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Advances in Neutron Activation Analysis of Large Objects with Emphasis on Archaeological Examples

Results of a Coordinated Research Project

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ADVANCES IN NEUTRON ACTIVATION ANALYSIS OF LARGE OBJECTS WITH EMPHASIS ON ARCHAEOLOGICAL EXAMPLES

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RESULTS OF A COORDINATED RESEARCH PROJECT

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Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
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For further information on this publication, please contact:

Physics Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
Email: Official.Mail@iaea.org

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FOREWORD

Compositional analysis is essential in many fields of science, ranging from environmental studies and geology, to advanced technology, food, nutrition and human health. Neutron activation analysis (NAA) is a non-destructive technique, preserving the sample as received, which uses nuclear properties to arrive at elemental composition. This publication explores an innovative variation known as large sample NAA (LSNAA), which is the only way to measure the bulk mass fractions of the elements present in a large sample non-destructively (up to kilograms in mass); examples include irregularly shaped archaeological artefacts, excavated rock samples, large samples of assorted ore and finished products such as nuclear reactor components.

The IAEA, in its endeavour to encourage innovative applications of research reactors in Member States, initiated a series of meetings that culminated in a coordinated research project (CRP) on the application of LSNAA techniques for inhomogeneous bulk archaeological samples and large objects. The aim of the CRP was to harmonize LSNAA procedures and to promote their use in research on precious samples, art objects, archaeological specimens or food packets, as well as market oriented applications in (industrial) waste, foodstuff to be exported and potable water, among others.

Fifteen Member States joined the CRP from 2009 to 2012, including both newcomers and Member States with established laboratories and proven facilities. During this time, several new facilities were built and innovative approaches were developed, and it was demonstrated that trustworthy results can be obtained with LSNAA. The latter was underpinned by a unique interlaboratory proficiency testing exercise in which replicas of an intact, clay pottery art piece were distributed among the participants. The degree of agreement among the participants was good, reflecting the power of the LSNAA technique and the relative simplicity of its implementation; details of the exercise are provided in this publication. LSNAA can be applied to many matrices that have relevance in archaeology, art pieces, foodstuff and ores, and can be extended to many other materials.

The objective of this publication is to make the information on LSNAA generated during the CRP available to Member States and potential stakeholders, and to explore the technique’s advantages, limitations, and scientific and technical requirements. LSNAA methodologies and approaches are described, and unique opportunities in developing infrastructure are highlighted with case studies developed during the CRP. Recent developments and a look to the future are also included. This publication serves as a reference of interest not only to the NAA experts, research reactor personnel and those considering implementing this technique, but also to various stakeholders such as industrialists and environmental and legal experts. An international network has been established in the frame of this CRP that will contribute to future use of LSNAA.

This publication is a compilation of the main results and findings of the CRP, and the accompanying CD-ROM contains country reports with additional relevant technical details. The IAEA acknowledges the valuable contributions of individual participants and the support of the international experts in contributing to and reviewing this publication, in particular P. Bode (Netherlands) and I. Stamatelatos (Greece). The IAEA officers responsible for this publication were D. Ridikas, N. Pessoa Barradas and A. Zeman of the Division of Physical and Chemical Sciences.

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Elemental analysis is often applied to decisively distinguish whether an object is genuine, or to provide information on its provenance. Archaeologists, art historians, conservators and museum curators generally do not allow visible destruction of their valuable and irreplaceable objects by removing a portion for analytical purposes. Intact objects are sometimes analysed using X ray fluorescence spectrometry but this technique provides only information on surface layers and not on the bulk composition of an object.

However, a breakthrough in elemental analysis came in the 1990s when it was demonstrated that reactor-based neutron activation analysis (NAA), applied to large intact objects, even up to several kilograms in mass, can provide reliable information on an objects' content of major and trace elements. The feasibility of this large sample NAA (LSNAA) technique was successfully demonstrated in inhomogeneous materials that are difficult to sub-sample, as well as in homogeneous objects having irregular shapes [1–4].

Analysis of large bulk samples by nuclear techniques is applied in mining exploration since the 1960s using well-logging tools [5] in coal, cement and other industries via on-line belt industrial analysers using either neutron generators or isotopic neutron sources [6–9] and in in-vivo studies such as Ca in bones or Cd in kidneys [10]. In all of these approaches, advantage is taken of the strong penetration of the neutrons and of the resulting emitted gamma-radiation (emitted either prompt during the nuclear reaction or delayed from the activation products). The industrial applications are mainly focused on raw material analysis and for product control of one or a few major constituents. These procedures are customised for the applications they have been developed for, and cannot be translated into a routinely applicable method for the analysis of a large variety of sample types.

The advantage of reactor-based LSNAA lies with the higher neutron fluxes and activation cross sections available, all leading to better sensitivities for trace elements than can be obtained with neutron generators and isotopic neutron sources, thus providing an outlook for full multi-element analysis.

LSNAA facilities are increasingly available at research reactors worldwide because of the unique niche of this technique. Applications have been reported in a variety of fields where sub-sampling is not allowed, for instance due to the rarity or value of the original intact and whole object, or not possible because of extreme difficulties in homogenization. As such, LSNAA is not limited to archaeology or cultural heritage, and is also applied on recycled electronic waste, household waste, food commodities, components for nuclear technology, ores and minerals, to name but a few.

Analysis of large samples by NAA and/or PGA finds its niche in the areas in which:

- Sub-sampling is not allowed: LSNAA and LSPGA are the only analytical techniques for measurement of chemical elements in the bulk of anything that is irreplaceable and therefore should not be damaged by removal of a small amount for testing. Objects related to archaeology and cultural heritage were already mentioned above, but similar considerations apply in other cases, for example cosmological materials such as meteorites, or materials from forensic studies. It will be demonstrated elsewhere in

this document that these techniques even provides the opportunity for obtaining information on the spatial distribution of chemical elements inside a large object;
- Homogenization is difficult or impossible, or expensive due to material properties: Representativeness of the composition of the test portion to the sample as received may therefore be at stake. Large sample analysis is cost effective as there is no need for sub-sampling and homogenization. Traditional solutions to this problem are to analyse a large number of sub-samples, or to sort the material and to perform individual homogenizations and, subsequently, individual analyses, thereby increasing the total project costs. The homogenization step can result in contamination of the sample. The contamination due to crushing or milling is not necessarily controlled on every sample type. When processing large series of samples careful interim cleaning is time-consuming and thus expensive, and may be overlooked;
- The degree of (in)homogeneity is subject of study: This can be the case e.g. for compositional studies of (suspected) repaired cultural objects, precious mineral nuggets within ores, aggregates within concrete, sedimentation layers in (soil, sediment) drill cores, etc.

Another advantage of LSNAA/LSPGA is that no special training of personnel for handling different varieties of samples is required because there is no sample preparation. The samples can be analysed by a single set of people in one laboratory using the same equipment without any chemical separations and irrespective of mass fraction levels. As no sample pre-treatment is required in this technique, the cost for analysis and labour is greatly reduced. Thus the techniques give savings in terms of optimum use of equipment as well as of required laboratory and staff numbers. LSNAA and LSPGA would be even easier to implement when customers are interested in a fast screening method.

With the availability of large sample analysis, studies can be carried out which hitherto were hindered by the limitation of conventional trace element methods. LSNAA and LSPGA offer an opportunity to researchers in various fields of science to obtain, non-destructively, information on the composition of their objects of interest which cannot be obtained by any other analytical technique. Research reactor institutions have an opportunity for a unique positioning of such a facility offered to a wide array of stakeholders and users.

1.2. OBJECTIVE

The IAEA organized in the period 2009-2012 a Coordinated Research Project (CRP) aimed to make the LSNAA technique available to end-users from different fields. The CRP focused primarily on the application of LSNAA in the areas of archaeology and geology; however it was also open for further exploration in other areas such as industry and life sciences as well as in basic research. The CRP contributed to establish the validation of the methodology, and, in particular, it provided an opportunity for developing trained manpower. The specific objectives of this CRP were to:

- Validate and optimize the experimental procedures for LSNAA applications in archaeology and geology;
- Identify the needs for development or upgrade of the neutron irradiation facility for irradiation of large samples;
- Develop and standardize data acquisition and data analysis systems;
- Harmonize and standardize data collection from facilities with similar kind of instrumentation for further analysis and benchmarking.

