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Development of Neutron Activation Analysis (NAA) protocols for NIRR-1 Irradiation and Counting Facilities after conversion to low enriched uranium (LEU) core

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Abstract

The first research reactor in Nigeria (NIRR-1) have been converted to LEU core in 2018 and characterized in 2022. The major analytical work with NIRR-1 is NAA which required development of protocols for the new LEU core. In this research, the experimental procedures for determination of over 30 elements of interest of geological and biological samples have been developed using Certified reference materials (CRM) and standard reference materials (SRM) In order to validate the experimental procedures the following standard reference materials, (IAEA-359, IAEA-336, IAEA 158, NIST 2690, and NIST1633C) were irradiated and analyzed. The concentrations in part per million (ppm) of the following elements Eu, Fe, Ga, Hf, In, K, La, Lu, Ca, Ce, Cl, Co, Cr, Cs, Cu, Mg, Mn, Na, Rb, Sb, Sc, Sm, Ta, Tb, Th, Ti, Al, As, Au, Ba, Br, Dy, U, V, Yb and Zn are in good agreement with the certified values. The capability of the technique and the facility was also validated as presented in the limit of detection (LOD).

Finally, the results of this research will serve as a database for the protocols and procedures for the use in NAA with NIRR-1 LEU core.

Keywords: NIRR-1, LEU, NAA, Irradiation and Counting Facility Standardization

Introduction

The Nigeria Research Reactor-1 (NIRR-1) low enriched uranium (LEU) core has been commissioned in 2018 at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria. NIRR-1 is tank-in-pool low power research reactor which was 1st critical in 2004 with HEU core [1-2]. The reactor was specifically designed for training and neutron activation analysis (NAA); therefore, our ability to analyze major, minor and trace elements in sample (biological and geological) have been greatly enhanced by the recent conversion from high enriched uranium (HEU) to LEU core.

In 2004, NIRR-1 was critical for the 1st time with HEU fuel enriched to over 90%. The reactor's irradiation and counting facilities were standardized for NAA in 2006 with the HEU core [2]. In 2018, NIRR-1 was converted to LEU with an enrichment of 13%.

The stability of neutron flux parameters is a clear feature of virtually all MNSR as reported by [1]. The unique feature of NAA which makes it attractive to use for routine analysis is it non-destructive nature and ability to detect many elements. These multi-element feature of NAA, it results reproducibility and it chemically independence. In this research, the experimental protocols by which sample can be analyzed were developed [1-3]. The protocols were based on sample preparation, irradiation regimes and counting scheme, which outer and inner irradiation channels neutron spectrum and radionuclide product half-life

were taking in to consideration for the adopted procedures.

Materials and Method

After conversion of NIRR-1 to LEU core with associated gamma-ray facility for radioactivity measurements and possible data acquisition system. The High-Purity Germanium (HPGe) detector with efficiency of approximately 10% with compatible software (MAESTRO) and multi-channel analyzer (MCA).

The major aim of this research is to develop method (protocols) on which NAA will be operated on by irradiating SRMs and CRMs based on two irradiation regime (short and long irradiation) putting in to consideration the capability and capacity of NIRR-1 [2-4].

Sample preparation for protocols validation

Standard reference materials (SRM) and certified reference material (CRM) where used in this research to validate the protocols of NAA in NIRR-1 new LEU core. The certified materials used are biological samples (IAEA-336, IAEA-359 and NIST-1547) and geological sample (IAEA-158, NIST-1633c, and NIST-2690). The samples were prepared as [2-1].

a) The vial and polyethylene films were prepared by soaking in HNO3 acid for 3 days and later washed with distilled water in the NAA NIRR-1 laboratory.
b) Sample was weigh and wrap in a polyethylene nylon for each sample:
i. Biological sample mass range to 0.200g to 0.300g
ii. Geological sample mass range is 0.150g to 0.200g
c) The weigh sample were then packed and sealed with in a polyethylene vial for both long and short irradiations.

