reduces high blood pressure.

These diseases occur in areas where selenium is low in the soil [5]. Severe deficiency of selenium over a long period can induce cancer, heart disease and low immune function [4]. Cereals, seafood and meat products are the richest sources of Se, whereas vegetables, fruits and beverages are generally low in Se [6].

Ionic sea minerals are natural sea salts containing no other added ingredients unless noted on the label, such as the activated charcoal in Cyprus Onyx™. This aids digestion and removal of impurities from the body. For example, the Alaea clay, the volcanic red clay found in our Pele Red Hawaiian™ used to make the white salts harvested from Molokai, red in colour, contains iron oxide. In addition to the elements listed above, natural sea salt contains the following trace amounts:

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Dysprosium, Scandium and other nutrients and minerals found in seawater [7].

Ionic minerals in liquid are found in electrolyte (or ionic) form [8]. Within the body, major trace minerals are found in a liquid environment (the blood stream, lymphatic, cellular, and extracellular fluids). In this condition, each mineral has a positive or negative electrical signature to essentially create a circuit to help the body move nutrients to the areas that need them the most. The electrical signatures in ionic minerals are also inextricably linked with the electrical impulses that operate in the entire nervous system [9] and [10]. These same sea-based minerals and trace nutrients have the same dynamic equilibrium as the body. In fact, sea water creates the same balance of liquid ionic signatures as healthy blood plasma and lymphatic fluid [11].

For many elements, an analytical period of as long as from days to several weeks is needed because the nuclides such as ^{75}Se (120d), ^{46}Sc (84d), ^{110m}Ag (250d), and ^{181}Hf (45d) have longer half lives. This makes the Instrumental Neutron Activation Analysis (INAA) competitive compared to other analytical techniques such as Inductively Coupled Plasma Mass Spectrometry (ICPMS). The use of the short lived nuclides of elements is preferred to their longer lived activation products, which can significantly reduce the analytical period and increase the number of samples possible to measured per day. This makes activation analysis more cost effective and comparative. Pseudocyclic Instrumental Neutron Activation Analysis (CINAA) is a technique of Neutron Activation Analysis for elemental analysis in which a sample is irradiated, decayed, counted, then irradiated with the process repeated for several times. This is done to improve the analytical precision and the detection limit for short-lived indication radionuclide.

Pseudocyclic INAA was applied in this research to determine the concentrations of ^{77}Se (17.45s), ^{46}Sc (18.75s) and ^{165}Dy (1.26min) in fishes from Cape Coast, Elmina and Biriwa, in the Central Region, Ghana. These concentrations were converted using [3], and the converted values were then compared to the Recommended Dietary Allowance of the Food and Nutrition of USA.

2. Relative Standardization

In the relative standardization method, a chemical standard (index *std*) of known mass, *W*, of the element is co-irradiated with the sample of known mass *W*. When the samples to be irradiated are short-lived radionuclide, then both the standard and sample are irradiated separately under the same conditions usually with a monitor of the same neutron flux rate, and both are counted in the same geometrical arrangements with respect to the gamma-ray energy. It is assumed that the neutron flux, cross section, irradiation times, and all other variables associated with the counting are constant for the standard and the sample at a particular sample-to-detector geometry. The neutron activation equation then reduces to

$$\rho_{sam} = \frac{\left[(P_A/t_c)\right]_{sam}\left[\rho WCD\right]_{std}}{\left[P_A/t_c)\right]_{std}.\left[WCD\right]_{sam}} \qquad (1)$$

Where $(P_A/t_c)_{std}$ and $(P_A/t_c)_{sam}$ are the counting rates for standard and sample, respectively; ρ_{std} and ρ_{sam} are the counting concentrations of the standard and the element of interest, respectively; C_{std} and C_{sam} are the counting factors for standard and sample, respectively; and D_{std} and D_{sam} are decay factors for the standard and sample respectively.

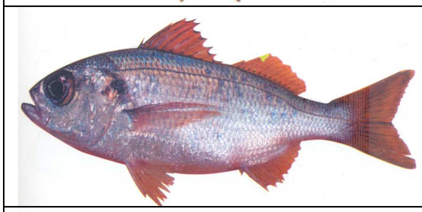
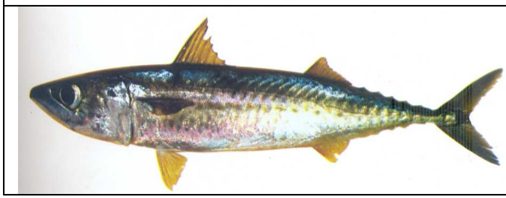
Eqn.1 can be reduced to

$$\rho_{sam} = \frac{\left[(P_A/t_c)CD\right]_{sam}W_{std}}{CD_{std}.W_{sam}SA} \qquad (2)$$

Where *SA* is defined as $\left[P_A/t_c\right]_{std}/\rho_{std}$ and is the sensitivity of the element. Using the number of counts under the photo-peak area from standardized irradiation and counting conditions, the concentration of the element of interest can be determined.

