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T. Vasilopoulou, F. Tzika, I. E. Stamatelatos

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Large Sample Neutron Activation Analysis: Developments and Perspectives

Theodora Vasilopoulou^{1,2}, Faidra Tzika¹ and Ion E. Stamatelatos¹

¹*Institute of Nuclear Technology - Radiation Protection, NCSR 'Demokritos', 15310 Aghia Paraskevi, Athens, Greece*

²*School of Applied Mathematical and Physical Science, National Technical University of Athens, 15780 Athens, Greece*

Abstract

Most of the available analytical techniques do not comply with the need for direct trace element analysis of samples of mass exceeding the order of grams. Instead sub-sampling methods are used to obtain representative sampling of the studied material. Large Sample Neutron Activation Analysis (LSNAA) is a powerful technique, which can fulfill this need in a non-destructive way, free of sample size restrictions due to the high penetrating properties of neutrons and gamma rays in matter. However, corrections are required in order to obtain quantitative analysis results. Due to its distinct advantage to allow for the analysis of whole objects, LSNAA has found successful applications in diverse fields of science and technology. In the present study, the LSNAA method and applications representative of the capabilities of the technique are presented. Moreover, recent developments and future perspectives of the technique are discussed.

Keywords: Neutron Activation Analysis, Large Sample

1. Introduction

Neutron Activation Analysis (NAA) is a non-destructive, multi-element analysis technique with excellent sensitivity, great accuracy, precision and linearity that has found a broad range of applications. NAA offers an overall simplicity in sample preparation since no sample digestion or dissolution is employed and therefore minimizes the probability of sample contamination at the laboratory. The technique involves neutron irradiation of the sample, usually in a research reactor facility, to produce radioactive isotopes. Subsequent analysis of the radioactivity of the sample using a gamma ray spectrometry system provides quantitative and qualitative information about the elements in the sample material. In conventional NAA, the mass of analyzed samples is in the range of milligrams to grams or of a few μl to ml in volume, representing a small portion of the bulk material. Nevertheless, there are

applications, such as authenticity and provenance studies, where the analyzed objects need to be preserved intact or representative sampling from the bulk material cannot be performed. Furthermore, in the case of heterogeneous materials (for example sediments or scrap) representative sub-sampling is often a very difficult or even impossible task.

The particular advantage of NAA being non-invasive and true multi-element technique is combined in Large Sample Neutron Activation Analysis (LSNAA) with the ability to analyze bulk objects, up to several liters in volume, as a whole. Based on the fact that both neutrons and gamma rays have mean free paths of several centimetres within materials, LSNAA enables non-destructive analysis of large samples, implying a number of additional advantages. First, since there is no need for sub-sampling, the technique provides the ability to analyze materials that are too precious to remove small parts from, such as art objects. Moreover, representative sampling and homogeneity problems are less important with large sample analysis of heterogeneous materials. Furthermore, facilities having relatively low neutron flux irradiation positions (10^6 - 10^9 cm⁻²s⁻¹), e.g. thermal columns in nuclear reactors, are adequate for carrying out analysis, since the loss in neutron fluence rate is compensated by the larger mass of the sample. This means that small and medium size reactors or reactor independent irradiation facilities (isotopic neutron sources or neutron generators) could also be used. In addition, since neutron irradiation of the large sample is performed at a lower neutron fluence rate (i.e. 10^7 cm⁻² s⁻¹) than that used for the conventional NAA (i.e. 10^{13} cm⁻² s⁻¹), the residual specific radioactivity of the sample is small and the sample can be removed from regulatory control within a minimum cooling time without any further sample radioactivity concern.

The ability to analyze whole objects distinguishes LSNAA among the analytical techniques since other established non-destructive methods (i.e. XRF, PIXE) can only analyze superficial layers of the sample and therefore provide limited information over the whole volume of the object. Moreover, LSNAA is not affected by post-depositional elemental alterations [1] since the analytical information is provided from the whole volume of the bulk object and not only from the surface layers of the material.