Irradiation of SRMs and CRMs

The neutron flux of irradiation samples was set at 5*1011 n/cm2 s which increase the sensitivities of analysis for the activated nuclides. To determine the unknown (blank) concentrations interested elements in the samples, two irradiation schemes were adopted based on the half-lives of the product radionuclides, capability and capacity of NIRR-1. For the short-lived activation, the prepared samples each was packed and sealed in a polyethylene vial and sent for activation in the outer channel of NIRR-1 (B4) with a 'soft' neutron spectrum in other to eliminate corrections due to nuclear interferences as a result of threshold reactions [1]. Similarly, samples going for long activation were packed in a single vial and irradiated for 6 h in the inner channel of NIRR-1 (B3) for maximum thermal neutron flux exposure since the previous features of HEU is maintained in this LEU core, this is because of the proximity of the inner channels of the NIRR-1 to the core which may lead to relatively higher ratio of fast-to-thermal neutrons.

Counting of irradiated SRMs and CRMs

Measurement of the activated samples was carried out by the PC-based gamma-ray spectrometry set-up. Following the short-live irradiation regime, the activated sample was counted using far geometry 'H2' (first count) and near geometry 'H1' after a decay period (second count). The previous counting scheme for HEU core was adopted, where by the first of the activated sample was counted for 10 min (S1) after a decay period of 2–15 min [2-1]. Samples was then placed on the sample holder "H2". The second count was also carried out for 10 min, following the short-live irradiation regime (S2) after a decay period of 180 min–240 min. Samples will be counted on a glass holder "H1".

Similarly, the long-live irradiation was counted for 30 min, following the long-live irradiation (L1) using the holder 'H1' after a decay time of 4–5 days. After 10-15 days of decay period, second count was carried out for 60 min (L2) at detector geometry "H1" (table 3.2).

Table 1: New irradiation and measuring procedure for routine NAA in NIRR-1 facility.

Neutron flux/Channel	Counting Regime	Geometry	Irradiation time		Decay time	Measuring Time	Activation Products
			Geological	Biological			
$2.5*10^{11}$ n/cm^2 s/ Outer Irradiation Channel (B4)	Short first count (S1)	14.80cm (H1)	1 min.	5 min.	2-15 min.	10 min.	^{66}Cu, ^{51}Ti, ^{52}V, ^{28}Al, ^{27}Mg, ^{38}Cl, ^{49}Ca,
	Short Second count (S2)	2.20cm (H2)	1 min.	5 min.	3-4 hrs	10 min.	^{24}Na, ^{42}K, ^{165}Dy, ^{56}Mn, ^{152m}Eu
$5*10^{11}$ n/cm^2 s/ Inner Irradiation Channel (B3)	Long First count (L1)	14.80cm (H1)	6 hrs	6 hrs	3-5 days	30 min.	^{153}Sm, ^{198}Au, $^{239}Np(U)$, ^{72}Ga, ^{122}Sb
							^{24}Na, ^{42}K, ^{76}As, ^{82}Br, ^{140}La
	Long Second count (L2)	2.20cm (H2)	6 hrs	6 hrs	10-15 days	60 min.	^{152}Eu, ^{177}Lu, ^{131}Ba, ^{86}Rb, ^{182}Ta
							^{46}Sc, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs
							^{160}Tb, ^{175}Yb, $^{233}Pa(Th)$, ^{65}Zn, ^{59}Fe, ^{181}Hf

Analysis of Irradiated SRM

For data processing analysis software WINSPAN 2004 was used for identification of gamma-ray of product radionuclides through their energies for every acquired spectrum. Based on these, the software requires that calibration factors be pre-determined by a multi-element standard reference material for elements of interest using adopted irradiation and counting regimes. In addition to NAA calculations, WINSPAN 2004 performs peak analysis, remote control of the MCA and other auxiliary functions such as efficiency calibration, and nuclear data generation as we venture to determine in this current research.

Determination of limit of detection (LOD) (minimal detection level (MDL))

NAA technique can detect element at very low trace level. The determination of lowest concentration level of the activated sample is referred to as the limit of detection (LOD) or minimal detection level (MDL). The ability to detect the elements of interest in the activated sample shows the applicability of NAA technique. The lower the detection limit of a technique the better the technique becomes [4].