This publication is one of the main outputs of the CRP. Its objective is to make the information on LSNAA generated during the CRP, and including further developments, available to Member States and potential stakeholders of the technique. It is intended to serve as the first authoritative reference on this innovative method of neutron activation analysis, of interest not only to the NAA experts, research reactor personnel and those considering implementing this technique, but also to various stakeholders such as industrialists, environmental and legal experts, and administrators.

1.3. SCOPE

The publication provides (i) examples of successful application of LSNAA and the analytical quality that can be obtained, (ii) a survey of existing facilities and approaches for LSNAA, (iii) guidance on how the technology could be implemented, (iv) developments in LSNAA that occurred after the end of the CRP and (v) an outlook for further improvements and developments.

Based on almost the same principles as NAA, prompt gamma analysis (PGA)[1] [11, 12] can also be applied to large samples (LSPGA). The emphasis in this documents lies, however, with LSNAA, which was the scope of the IAEA Coordinated Research Project (CRP) that led to the work presented here and is more commonly available in NAA laboratories worldwide.

To this end, the following topics are covered:

- Analytical quality of results: The world's first laboratory intercomparison of chemical element analysis of a large object was carried-out during the CRP, the most important effort to date to establish the degree of accuracy in LSNAA of large objects relevant to archaeological studies;
- The actual status of LSNAA in the world: Various technical and infrastructural aspects of implementing LSNAA are discussed. Indeed, there are a few infrastructural limitations to its applicability that must be considered, such as the security of the objects, the logistics of handling them, their processing and management and the ultimate free-release after completion of the analysis;
- Irradiation facilities: Usually, irradiation facilities at research reactors are designed for handling and transferring objects of a few to maximum several tens of cm^3. Irradiation of irregularly shaped samples, such as intact objects with sizes of litres and masses up to kilograms, require new facilities. The realization of such facilities depends on the reactor design (or other neutron source) and accessibility;
- Counting conditions: As in normal NAA, the induced activity is measured using semiconductor gamma ray spectrometry. However, standard sample changers and detector systems may not be suitable for large irregularly shaped objects;
- Physics and software: Physical and empirical approaches correcting for the neutron self-shielding, gamma ray self-attenuation and deviation from the point source geometry are discussed;

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[1] Note that in prompt gamma analysis the radiation is measured following the de-excitation of the compound nucleus — which often may even be a nucleus of a stable nuclide; and not the radiation from the decaying radionuclide, as in the principle of NAA. As such, the often used term 'prompt gamma (neutron) activation analysis' is, strictly speaking, incorrect and the annotation 'prompt gamma analysis' is preferred.

- Calibration: Calibration in LSNAA is not trivial. Several approaches are discussed, including the standardless method, the internal standard method, the relative method and the k_0 method for standardization [11];
- Trueness control, analytical interpretation and best measurement capability: Differently from normal NAA, the degree of trueness cannot easily be accessed by analysis of common certified reference materials (CRMs). CRMs are available as extremely homogenized (powdered) materials and thus differ fundamentally from the types of large samples measured by LSNAA. Various approaches for assessing the degree of trueness are discussed;
- Design considerations: Positioning large objects that absorb or scatter neutrons near the reactor core may have an impact to the reactor's reactivity. Similarly, positioning a large neutron absorbing object into an external neutron beam may render a significant source of prompt gamma rays. In extreme cases, radiation damage may occur. Large objects with significant activation cross sections can generate substantial amounts of induced radioactivity for relatively modest neutron exposures. This aspect is perhaps the largest safety consideration between large-sample and traditional NAA;
- The steps required for implementing LSNAA are described in detail;
- Further developments and outlook: LSNAA continued to be developed after the end of the CRP in 2012. Recent developments and opportunities for additional innovative expansion of LSNAA and LSPGA in analytical and applied research using large samples are included in this publication. It is discussed, amongst other aspects, that hybridisation with additional techniques such as X ray fluorescence, computer-aided tomography and neutron radiography/imaging can provide important compositional spatial information as input for e.g. the neutron self-shielding and gamma ray self-attenuation correction.

1.4. STRUCTURE

This report consists of this introduction, four technical sections, list of references, a bibliography containing the published output of the CRP, list of contributors to drafting and review and list of individual paper contributors together with their affiliations and individual paper titles. This publication also includes an attached CD-ROM, in which the individual reports from the countries participating in the CRP are included.

The four technical sections constitute the main part of this publication. Section 2 reports on the results achieved during the CRP, namely on the laboratory intercomparison performed. Section 3 describes the current status of development of LSNAA worldwide, including infrastructural and technical aspects such as irradiation facilities, counting conditions, physics and software, calibration approaches, quality control and design considerations. Section 4 discusses some aspects that should be considered before deciding to implement LSNAA. Finally, section 5 documents recent developments in LSNAA, and discusses the outlook of the technique.

Annex I gives some examples of stakeholder-driven use of LSNAA. These case studies constitute a collection of different approaches of LSNAA showing the versatility of the method. Annex II, with the individual reports from the countries, describes in detail the output of the participants in the CRP, their driving forces, approaches and accomplishments. This covers a wide variety of reactor-types, instrumentation approaches, broad range of samples and materials, as well as different methodologies for correction and calibration.

2. CRP EXPERIMENTAL METHODOLOGY AND RESULTS ACHIEVED

2.1. INTRODUCTION TO ANALYTICAL QUALITY OF LSNAA

Various modes of LSNAA have been implemented during the CRP, with different approaches for applying all necessary corrections resulting from the size difference of the objects studied and the ideal point source geometry. By definition, large samples refer to test portions larger than the usual size practised in NAA, which ranges from about 100 mg to about 300 mg.

Two interlaboratory comparisons have been implemented during the CRP on the following materials:

- A large, intact and irregularly shaped object of known element composition of approximately 20 cm height and 0.75 kg mass;
- Powdered pottery samples with approximately 5 g mass.

Both examples reflect the opportunities of LSNAA: sample masses of 5-1000 g can be beneficial for compensating low neutron fluxes; intact objects of e.g. one or more kilogram cannot be analysed by other techniques other than NAA (and PGA) for their bulk element content. The availability of both materials was facilitated with the help of the Peruvian Institute of Nuclear Energy (IPEN), one of the participants in the CRP.

2.2. EXPERIMENTAL METHODOLOGY

2.2.1. Large object preparation

The samples used for these tests were replicas of a pseudo Peruvian archaeological pottery object, being a free recreation of a pottery subject of the Mochica Culture (see Figure 1). The approximated dimensions were about 110 mm wide and 210 mm high.

A set of 20 nominally identical replicas were prepared by the same Peruvian artisan, from a well homogenized and fine-textured paste (clay + tempering agent). The prepared replicas had an average mass of 720±30 grams. Because of Peruvian legal regulations against illicit traffic of cultural objects, each replica was examined prior exportation by experts of the Peruvian Ministry of Culture and received a certificate stating that the examined replica is not part of the Peruvian Cultural Patrimony. Each participant received one replica and was asked to analyse it, using the method developed in their laboratory. A spreadsheet form was sent to each participant, providing a uniform template to report the measurement results and associated combined standard uncertainties, as well as complementary information. This complementary data included general information about the laboratory, description of the analytical methodology and of the estimation of uncertainties, and specific quality assurance and quality control (QA/QC) aspects.

FIG. 1. Replica of a pseudo Mochica style pottery used as entire sample for the LSNAA intercomparison.

2.2.2. Small sample reference analysis

IPEN has participated since 2011 in the Proficiency Testing by Interlaboratory Comparison of NAA laboratories. This testing mechanism is implemented by the IAEA in conjunction with the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) [13]. IPEN has demonstrated consistently the high degree of trueness of its NAA results.

As such, the participants in the CRP agreed that IPEN would provide reference data on the elemental composition of the material of the replicas by analysis of small amounts thereof. Before the distribution of the large samples, about 1 gram of material was scraped from different parts of each replica and collected in separate vials. The contents of each vial were carefully homogenised and kept for the analysis. Eleven vials were chosen at random, and their contents were analysed by k_0-based NAA [14].