3. Fish Samples Used

Fish samples were randomly collected from Elmina habour, Biriwa landing site and Cape Coast landing sites between the months of June and September 2005. These samples are shown below.

	***Decapterus*** **rhonchus (False scad, Mackerel scad)**
	***Dactyloterus*** **volitans (Flying gurnard)**
	***Selar*** **crumenophthalmus (Bigeye scad)**
	***Selene*** **dorsalis (African lookdown/moonfish)**
	***Brachydeuterus*** **auritus (rubberlip grunt, burrito, bigeye grunt)**
	***Auxis*** **tharzard (frigate tuna)**
	***Pagellus*** **bellottii (Red pandora)**
	***Scomber*** **japonicus (Chub mackerel)**

	***Sargocentron* hastatus (Red squirrelfish)**
	***Citharicthys* stampflii (smooth flounder)**
	***Hermiramphus* balao (baloa halfbeak)**
	***Pomadasys* peroteti (Parrot grunt)**
	***Calappa* pelii (Spiny box crab)**
	***Neorossia* caroli (Carol bobtail)**

4. Experimental Procedure

Each set of the cleaned fishes was bagged in polyethylene bag and freeze dried for one week. The samples were grinded separately in an agate mortar to homogenize them into a fine powder or refined form and then sealed in a polyethylene bag. 200 mg of eight of each of the fish samples were then weighed using analytical balance. The standards samples were orchard leaf, oyster tissue and peach leaf.

In this method, the samples heat-sealed in the 7 ml capsule were repeatedly irradiated using pneumatic system of the reactor in one of the inner irradiation sites of the GHARR-1 operating at air pressure of 0.25 psi for 30sec, at this site the thermal neutron flux is 1.0 x 10^{12} n/cm^{2}S and operates at 30 kW. The irradiated samples were then delayed for 10sec and then were taken to a modern gamma measuring systems consist of a gamma detector, i.e., N-type High Purity Germanium Detector (HPGe detector) connected to a multichannel analyzer [12] and [13].

5. Qualitative and Quantitative Analysis

The qualitative analysis involves the determination of the Se, Sc and Dy in the fish samples by the identification of the spectra peaks and assigning corresponding radio-nuclides and hence the elements present.

The quantitative analysis, involves the calculation of the areas under the peaks of the identified elements and converting them into concentrations using an appropriate software or equation(s). The qualitative analysis was achieved by means of ORTEC EMCAPLUS Multi-channel Analyzer (MCA) Emulation software. The quantitative measurements were done using the concentration equation (Eqn.(1)) in an Excel programme for calculating the elemental concentrations in µg/g.

6. Results

Table 1: Daily Intake of Se, Sc and Dy from fish Samples.

Sample Codes	Se µg/d	Dy µg/d	Sc µg/d
SD	7.7±1.2	DL	0.46±0.0
LP	8±0.0	841±5.4	0.72±0.0
BA	DL	499±4.8	0.48±0.6
SC	128±3.0	350±6.0	0.36±0.0
SH	DL	205±8.4	0.55±0.0
DV	40±1.2	562±1.2	1.63±0.0
HB	125±1.2	505±1.2	0.11±0.0
AT	36±1.8	866±3.0	DL
PB	125±3.0	749±4.2	2.59±0.0
CS	100±0.6	332±1.8	1.63±0.0
NC	26±2.4	807±5.4	0.24±0.0
SJ	48±1.2	997±4.2	1.09±0.0
CG	25±0.0	254±7.4	0.60±0.0
DR	55±3.0	385±5.7	1.15±0.0

The detection limits (DL) for Dy; 39ppm, Sc; 60ppb, and Se; 11ppb. The daily intake in gram per capita for various elements was calculated using the data from [3], 22kg/capita/year.

Table 2: Recommended Dietary Allowable (RDA) and Maximum Upper Limit (UL) Infant, Children, Pregnant & lactation, Adults male and female for Se.

Life Stage Groups			Se RDA/AI µg/d	Se UL µg/d
Infants	0-6 months	(AA)	15	45
	7-12 months	(BB)	20	60
Children	1-3 yrs	(CC)	20	90
	4-8 yrs	(DD)	30	150
Pregnant Women	≤18 yrs	(AH)	60	400
	19-30 yrs	(AI)	60	400
	31-50 yrs	(AJ)	60	400
Lactation Women	≤18 yrs	(AK)	70	400
	19-30 yrs	(AL)	70	400
	31-50 yrs	(AM)	70	400
Adults Males & Females	9-13 yrs	(AB)	40	280
	14-18 yrs	(AC)	55	400
	19-30 yrs	(AD)	55	400
	31-50 yrs	(AE)	55	400
	51-70 yrs	(AF)	55	400
	>70 yrs	(AG)	55	400

(Food and Nutrition, [14])

ND = Not determinable due to lack of data of adverse effects in this age group and concern with regard to lack of ability to handle excess amounts. Source of intake should be from food only to prevent high levels of intake.