2. Method

In LSNA the sample is irradiated in a neutron field, usually at a research reactor graphite thermal neutron column, and subsequently transferred to a gamma-ray spectrometry system to be counted either as a whole or using a scanning geometry counting configuration. Analysis of the acquired gamma spectra allows the determination of the elements present as well as the calculation of their concentration in the studied sample. Neutron source, gamma ray detector, experimental configuration and method of analysis have been optimized on the basis of the individual application and elements of interest.

Several reactors have developed or are in the procedure of developing new irradiation facilities appropriate for large sample analysis. Neutron sources used for activation range from miniature to high power reactors, neutron generators and neutron beams. Some of these facilities are listed in Table 1, based on data provided by International Atomic Energy Agency (IAEA) [2]. A schematic representation of the thermal column irradiation facility at the Greek Research Reactor (GRR-1) is shown in Figure 1.

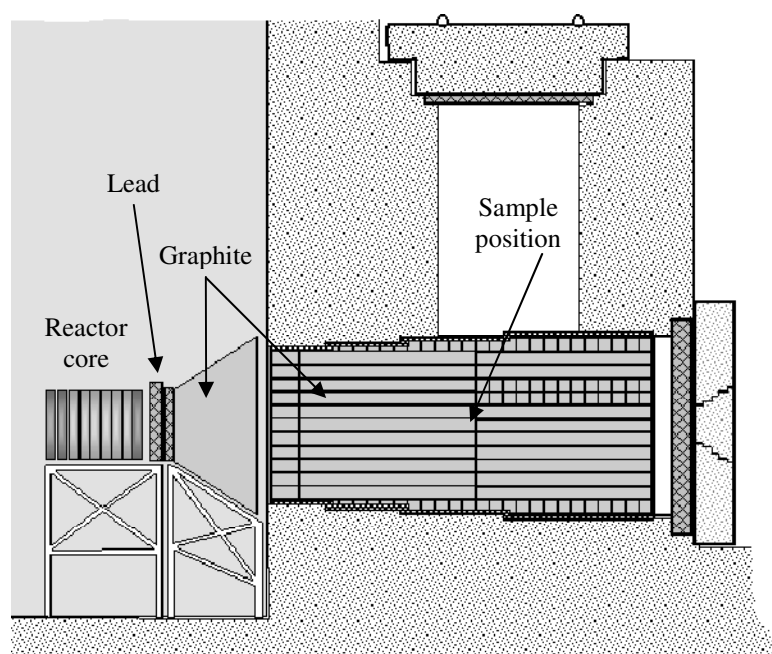


Fig. 1 Schematic representation of the GRR-1 irradiation facility (vertical cross-section)

Country	Facility available	Calibration Technique	Main Applications	Reference
Brazil	Pool	Comparative	Archaeology	[3]
China	N-generator	Comparative	Archaeology	[4]
Egypt	Thermal column	Comparative	Archaeology, Geology	[5]
Ghana	Pool, isotopic source	Comparative, k0	Archaeology, Geology	[6]
Greece	Thermal column	Comparative, absolute	Archaeology, Waste	[7]
India	Thermal column & pool	Internal monitor	Archaeology, Food, Geology, Waste	[8]
Japan	Pool	PGNAA, comparative	Extra terrestrial	[9]
Malaysia	Isotopic source	PGNAA, comparative	Archaeology, Geology	[10]
Netherlands	Thermal column & pool	k0	Biomedical	[11]
Peru	Pool	Comparative	Archaeology Pottery	[12]
Romania	Dry channel	Absolute or k0	Archaeology	[13]
Russian Federation	Dry channel & water channel	Comparative & absolute	Geology, Oil	[14]
Syrian Arab Republic	Pool	Absolute	Waste	[15]
Thailand	Thermal column & pool	Comparative & absolute	Food, Soil, Geology	[16]
USA	Pool, Thermal column cell	Comparative	Soil, Environmental	[17]