Two test portions of about 250 mg each were taken from each vial and weighed into smaller polyethylene vials. These small vials were irradiated for 20 minutes, together with similar vials containing known amounts of a sodium containing compound, acting both as flux monitor and comparator for the standardization based on the k_0 constants. The irradiations were performed with the pneumatic transfer system of the 10 MW Peruvian RP-10 nuclear research reactor, at a thermal flux of 1.9×10^{13}cm^{-2} s^{-1} and epithermal flux of 3.2×10^{11}cm^{-2}s^{-1}.

After a decay time of 5 days, a first measurement of the samples was performed for 5000 to 6000 s, using a gamma ray spectrometer equipped with a CANBERRA GC 1518 HPGe detector (relative efficiency: 15%; FWHM: 1.8 keV at 1332.5 keV ^{60}Co). The flux monitors/comparators were measured for 1000 s after 6 days of decay in an identical geometry. Under these conditions ^{76}As, ^{42}K, ^{140}La, ^{24}Na, ^{239}Np, ^{122}Sb, ^{153}Sm, and ^{175}Yb were measured. A second measurement was carried out after 15–17 days decay for 10000 s with another CANBERRA HPGe detector (relative efficiency: 70%, FWHM: 1.9 keV at 1332.5 keV ^{60}Co). The nuclides measured were ^{131}Ba, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{177}Lu, ^{147}Nd, ^{86}Rb, ^{46}Sc, ^{85}Sr, ^{182}Ta, ^{160}Tb, and ^{233}Th.

Test portions of the reference material Old Ohio Red Clay [15, 16] were used for quality (trueness) control of the procedure. The degree of trueness of the analysis results of this Old Ohio Red Clay was independently verified by analysis of NIST SRM 1648 Urban Particulate Matter [17].

2.2.3. Large sample analysis

Ten laboratories (from Netherlands, Romania, Greece, Egypt, Russia, India, Thailand, Brazil, Peru and USA) reported their measurement results using LSNAA. The laboratory in Brazil took both homogenized 200 mg samples and about 5 g subsamples from the vase. The laboratory in India analysed also small amounts of material scraped off the vase for measuring the Na content, which serves as an internal standard in their LSNAA methodology. The laboratory in Japan reported data for traditional small sample NAA using subsamples taken of the pottery objects.

The experimental conditions and the technical description of the irradiation and gamma counting facilities used are given in Section 3.2 and experimental details are given in the individual country reports in Annex 2.

2.2.4. Powdered material preparation

A piece of pottery made of a well homogenized and fine-textured paste (clay together with a tempering agent) was available at IPEN, Peru. It should be noted that this was a preparation from a batch different from the one used for preparing the large object described in paragraph 2.2.3, and, from a methodological point of view, it would have been preferable to use clay from the same pottery used in the intercomparison.

A fragment of this piece of pottery was sent to the NAA laboratory of the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN), in Belo Horizonte, Minas Gerais, Brazil. The fragment was powdered at CDTN; a 5 g sample was used for NAA analysis at CDTN; about 10 g of the material was sent to the NAA laboratory at the Jožef Stefan Institute (JSI) in Ljubljana, Slovenia for analysis at the 200 mg scale.

2.2.5. Measurement at IPEN, Peru

Small samples of about 250 mg were used for analysis and two replicate analyses were performed for each vial. The analyses at IPEN were done similar to the methodology described above under paragraph 2.2.2.

2.2.6. Measurement at CDTN, Brazil

About 5 g of powdered clay sample was sealed into a pure polyethylene vial. The sample and neutron flux monitors (IRMM-530R: Al-0.1%Au disc 6 mm in diameter and 0.1 mm high) were stacked together and fixed in the polystyrene vial and irradiated for 8 hours in the carousel facility (CF-7) of the TRIGA MARK I IPR-R1 reactor at a thermal neutron flux of 6.4×10^{11} cm^{-2} s^{-1}.

The gamma spectrometry was performed after 4, 8-11 and 30 days cooling time using an HPGe detector (CANBERRA, USA, 25 % relative photopeak efficiency for the 1332 keV gamma ray of ^{60}Co) of which an absolute photopeak efficiency curve was available.

The HyperLab (HyperLab 2002 System, 2009 [18]) program was used for net peak area evaluation. The "Cd-ratio" method for multimonitors was applied to determine f (thermal to epithermal flux ratio) and α (epithermal flux deviation from the ideal 1/E distribution) parameters. These measurements resulted in $f = 22.3$ and $\alpha = -0.002$ [19], used as input parameters to the software package Kayzero for Windows [20] which served to calculate the effective solid angle during gamma ray spectrometry as well as the elemental mass fractions.

2.2.7. Measurement at JSI, Slovenia

The moisture fraction of the clay was estimated by drying about 1 g of the sample in a ventilated oven at 105 °C until constant mass was attained. It resulted in a correction factor of 1.0162. About 180 mg of powdered (dried) clay was sealed into a pure polyethylene vial (Posthumus Plastics, Beverwijk, Netherlands). A clay sample and a standard (Al-0.1%Au alloy (IRMM-530R) disc 6 mm in diameter and 0.1 mm high) were sandwiched and fixed in the polyethylene vial and irradiated for 13 hours in the carousel facility of the Institute's TRIGA reactor at a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1}.

The induced activities of the samples were measured after 4, 8-11 and 40 days cooling time on absolutely calibrated HPGe detector (CANBERRA, USA, with 45 % relative efficiency).

The HyperLab (HyperLab 2002 System, 2002 [18]) program was used for net peak area evaluation. The "Cd-ratio" method for multimonitor was applied to measure the f and α parameters [21] resulting in $f = 28.6$ and $\alpha = -0.001$. The software package Kayzero for Windows [20] was used to calculate the effective solid angle during gamma ray spectrometry as well as for the elemental mass fractions.

For QA/QC purposes of k_0-NAA (trueness control) the certified reference material BCR-320R Channel Sediment was used.

2.2.8. Uncertainty budget

The uncertainty budget of k_0-NAA includes contributions from the following uncertainties: uncertainties published in literature for $t_{1/2}$, $\bar{E}_r$, Q_0 and k_0; uncertainties known, calculated or estimated in the irradiation, decay and measuring times; in the true-coincidence correction factor; in the mass fraction of Au in the Al-0.1%Au alloy; in the masses of the sample and the standard (Al-0.1%Au alloy); in the dry mass correction; and in the previously determined neutron flux parameters (f and α); and in the detection efficiency. The combined standard uncertainty (u_c) of the k_0-NAA in this study is calculated as:

$$u_c = \sqrt{(St.dev.)^2 + u_{method}^2} \tag{1}$$

where *St.dev.* is the reproducibility standard deviation (SD), i.e. the variability between single test results (n=5) and u_{method} is the estimated combined standard uncertainty of the contributions mentioned in the above (approximately 3.5% with a coverage factor k=1).

Measurement results and associated uncertainties are given in Table 3, and the results were based on dry sample mass.

2.3. RESULTS AND DISCUSSION

2.3.1. Large object analysis

2.3.1.1. Reference values

The results of the analysis at IPEN of the small subsamples taken from all large objects are given in Table 1. All data are rounded off in agreement with the uncertainty of measurement.

The 200 mg and 5 g small sample analysis results of the vase pottery by the laboratories in Japan and Brazil, respectively, are given in Table 2 for comparison of the degree of equivalence with the Peruvian small (250 mg) sample results.

There is excellent agreement for several elements reflected by the low *zeta* scores but also remarkable differences occur, such as the low value found in Japan for Fe and the differences in the K content. Zeta is defined as

$$zeta = \frac{x_{obs} - x_{ref}}{\sqrt{(u_{ref}{}^2 + u_{obs}{}^2)}}, \tag{2}$$

with $x_{ref,obs}$ being the reference and observed mass fractions, and $u_{ref,\ obs}$ being the measurement uncertainty of the reference and observed mass fractions (one standard deviation, k=1).