7. Discussion

Codes of fishes that were used are as follows: *Selene* dorsalis-SD, *Pomadasys* peroteti-LP, *Brachydenterus* aurita-BA, *Selar* crumenophthalmus-SC, *Sargocentron* hastatus-SH, *Dactylopterus* volitans-DV, *Hemiramphus* balao-HB, *Auxis* tharzard-AT, *Pagellus* belloti-PB, *Citharicthys* stampflii-CS, *Neorossia* caroli-NC, *Scomber* japonicus-SJ, *Calappa* pelii-CG, and *Decapterus* rhonchus-DR.

Various RDAs and UL for all life stage groups will use the following codes; infant [0-6month (AA) and 7-12months (BB)], children [1-3yrs (CC), and 4-8yrs (DD)], Male adults [9-13yrs (AB), 14-18yrs (AC), 19-30yrs (AD), 31-50yrs (AE), 51-70yrs (AF), >70yrs (AG)], Female adults [9-13yrs (AB), 14-18yrs (AC), 19-30yrs (AD), 31-50yrs (AE), 51-70yrs (AF), >70yrs (AG)], pregnant women [≤ 18yrs (AH), 19-30yrs (AI), and 31-50yrs (AJ)], and lactation women [≤18yrs (AK), 19-30yrs (AL), and 31-50yrs (AM)].)]. Asterisks (*) on each code signifies the UL for the various codes for each life stage groups. These codes will be used in the analysis and discussions.

From Table 1, SC registered the highest daily intake of Se in fish with 128µg/d, which falls within the RDA and UL for both males and females in Table 2. LP registered the least daily intake of Se, with 8µg/d and is below the RDA.

Four of the daily intake of Se from the fishes, SC (128 µg/d), HB (125 µg/d), PB (125 µg/d) and CS (100 µg/d) are above the RDA of Se with 55 µg/d for life stage groups. DR provides a comparable daily intake of Se of 55µg/d for an adult male.

The UL of Se for life stage groups AC, AD, AE, AF, and AG for males is 400µg/d, whilst that of their RDAs is 55µg/d. This signifies that, SC is a good source of Se for the life stage groups mentioned above as well as HB, PB, and CS.

CG with 997µg/d registered the highest daily intake of Dy, whilst SD with 39µg/d registered the least daily intake of Dy. With one exception, all the fishes registered an appreciable amount of Dy. Dy is one of the trace elements, which is essential but not vital, and does not have any RDA or UL. Therefore, Dy sources must be from food only.

The daily intake of Sc for PB (2.59µg/d) registered the highest. AT registered the least of the daily intake with 0.06µg/d. Sc is also another trace element, which is essential but not vital, and does not have any RDA or UL. Therefore Sc sources must be from food only.

8. Conclusion

This paper was set out to adopt Pseudocyclic Instrumental Neutron Activation Analysis to determine Selenium, Scandium and Dysprosium in fourteen fishes (*Selene* dorsalis-SD, *Pomadasys* peroteti-LP, *Brachydenterus* aurita-BA, *Selar* crumenophthalmus-SC, *Sargocentron* hastatus-SH, *Dactylopterus* volitans-DV, *Hemiramphus* balao-HB, *Auxis* thazard-*AT*, *Pagellus* belloti-PB, *Citharicthys* stampflii-CS, *Neorossia* caroli-NC, *Scomber* japonicus-SJ, *Calappa* pelii-CG, and *Decapterus* rhonchus-DR) from Cape Coast, Elmina and Biriwa using Low Power Ghana Research Reactor-1 (GHARR-1). An experiment was conducted by developing Pseudocyclic INAA, which was used to improve the detection sensitivity of short-lived radionuclides, Selenium (^{77}Se), Scandium (^{46}Sc) and Dysprosium (from the fish samples). With these methods, 94.7% accuracy was achieved by analyzing International Atomic Energy Agency (IAEA) certified standard reference materials. *Relative standardization* method was used in the quantification of all the elements.

Out of the fourteen fishes sampled, four of them (with fish codes LP, DV, HB and SJ) contain all the trace (Se, Sc, and Dy) elements.

Fifty percent (50%) of the fishes under investigation; SC (128 µg/d), HB (125µg/d), PB (125µg/d), CS (100µg/d), DR (55µg/d), SJ (48µg/d) and DV (40µg/d) show significant amounts of Se with the rest below the RDA for all life stage groups. This indicates that, marine fishes under investigation in Cape Coast, Elmina and Biriwa area can be good sources of Se.

The fish coded SH did not register any sizable daily intake of trace elements. All the daily intake trace elements under investigation in this fish were below the RDAs for all life stage groups. Therefore, daily intake of *Sargocentron* hastatus (SH) may cause malnutrition if people in the catchment area continue to take this fish for longer period.

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