Table 1. Characteristics of the facilities used for LSNA and type of samples analyzed in each facility

Gamma spectrometry systems are usually based on High Purity Germanium (HPGe) detectors. Most of the gamma counting configurations designed to facilitate large sample measurements consist of high relative efficiency detectors surrounded by lead shielding for background radiation reduction and sample holders with rotation and vertical adjustment capabilities to allow for the scanning of the large sample. They also provide the ability to perform photon transmission measurements in order to assess the effective linear attenuation coefficient of the sample material. The GRR-1 gamma counting system used for LSNA is shown in Figure 2.

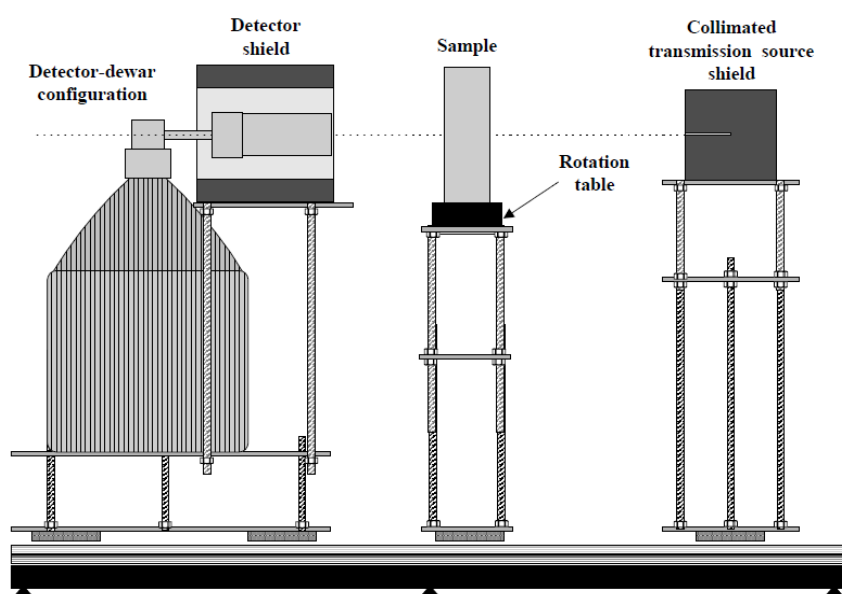


Fig. 2 Schematic representation of the GRR-1 gamma measurement facility (vertical cross-section)

The insertion of the large sample in the irradiation position (graphite pile) causes significant perturbation of the neutron field in the sample volume as well as in the vicinity of the sample, due to neutron scattering and attenuation within the sample material. Moreover, gamma counting of the activated large sample differs from that of a point source since an extended source geometry results in different detection efficiency and moreover, the attenuation of gamma rays within the sample material needs to be taken into account. Thus, in order to produce quantitative results, corrections are required for the effects of thermal neutron self-shielding during sample irradiation, self-attenuation of gamma rays, heterogeneity of the sample and geometric factor during gamma counting. These factors depend on the irradiation facility, the gamma ray detection system employed and the sample characteristics.

Several calibration techniques such as the comparative method [18] and the internal standard method [19] have been proposed. Furthermore, the theoretical modelling of the irradiation and measurement processes and the employment, in particular, of Monte Carlo simulations for the study of thermal neutron self-shielding and gamma ray attenuation within large samples have been presented [20, 21].