TABLE 1. RESULTS FOR SMALL SAMPLE NAA OF VASE POTTERY AND OLD OHIO RED CLAY, AND ZETA SCORE FOR OLD OHIO RED CLAY RESULTS IN COMPARISON TO REFERENCE VALUES

	IPEN results: Vase Pottery, N = 22, mg/kg	1 SD, mg/kg	IPEN results: Old Ohio Red Clay, N = 3, mg/kg	1 SD, mg/kg	Reference value Old Ohio Red Clay [15, 16], mg/kg	1 SD, mg/kg	zeta score Old Ohio Red Clay
Na	20400	600	1380	30	1400	25	-0.5
Mg	13100	700	9650	120			
Al	83000	2000	96500	1200	94500	2350	0.8
K	16600	1500	29000	2000	35200	500	-3.0
Sc	16.5	0.8	18.1	0.2	18.95	0.48	-1.6
Ti	4500	300	6500	150	5940	390	1.3
Cr	25.1	1.9	85.4	1.3	90.7	2.65	-1.8
Mn	840	20	249	4	253	4	-0.7
Fe	33500	900	48700	400	53300	7000	-0.7
Co	14.8	0.4	23	1.4	20.2	0.2	2.0
As	34	2	15.6	0.09	14.1	0.45	3.3
Rb	100	2	180	1.4	184	5.5	-0.7
Sr	420	20	N. A				
Sb	5.1	0.5	1.19	0.07	1.39	0.45	-0.4
Cs	11.4	0.3	10.2	0.12	10.6	0.35	-1.1
Ba	680	10	608	9	668	16.5	-3.2
La	25	2	48.9	1.7	50.9	1.1	-1.0
Ce	51	3	108.6	0.5	105.5	2.25	1.3
Nd	26	5	50	2	42.3	1.3	3.2
Sm	5.8	0.3	10.2	0.3	8	0.2	6.1
Eu	1.1	0.01	1.55	0.02	1.54	0.05	0.2
Tb	0.65	0.04	1.07	0.03	1.06	0.03	0.2
Yb	2.3	0.1	4.27	0.18	4.17	0.055	0.5
Lu	0.36	0.02	0.66	0.02	0.64	0.045	0.4
Hf	5.1	0.3	6.9	0.15	7.16	0.21	-1.0
Ta	0.55	0.04	1.36	0.03	1.65	0.08	-3.4
Th	10.8	0.6	14.8	0.1	15.1	0.3	-0.9
U	2.9	0.2	3.2	0.2	2.96	0.21	0.8

The results from IPEN, Peru have been used as reference values for comparison with the complete object analysis results.

3.3.1.2. Large object analysis results

The participating laboratories using LSNAA reported a total of 193 results for elements such as Na, Mg, Al, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Zn, Ga, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th and U; typically with between 2 and 10 values for each element.

TABLE 2. SMALL SAMPLE NAA RESULTS FROM PERU, JAPAN AND BRAZIL AND ZETA SCORES IN COMPARISON TO THE PERUVIAN RESULTS

	Peru small 250 mg		Japan small 200 mg			Brazil small 5 g		
Analyte	Result (mg/kg)	1 SD (mg.kg)	Result (mg/kg)	1 SD (mg/kg)	zeta	Result (mg/kg)	1 SD (mg/kg)	zeta
Na	20400	600	20400	700	0.0	22000	500	2.0
Mg	13100	700	21800	800	8.4			
Al	83000	2000	83000	4000	-0.1			
K	16600	1500	20100	500	2.2	19600	600	1.9
Ca			32700	110		32100	1600	
Sc	16.5	0.8				17.1	0.3	0.8
Ti	4500	300	4380	180	-0.3			
Cr	25.1	1.9	27	2	0.6	27.5	0.6	1.2
Mn	840	20	880	20	1.0			
Fe	33500	900	30000	400	-15.0	46600	800	1.8
Co	14.8	0.4	15.7	0.4	1.6	15.2	0.3	0.7
Zn			170	30		140	3	
As	34	2				35.3	0.5	0.6
Br	100	2				3.93	0.17	-0.3
Rb	420	20				98	2	-0.5
Sb	5.1	0.5	5.38	0.16	0.6	5.08	0.06	0.0
Cs	11.4	0.3	15.8	0.3	10.3	11.65	0.14	0.8
Ba	680	10	610	20	-2.6	592	18	-3.7
La	25	2	24.9	1.2	0.0	25.6	1.1	0.3
Ce	51	3				52	2	
Nd	26	5				25.8	1.4	
Sm	5.8	0.3	5.59	0.18	-0.6	5.08	0.11	-2.4
Eu	1.1	0.01				1.274	0.017	
Tb	0.65	0.04				0.678	0.013	
Yb	2.3	0.1				2.41	0.18	
Hf	5.1	0.3		0		5.6	0.3	
Ta	0.55	0.04				0.568	0.019	
Th	10.8	0.6	11.1	0.6	0.3	11.1	0.7	0.3
U	2.9	0.2	2.15	0.08	-4.2	3	0.3	0.1

Zeta scores were calculated from the LSNAA results in comparison to the IPEN reference small sample mass fraction values, as well as the relative differences (bias, in %) to the reference mass fraction value provided by Peru on basis of the small sample analysis of the pottery as described in paragraph 2.2.2. and given in Table 1. These results are shown for all participating laboratories in Figures 2-6. The bias is defined as

$$bias = \frac{x_{obs} - x_{ref}}{x_{ref}} * 100\% \qquad (1)$$

with $x_{ref,obs}$ being the reference and observed mass fractions.

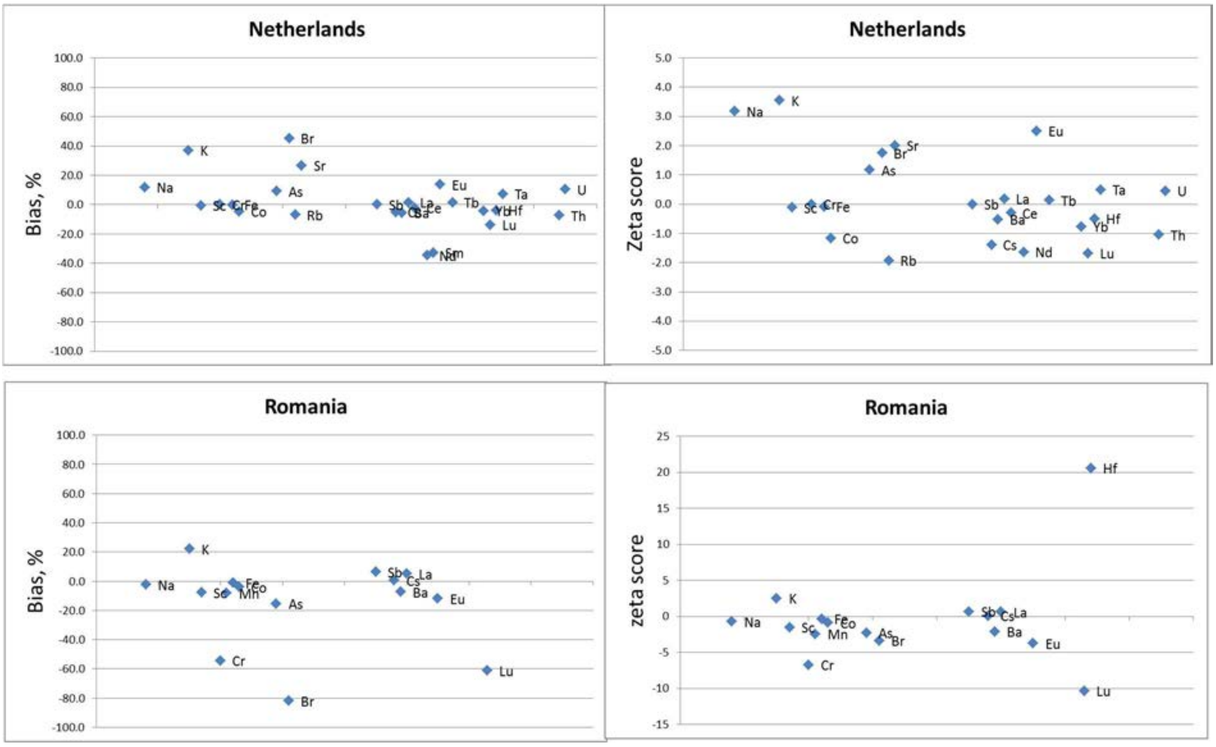

FIG 2. Relative bias and zeta scores for LSNAA results reported by participants from Netherlands and Romania.