The LOD is increased by increasing the neutron flux which also increase the probability of having good minimum detectable activity (MDA). The ability of a detector to measure lower activities concur with small LOD. These means that, element's LOD is proportional to the detector's MDA for the irradiated nuclide(s) of that element and S/N. Better quality detector with better efficiencies and lower S/N will give better NAA result with lower LOD.

Similarly, longer counting period gives better MDA because the MDA is based upon the probability of interaction of emitted gamma energy with the active medium of a detector. The LOD of the technique can determine from following formula [5].

$$L_d = \frac{4.75\sqrt{\sum_{i=i_0-l}^{i_0+l} A_i}}{\gamma * \varepsilon * T_c} \quad (1)$$

Where:

Ai total count of channel i, including peak count and background count Bi.

i_o Peak location

l = n/2 = 2.5*FWHM Integral width to calculate LOD

T_c Measuring time

γ γ-ray emission probability (number of γ-rays emitted in each nuclear decay)

ε Detection efficiency for this γ-ray

L_D is the limit of detection.

Results and discussion

The certified reference materials (CRM) and standard reference materials were irradiated, counted and analyzed with WINSPAN multi-element gamma-ray software to validate the protocols as presented in table 1. Result in Table 2 present limit of detection and mean concentrations of over 30 elements within the limit of experimental errors. The deviation reported are within the uncertainties of at least three analyses replicate.

Table 2: Limit of detection and Mean concentration of biological and geological sample.

Product Isotopes	Half-live	Gamma-Energy (keV)	LOD of Samples
Na-24	14.96h	1368.6	0.00023
Al-28	2.24min	1778.99	0.08
K-42	12.36h	1524.58	0.004
Sc-46	83.81d	889.28	0.111
Ca-49	8.72min	3084.54	0.214
Cr-51	27.7d	320.98	0.639
V-52	3.75min	1434.08	7.922
Mn-56	2.58h	846.76	0.652
Fe-59	44.5d	1099.25	0.019
Co-60	5.27y	1173.2	0.695
Zn-65	243.9d	1115.55	8.329
As-76	26.32h	559.1	0.069
Br-82	35.3h	776.5	0.652
Sr-89	50.55d	909.15	47.57
Rb-86	18.8d	1076.6	0.652
Sb-122	64.8h	564.24	0.045
Cs-134	2.06y	795.85	0.28
Ba-131	11.8d	496.3	10.49
Nd-149	1.72h	211.31	0.461
La-140	40.3h	1596.21	0.063
Eu-152	13.3y	1408.5	52.22

Sm-153	46.27h	103.18	2.519
U-238	23.47m	74.66	0.024
Dy-165	2.33h	94.7	21.36
Lu-177	6.71d	208.36	2.277
Hf-181	42.4d	482.2	193.8
Th-232	22.3min	459.31	0.104

The result presented in Tables 3 and 4 were analyzed using WINSPAN software to determine the correctness of our analytical method and efficiency calibration with different matrix as in CRM and SRM certificates. Large percentage of the concentration reported in this work are in good agreement with certified value. The limit of detection reported in Table 2 for the adopted protocols gives us the ability to detect elements at very low trace level. The ability to detect the elements of interest and to measure lower activities of irradiated samples shows the applicability of NAA technique and concur with smaller LOD as presented in Table 2. That is, the lower the detection limit of a technique the better the technique becomes [4].