NCSR ‘Demokritos’ group used Monte Carlo neutron transport code MCNP to model the irradiation and counting facilities and derive the respective correction factors for a set of materials of interest for LSNA [7, 21-22]. In Figure 3 the estimated neutron self-shielding correction factor, f_n , is plotted as a function of the dimensionless parameter x_0 , which expresses the mean sample size in units of thermal neutron diffusion length in the sample material. Variable x_0 is defined to be equal to $\frac{r \times h}{(r + h) \times L}$, where r : sample radius, h : sample height, L : thermal neutron diffusion length in the sample material. Figure 4 shows the efficiency correction factor, f_γ , as a function of the dimensionless variable $\frac{\mu \times r \times h}{r + h}$, where μ is the linear attenuation coefficient of the sample material. This dimensionless variable expresses the mean sample size in units of photon mean free path within the sample material, for specific photon energy. The curves shown in Figures 3 & 4 can be used for the determination of correction factors for samples of different shapes and volumes, provided that the matrix composition or at least the main components of the sample matrix are known. Moreover, the NCSR “Demokritos” group proposed a method to predict neutron self-shielding and efficiency correction factors of unknown samples using the thermal neutron fluxes measured at the surface of the sample and the linear attenuation coefficients assessed by transmission measurements, respectively.

Advantages of the Monte Carlo approach include the better representation of the actual neutron and gamma-ray fields and the flexibility in the geometrical representation of the sample. Furthermore, the computations can easily be extended to any size, shape and material of interest. The latter is important for the analysis of objects with a non regular shape that is often the case in authentication, environmental or waste management studies.

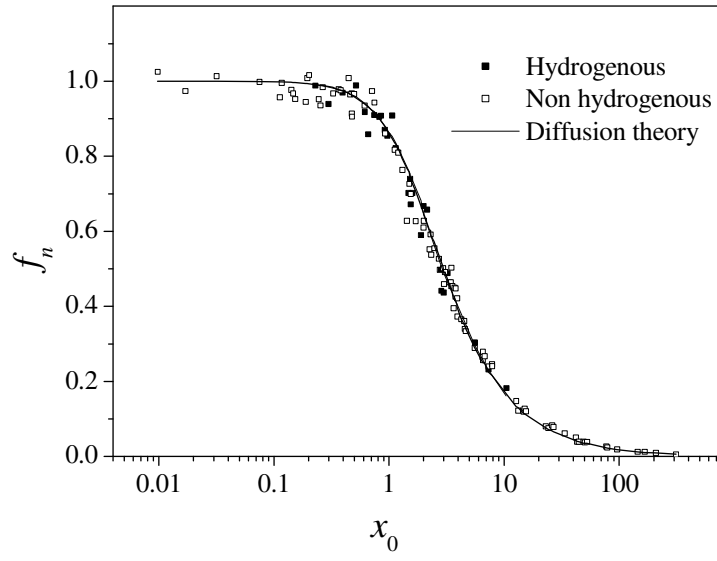


Fig. 3 Dependence of neutron self-shielding correction factor, f_n , on the dimensionless sample parameter

$$x_0 = \frac{r \times h}{(r + h) \times L}$$

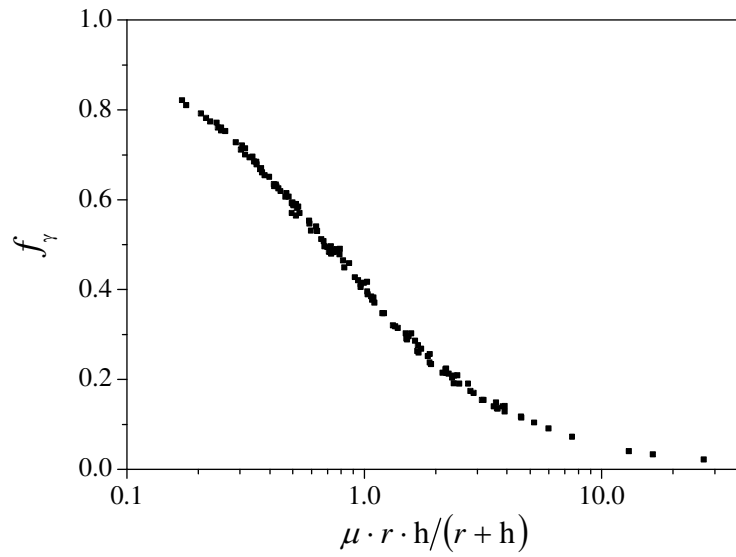


Fig.4 Dependence of efficiency correction factor, f_γ , on the dimensionless variable $\frac{\mu \times r \times h}{r + h}$

3. Applications

The numerous advantages of the technique have lead to a number of new and unique applications involving analysis of materials that are difficult to homogenize or the objective of the study does not allow grinding or mixing of components.