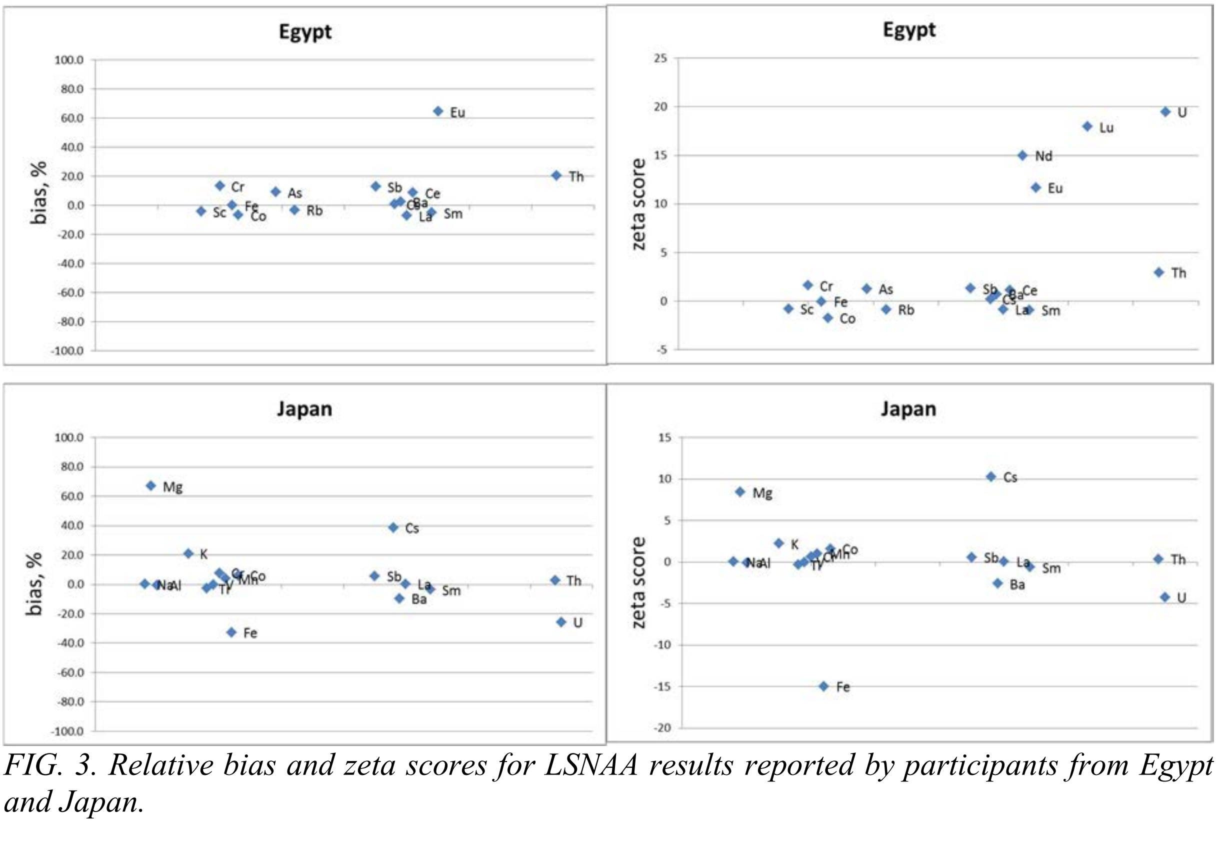

FIG. 3. Relative bias and zeta scores for LSNAA results reported by participants from Egypt and Japan.

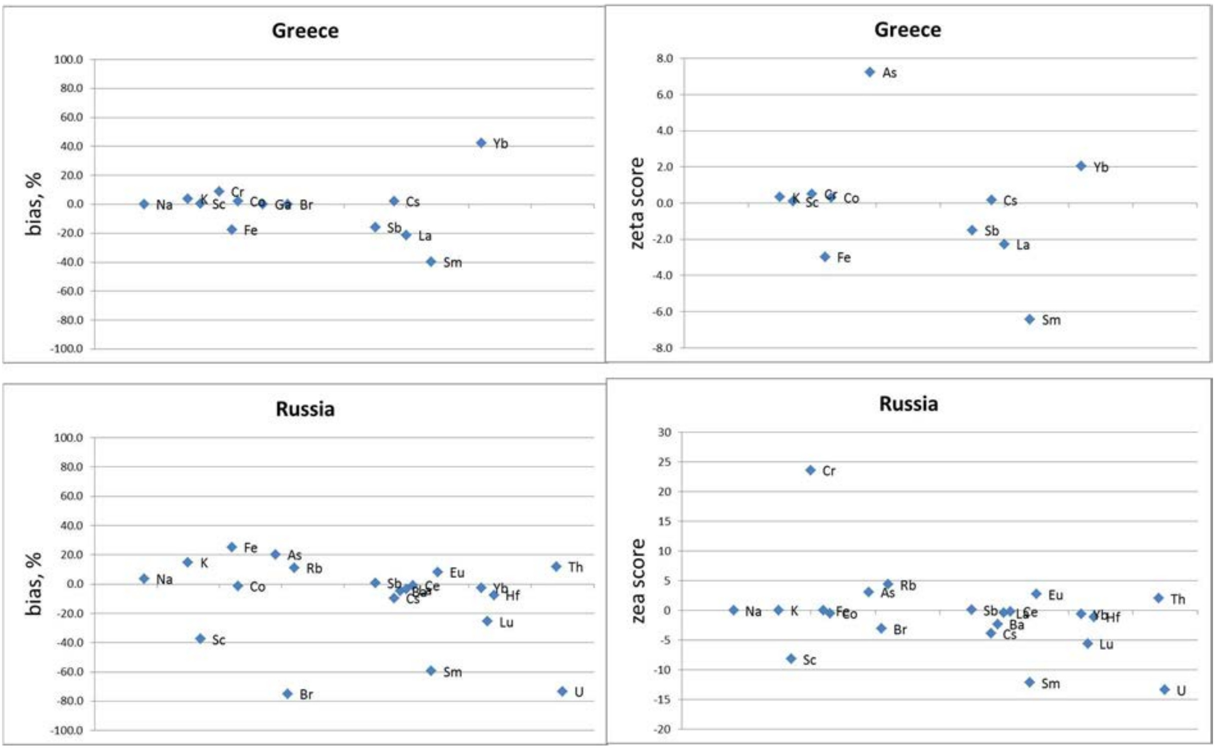

FIG. 4. Relative bias and zeta scores for LSNAA results reported by participants from Greece and Russia.