Table 3: Result of geological CRM and SRM samples compare with certified values in ppm

ELEMENT	NIST 2690 Conc.		NIST 1633C		IAEA 158	
	Cert. Value	This work	Cert. Value	This work	Cert. Value	This work
Mg	15300±500	16560 ± 249	4980± 520	5012 ± 246	10390±960	10854 ± 233
Al	123500±2800	126950 ± 770	132800 ± 6100	133700 ± 1070	51.8±3.4	47.0 ± 3.7
Ca	57100±1300	BDL	13650± 400	13740 ± 1855	64.9±5.8	70.4 ± 3.8
Ti	5200±100	4765 ± 329	---	7247 ± 457	4390±170	2073 ± 255
V	---	123.4 ± 5.4	286.2±7.9	288.1 ± 8.1	140.6±9.5	BDL
Mn	300	297 ± 4	---	241.8 ± 4.1	356±24	360.8 ± 5.1
Dy	---	5.8 ± 0.7	18.70±0.30	18.82 ± 1.26	---	3.25 ± 0.22
K	10400±400	10960 ± 241	17730± 660	17100 ± 274	20000±1600	22210 ± 1066
Mn	---	278.1 ± 1.9	240.2±3.4	242.6±1.9	---	363.1 ± 2.2
Sr	2000	2186 ± 121	901±56	1010±87	---	---
Na	2400±200	2522 ± 8	1707± 59	1773 ± 5	23800±1000	24090 ± 48
As	26	25.28 ± 0.21	186.2±3.0	191 ± 1	11.5±1.2	10.96 ± 0.46
Cd	---	---	0.758±0.005	BDL	0.372±0.039	BDL
La	---	65.48 ± 0.26	87.0±2.6	89.61 ± 0.27	30.2±2.2	29.98 ± 0.27
Sm	---	9.3 ± 0.03	---	19.63 ± 0.04	---	4.41 ± 0.03
Ho	---	46.1 ± 2.4	---	108.4 ± 3.3	---	18.69 ± 4.24
U	---	12.8 ± 0.23	9.25±0.45	9.029 ± 0.235	2.42±0.28	2.459 ± 0.275
Sc	17	18.09 ± 0.11	37.6±0.6	37.6 ± 0.2	8.32±0.39	8.673 ± 0.078
Cr	67	72.45 ± 4.19	258±6	258 ± 5	74.4±5.8	75.81 ± 2.88
Fe	35700±600	36170 ± 398	104900± 3900	104900 ± 629	26300±140	26860 ± 349
Co	19	19.03 ± 0.51	42.9±3.5	42.9 ± 0.7	9.2±1.1	11.68 ± 0.46
Zn	120	137.8 ± 11.3	235±14	235 ± 14	---	166.7 ± 10.3
Rb	---	68.06 ± 5.31	117.42±0.53	117.4 ± 7.4	82±10	77.08 ± 5.09
Sb	6	5.848 ± 0.123	8.56±0.29	8.56 ± 0.15	---	1.34 ± 0.08
Cs	8	9.302 ± 0.493	9.39±0.22	9.39 ± 0.63	3.73±0.34	4.001 ± 0.372
Ba	5800	6445 ± 77	1126± 33	1126 ± 55	1028±46	1060 ± 43
Eu	2	2.027 ± 0.164	4.67±0.07	4.67 ± 0.23	1.079±0.061	1.4 ± 0.1
Tb	---	1.29 ± 0.14	3.12±0.06	3.12 ± 0.21	---	---
Yb	---	4.04 ± 0.16	---	7.7 ± 0.2	2.08±0.18	1.745 ± 0.124
Lu	---	0.74 ± 0.03	1.32±0.03	1.32 ± 0.03	0.306±0.03	0.3593 ± 0.0219
Hf	8	7.223 ± 0.274	---	6.0 ± 0.3	6.23±0.4	5.383 ± 0.247
Ta	---	1.517 ± 0.149	1.58±0.03	1.58 ± 0.21	0.97±0.12	1.067 ± 0.126
Th	25	25.9 ± 0.3	23.0±0.4	23.0 ± 0.3	---	8.566 ± 0.214

Table 4: Result of biological CRM and SRM samples compare with certified values in ppm.