LSNAA has been proven particularly useful in provenance and authentication studies, where compositional profiles of individual artifacts and source materials are used in order to trace the artifacts to their place of origin. A characteristic example of the application of the technique in cultural heritage studies was the analysis of a ceramic vase representing an archaeological object [23]. The LSNAA results were compared to reference values obtained by Instrumental Neutron Activation Analysis (INAA) of small samples. As shown in Table 2, a satisfactory agreement was observed, demonstrating the feasibility of performing non-destructive whole-object analysis of valuable art pieces.

Element	Ratio LSNAA/Reference
Eu	0.70 ± 0.17
Sm	0.75 ± 0.05
Ce	0.76 ± 0.09
Sc	0.86 ± 0.05
Cr	0.86 ± 0.05
Fe	0.89 ± 0.06
Co	0.90 ± 0.06
W	0.96 ± 0.28
Ca	0.99 ± 0.15
Yb	0.99 ± 0.22
As	1.01 ± 0.17
Cs	1.03 ± 0.14
La	1.05 ± 0.06
Sb	1.20 ± 0.18
Rb	1.27 ± 0.21

Table 2. Ratio of LSNAA to Reference concentration values per studied element
(data from [23])

Other examples include provenance studies of Brazilian Tupi-Guarani tradition pottery [3] and Peruvian ceramics [12], analysis of large and non-standard

geometry archaeological samples [24], compositional studies on ancient pottery samples obtained from Buddhist sites of Andhra Pradesh in India [25] as well as authenticity identification of intact ancient Chinese porcelain ware [4].

In the field of geology, Fernandes and Bode have employed LSNA to study uranium mining waste rocks [26]. Moreover, the application of the technique for non-destructive analysis of bulky meteorite samples has been demonstrated by Islam et al [9]. A method for the evaluation of the presence of inhomogeneity and determination of the spatial distribution of radioactivity in the sample has been developed by Baas et al [27] and successfully applied for testing trace element homogeneity in Brazilian coffee beans [28].

LSNA technique has been also used in life sciences for the *in vivo* determination of elemental concentrations in small animals [29] and the analysis of large organic samples [30]. Material technology and waste characterization studies are included in the wide variety of LSNA applications. Acharya et al have employed LSNA to study irregular shape and size nuclear cladding materials of zircalloys, stainless steels and aluminum as well as large size synthetic solid and liquid samples [31-33]. Activation analysis studies of large volume electronic waste material and municipal solid waste have been reported by Segebade et al [34] and Haddad and Alsomel [15] respectively.

Furthermore, the capabilities of LSNA in the case of large inhomogeneous samples have been discussed. Vasilopoulou et al [35] demonstrated the feasibility of high-quality quantitative analysis of non-homogeneous samples using an in-house developed reference material.

4. Developments and Perspectives

Previous studies have shown that trueness of LSNA depends on the inhomogeneity of the sample material and investigated the uncertainties associated with the presence of inhomogeneities in a large sample [36, 37]. The results of these studies suggested that some *a priori* knowledge on the distribution of activity within the sample is necessary in order to perform accurate quantitative analysis. The development of a technique capable to provide such information has been presented by Vasilopoulou et al [38]. The technique was based on collimated gamma scanning to obtain the activity pattern in the sample and Monte Carlo simulations to correct the experimental data for the effect of the inhomogeneous activity distribution. The

method was experimentally evaluated in the case of a large cylindrical sample containing quartz as matrix material and a known source of radioactivity placed (a) on axis and (b) off axis. As it can be seen from Figures 5a & 5b, collimated gamma scanning enabled the precise determination of the activity distribution in the sample volume, confirming in both cases the position of the radioactive source.