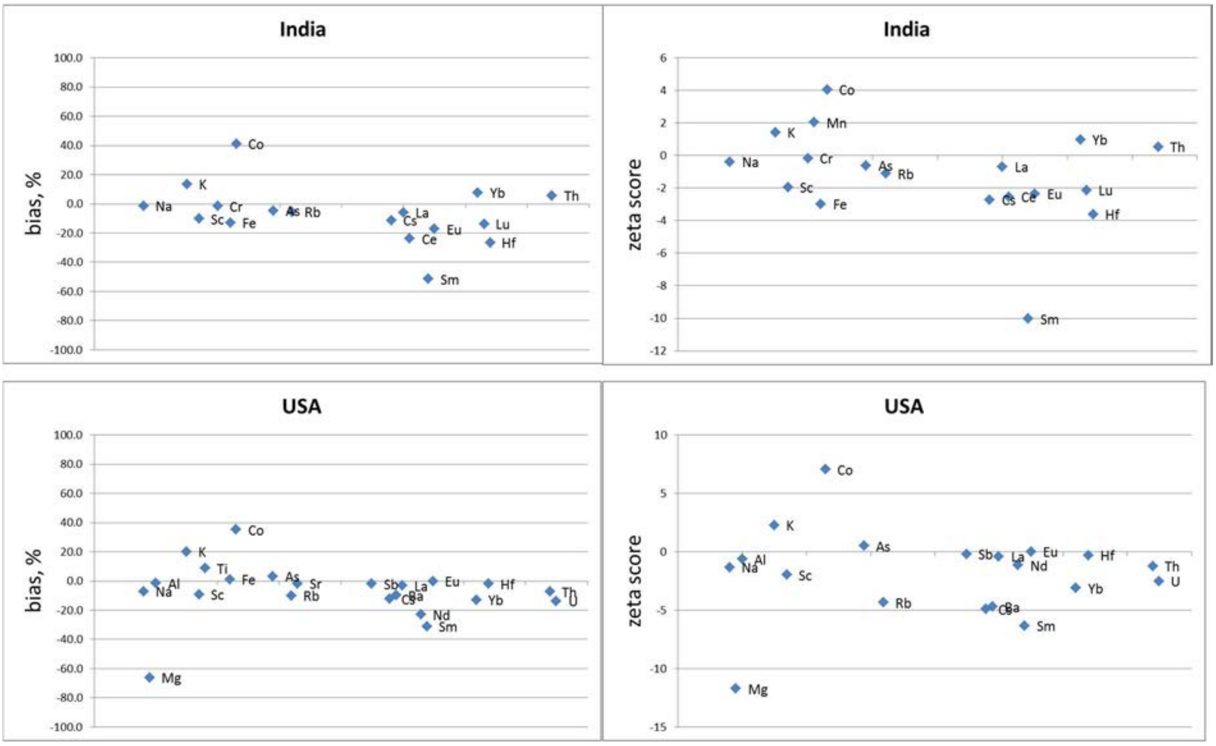

FIG. 5. Relative bias and zeta scores for LSNAA results reported by participants from India and USA.

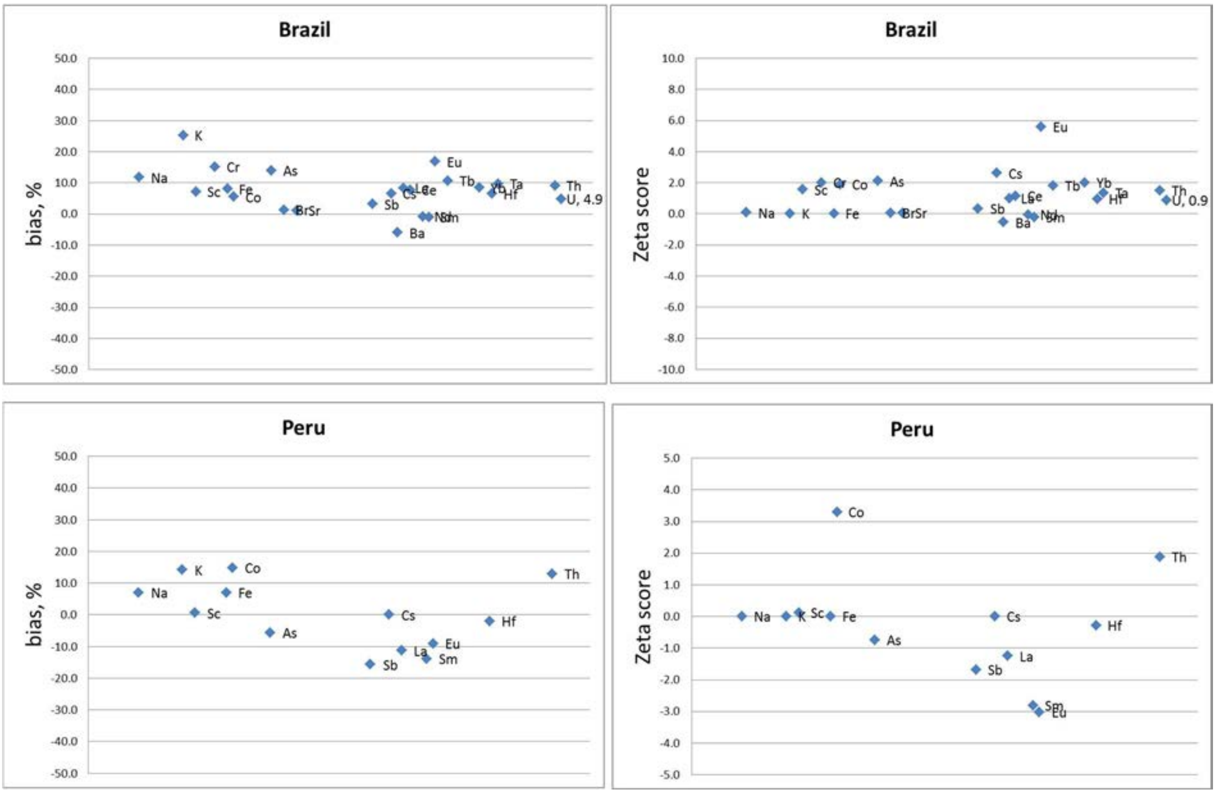

FIG. 6. Relative bias and zeta scores for LSNAA results reported by participants from Brazil and Peru.

The fraction of the reported LSNAA data for which |zeta| < 3 or |bias| is < 20 % or are shown in Figs. 7 and 8.

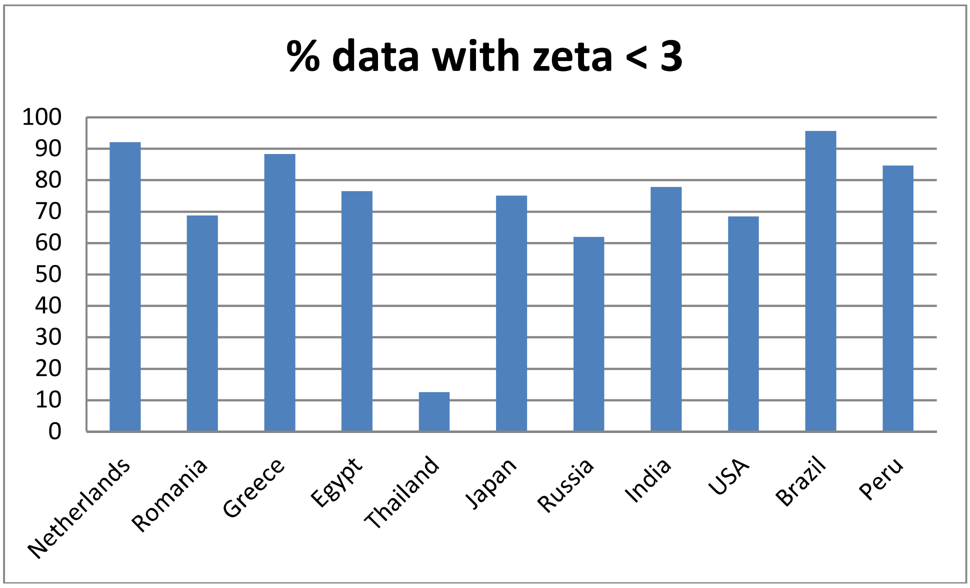

FIG. 7. Percentage of data reported with |zeta|< 3.

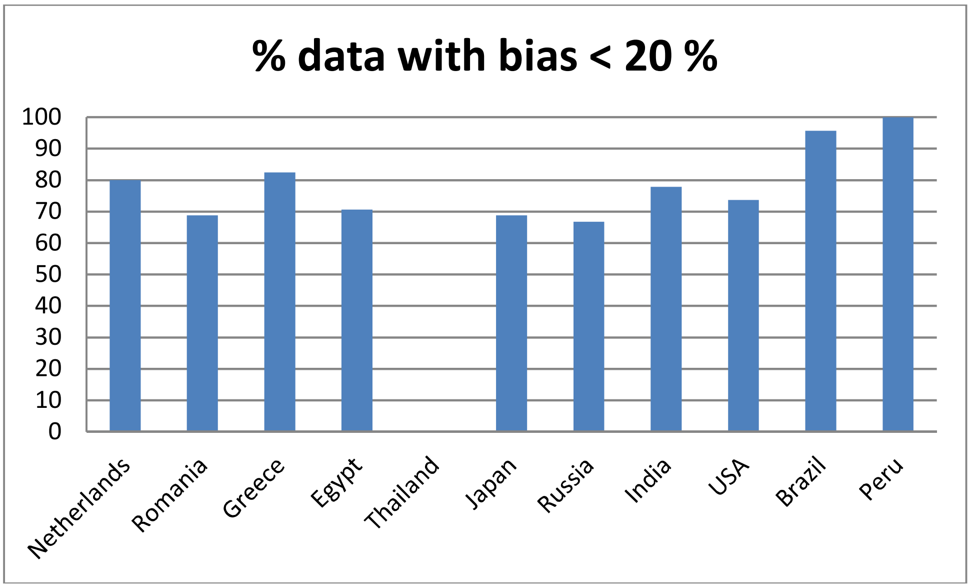

FIG. 8. Percentage of LSNAA data reported with absolute bias (difference between LSNAA result and reference value) < 20 %.