ELEMENT	NIST 1547 Conc.		IAEA 336 Conc.		IAEA 359 Conc.	
	Cert. Value	This work	Cert. Value	This work	Cert. Value	This work
Mg	4320±150	4320 ± 91	---	664.6 ± 57.8	2110-2210	2109 ± 86
Al	248.9 ± 6.5	249 ± 6	570-790	707.1 ± 7.1	---	169.8 ± 5.4
Cl	361±14	360 ± 16	1600-2200	1868 ± 32	---	9152 ± 73
Ca	15590±160	15600 ± 546	---	3720 ± 275	17990-19010	19210 ± 595
V	0.367±0.038	0.37 ± 0.05	1.25-1.69	1.139 ± 0.076	---	---
Cu	3.75±0.37	BDL	3.1-4.1	BDL	5.49-5.85	BDL
Mn	97.8±1.8	98 ± 1	---	58.31 ± 0.64	31.3-32.5	32.97 ± 0.53
I	0.3	BDL	---	0.6459 ± 0.0943	---	---
Na	23.8±1.6	28.91 ± 2.22	---	168.9 ± 2.4	567-601	611.4 ± 6.7
K	24330±380	24440 ± 464	1640-2040	1868 ± 120	31810-33190	33060 ± 364
Mn	---	---	56-70	60.65 ± 0.30	---	33.33 ± 0.23
Sr	53.0±5.0	57.7 ± 3.4	8.2-10.4	BDL	47.8-50.6	BDL
Na	---	52.3 ± 0.5	280-360	320 ± 1	---	629.6 ± 1.9
As	0.062±0.014	0.056 ± 0.033	0.55-0.71	0.63 ± 0.03	0.096-0.104	BDL
La	9.00	10.47 ± 0.06	0.56-0.76	0.66 ± 0.03	---	0.11 ± 0.03
Sm	1.000	1.101 ± 0.007	0.092-0.120	0.106 ± 0.003	---	0.0178 ± 0.003
Sc	0.040	0.041± 0.006	0.15-0.19	0.17 ± 0.01	---	---
Cr	1.00	1.17 ± 0.07	0.89-1.23	1.06 ± 0.28	1.24-1.36	BDL
Fe	219.8±6.8	229.4 ± 6.4	380-480	430 ± 33	144.1-151.9	158.9 ± 35.3
Co	0.07	BDL	0.24-0.34	0.29 ± 0.04	---	0.20 ± 0.05
Zn	17.97±0.53	15.06 ± 5.48	27.0-33.8	30.4 ± 3.1	37.9-39.3	32.45 ± 3.08
Br	11	12.0 ± 0.4	11.2-14.6	12.9 ± 0.5	---	7.84 ± 0.40
Rb	19.65±0.89	18.81 ± 1.08	1.54-1.98	BDL	---	2.15 ± 0.59
Sb	0.02	BDL	0.063-0.083	0.073 ± 0.017	---	0.09± 0.02
Ba	123.7±5.5	127.9 ± 2.6	5.3-7.5	BDL	10.5-11.5	BDL
Nd	7	BDL	0.42-0.78	BDL	---	---
Eu	0.17	BDL	0.019-0.027	0.023 ± 0.006	---	---
Tb	0.1	BDL	0.012-0.016	BDL	---	---
Yb	0.2	0.18 ± 0.02	0.025-0.049	BDL	---	---
Th	0.05	BDL	0.12-0.16	BDL	---	---

In this project, the protocols by which sample can be evaluated have been developed. These include minimum sample preparation for biological and geological, two irradiation regimes and four counting strategies have been adopted on the basis of the half-life of product radionuclides and the neutron spectrum parameters in the inner and outer irradiation channels of NIRR-1.

Finally, the LODs were determine using a well-defined method [6-7]. to check the capabilities of the NIRR-1 and correctness of the protocols. The count rate under peak of interest of background spectrum was compared with that of SRMs and CRMs. As presented Table 3 and 4, there is very good sensitivities in NIRR-1 facility for all elements of interest determined in this research.

Conclusions

NAA protocols for routine analysis in NIRR-1 laboratory have been developed for more than 30 elements ofbiological and geological matrices. The obtained results show a very good agreement with certified values. As can be seen the irradiation and counting protocols are comparable with that of the HEU which indicate that the conversion to LEU has compromised the utilization of NIRR-1 for NAA. The result of this work will serve as database for the protocols and procedures for the various NAA lines in NIRR-1 LEU core. All future NAA experiments will be compared to the results found in the database.

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