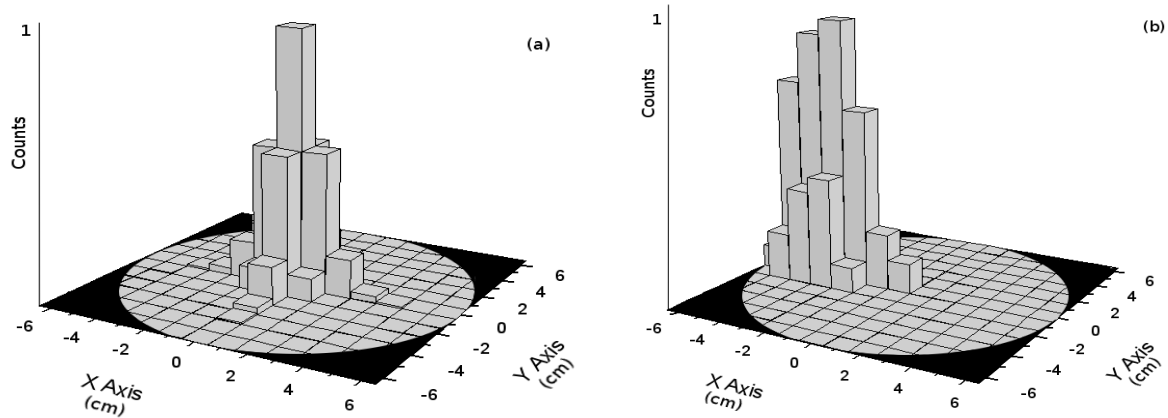


Fig. 5 Activity distribution obtained for the two source cases studied (a) on axis and (b) off axis
(plot corresponding to the vertical layer of maximum activity)

The results of the calculations were then combined with the acquired gamma spectrometry data in order to evaluate the activity of the sample. The calculated activity was compared against the reference one and an excellent agreement was observed in the case where the inhomogeneity distribution was taken into account and applied on the experimental data (Table 3).

Source	Collimator	Distribution	Evaluated to Reference activity ratio	Z-score
On axis	No	Homogeneous	0.75 ± 0.03	-5.91
	Yes	From fig. 5a	1.00 ± 0.05	0.09
Off axis	No	Homogeneous	0.90 ± 0.04	-2.41
	Yes	From fig. 5b	1.03 ± 0.06	0.59

Table 3. Evaluated to Reference activity ratio and Z-score for each of the cases studied along with their combined standard uncertainties (data from [38])

The development of the collimated scanning technique complemented and significantly extended the capabilities of LSNAА enabling high quality analysis of inhomogeneous samples. Further work could be focused on determination of detection limits, optimization of scanning procedure and image reconstruction algorithms in order to allow accurate neutron induced gamma ray tomography to be performed [39].

5. Conclusions

Unlike most of the multi-element techniques which usually analyze small amounts of material, LSNAА enables non-destructive analysis of bulk samples, up to several liters in volume, as a whole. Therefore, LSNAА is an ideal technique for analysis of precious objects and artifacts that cannot be damaged for sampling purposes as well as of inhomogeneous samples and sediments in which representative sampling cannot be performed. The ability to analyze whole objects distinguishes LSNAА among the analytical techniques since other established non-destructive methods can only analyze superficial layers of the sample and simultaneously implies a variety of applications in several fields of science and technology.

In the present work, the advantages and the new possibilities arising from the direct analysis of voluminous samples have been discussed and selected applications of the technique have been demonstrated. New improvements of the LSNAА method, such as the development of a collimated scanning technique to be used for the analysis of large samples with inhomogeneous activity distribution, were presented. It was shown that LSNAА is a powerful technique which extends the analytical tools available for compositional studies providing unique applications of non-destructive analysis of large samples and whole objects.

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