These results are also sorted by the element to assess if the various methodologies had corroborating difficulties for measuring specific elements. The outcome thereof is shown in Figs. 9-11.

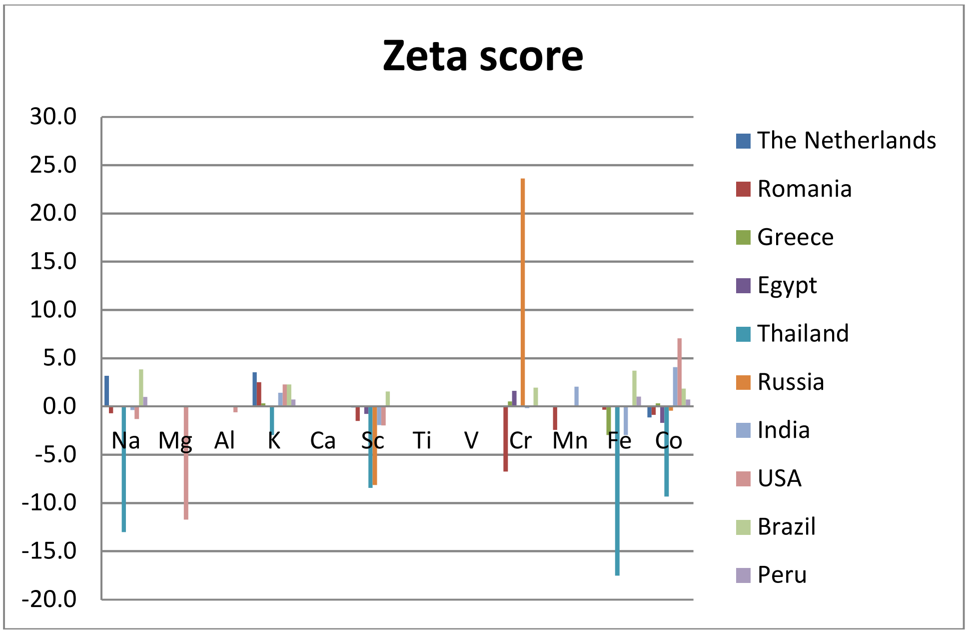

FIG 9. Zeta scores for the elements as measured by LSNAA.

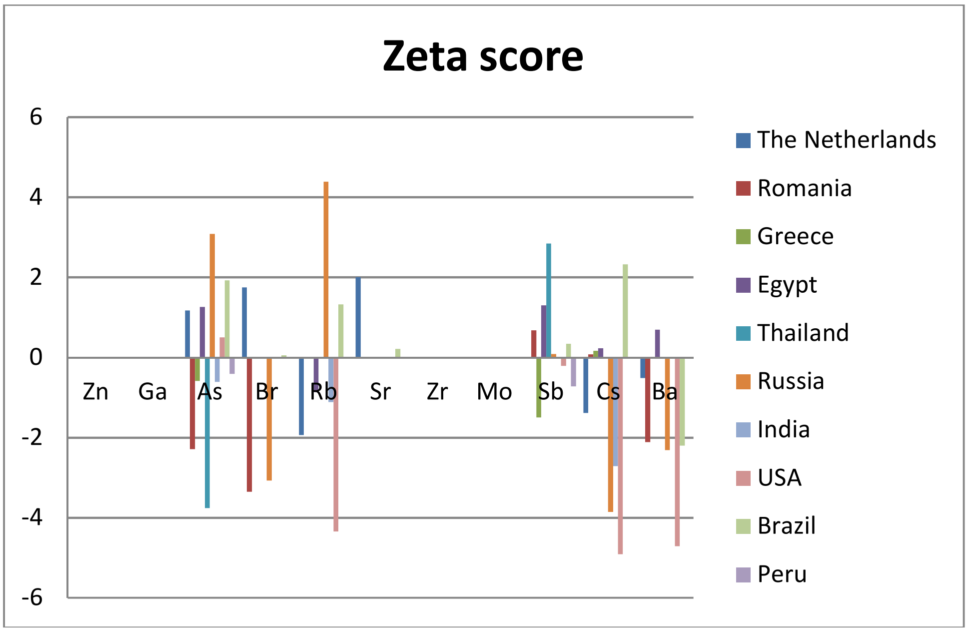

FIG. 10. Zeta scores for the elements as measured by LSNAA.

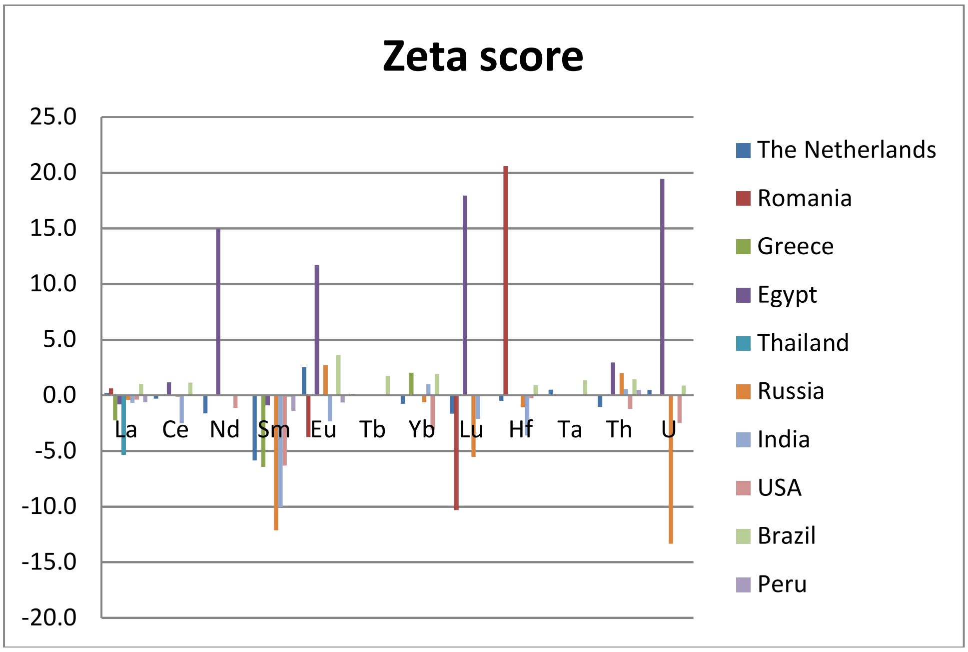

FIG. 11. Zeta scores for the elements as measured by LSNAA.

2.3.2. Powdered object analysis

The results of the powdered sample analysis in Peru (normal NAA, 250 mg), Brazil (5 g powdered LSNAA) and Slovenia (normal NAA, 180 mg) are shown in Table 3. It should be noted that the material was from a different batch than the material used for preparing the large object.

TABLE 3. INTERCOMPARISON RESULTS FOR THE LSNAA METHOD DEVELOPED BY BRAZIL, FOR THE ANALYSIS OF SETS OF GRAM AMOUNTS OF POWDERED POTTERY. ZETA SCORES REFER TO COMPARISON WITH THE DATA FROM PERU

	Peru (250 mg)		Brazil (5 g)			Slovenia (180 mg)		
Analyte	Result (mg/kg) (N=18)	1 SD (mg/kg)	Result (mg/kg) (N=3)	1 SD (mg/kg	zeta	Result (mg/kg) (N=5)	1SD (mg/kg)	zeta
Na	13000	1800	10100	400	-1.5	10300	400	-1.4
K	27900	1300	26000	3000	-0.6	28100	1100	0.1
Ca		0	66500	1700		68000	3000	
Sc	14.1	0.3	15.4	0.4	2.6	15.7	0.5	2.6
Cr		0	47,0	1.5		45.3	1.6	
Fe	37300	600	40600	900	3.0	41600	1500	2.7
Co	17.5	1.3	17.9	0.4	0.3	18.5	0.6	0.7
As	54	3	50	4	-0.9	53.8	1.8	-0.1
Br		0	1.24	0.15		1.08	0.09	
Rb		0	159	5		171	6	
Sr		0	333	10		332	13	
Sb	5.7	0.4	5.20	0.10	-1.2	5.12	0.20	-1.3
Cs	56	8	75	3	2.2	79	3	2.8
Ba		0	6004	30		650	20	
La	31.3	0.8	3.0	0.7	2.5	33.7	1.2	1.7
Ce		0	70.5	1.3		68	2	
Nd		0	34.0	0.7		32.8	1.7	
Sm	5.10	0.14	5.80	0.15	3.5	5.9	0.2	3.1
Eu	1.10	0.07	1.40	0.05	3.5	1.50	0.09	3.5

It can be derived that the LSNAA results from Brazil agree very well with the small sample results from Slovenia, and that there is also good agreement for the results of most elements between the small sample analysis of Slovenia and Peru. Differences between the Peruvian, Brazilian and Slovenian results may possibly be attributed to homogeneity differences in the original fragments. For some particular elements, further comments can be made:

- Na: The measured mass fraction can be higher after 5 d of cooling time due to interference of the ^{124}Sb Eγ = 1368.2 keV line to the ^{24}Na line at 1368.6 keV. One could infer from the results a relatively high content of Sb in the sample;
- Sm: The measured mass fraction can be lower due to different attenuation corrections in the sample and in the standard at the 103.2 keV line of ^{153}Sm. There is also a possible interference of ^{239}U/^{239}Np at 103.7 keV;
- Eu: The measured mass fraction can be lower if the content is calculated via ^{152}Eu, which is a non *1/v* absorber, and the data in k_0-library are not recommended. One should take into account the Westcott g-factor, which is a quantitative measure of the deviation of the cross-section from *1/v* below the cadmium cut-off energy (0.55 eV). Alternatively, the mass fraction can be measured via ^{154}Eu, which is a *1/v* absorber.

2.3.3. Discussion

The results represented in Figures 7-9 show a striking difference in performance between most laboratories and the one in Thailand. Indeed, the Thai laboratory confirmed in 2012 that their methodology needs more elaboration as large deviations had also been found in analysing a homogeneous large sample of well-defined geometry.

Quantitative results for 16 to 23 elements were reported by most laboratories. This is a normal number for an activation analysis of this type of material, clay. It should be noted that elements measured via short half-life radionuclides (e.g., Al, Mg, Ti and/or V) were not reported as the irradiation facilities are not (yet) suitable for fast transfer of the object after the irradiation.

The laboratories in Netherlands and Greece have experience in LSNAA since the 1990s which is reflected by the large number of acceptable results ($|z|<3$). The other laboratories show, on average, a fairly equivalent performance which may be considered as very promising. It should be noted that high zeta scores may also result from an underestimation of measurement uncertainties. Several newcomer laboratories used only the contribution of the counting statistics in their estimation of the uncertainty of measurement as it was too complicated to account for all contributions to the uncertainty, including the contributions from the correction factors.

The zeta-score graphs in Figures 2-6 indicate that there are no cases in which all of the LSNAA results are over- or underestimated with respect to the reference values as set by the small sample analysis in Peru. The data in Figures 9-11 show a tendency that the LSNAA results are lower than the reference values. It can also be derived from Figures 9-11 that almost none of the laboratories have difficulties in measuring elements such as Na, As, Sb and Th. This indicates that corrections for voluminous efficiency and neutron self-attenuation — the latter being not very significant for this material — are well estimated. The existing deviations for some elements may be ascribed either to overestimation of the gamma ray self-attenuation (e.g. for the elements Sm and Lu) or to the element calibration applied, e.g. for the lanthanide elements.

It should be noted that no *a priori* information was available on the composition and physical properties of the material. Gamma ray self-attenuation parameters had to be measured or estimated. The estimation of the voluminous full-energy photopeak efficiency had to be based on first order approximations of the shape and size of the object. Improvements can be expected by adding X ray tomographic data to LSNAA.

One should be careful in extrapolating these results towards a generalized characterization of the capabilities of LSNAA. Firstly, the material analysed was approximately homogeneous in composition over its entire shape. Secondly, there was no substantial neutron self-attenuation and also the gamma ray self-attenuation was limited. More difficulties may arise when similar objects have to be analysed that are (unknowingly) inhomogeneous and composed of materials different in composition. Mass fractions — as reported in the studies described here — are implicitly based on an assumed homogeneity throughout the object tested. It might therefore be metrologically more correct to report, for objects of (un)known degree of homogeneity, masses measured rather than the mass fractions calculated, and leave the interpretation thereof to the end-user.

2.4. CONCLUSION

The evaluation of the results reported from the intercomparisons indicate that the experienced LSNAA laboratories are able to reach results in LSNAA within 25% of the approximate expected value for an irregular, intact large object made of clay, considered homogeneous for most chemical elements. These experienced laboratories reached a degree of accuracy (zeta score, reflecting trueness and precision) for almost all elements measured in this intercomparison equivalent to what is usually reached in normal NAA. Other laboratories showed some minor shortcomings in their methodology in 2012, as they had starting-up problems of known origin. NAA is based on processes described by physics, and therefore the source(s) of deficiencies should be relatively easy to find. As such, also the newcomer laboratories will eventually have the opportunity to perform LSNAA at the desired level of quality.

3. CURRENT STATUS OF LSNAA

3.1. ADVANTAGES AND CHALLENGES OF LSNAA

The uniqueness of LSNAA (and LSPGA) is that an intact object is irradiated directly with neutrons for analysis, i.e., without pre-treatment. Sample handling and preparation, particularly grinding and mixing to make a representative test portion, can be avoided altogether. Concerns about inadvertent contamination of the test portion during this process are avoided. Moreover, the contribution of the blank, e.g., the element content of the packaging, may effectively be absent given the large difference in mass of the test portion and its packaging. Concern that the test portion is representative of the sample 'as received' is also avoided: the sample 'as received' is the test portion. The procedure in LSNAA, including the irradiation and counting of large samples can be less time-consuming or simpler than traditional NAA methods, and may result in an equivalent level of accuracy. The widespread use of Marinelli beakers to measure the activity of radionuclides in water and powdered samples is a common example of the ease of using large samples, whereas the degree of accuracy of these approaches has been thoroughly assessed.

Implementing a method for NAA (and PGA) of large samples presents distinct technological and scientific challenges in how to irradiate these large samples, count the induced activity and perform the analysis and interpretation of the results. With traditional NAA/PGA methods, neutron self-shielding within the sample is seldom so significant that it complicates the analysis. The same applies to gamma self-attenuation which, for samples with masses up to a gram is almost always negligible. However, neutron self-shielding, scattering, and sometimes changes to neutron self-moderation as well as the gamma ray self-attenuation of the emitted gamma rays, should always be considered for large samples of several grams and more. Also for traditional NAA and PGA, point source geometry can be used for the vast majority of samples, simplifying estimation or calculation of the photopeak efficiency. A mathematical description of, e.g., an irregularly shaped cultural object for estimating the 3-dimensional activation and voluminous detection efficiency can be less trivial. In normal NAA, many laboratories apply the comparator method using reference materials (widely available for almost any sample matrix) which eliminates the need for detailed knowledge of the spatial distribution of the neutron flux impinging on the sample, as this is almost the same for sample and comparator. This absence of reference materials for large (irregularly shaped) samples resulted in the development of several new LSNAA methodologies during this CRP. These aspects of LSNAA are all discussed in depth in the next paragraphs of this Section.

Inhomogeneities in normal small sample NAA/PGA do not usually create a problem in the calculation of the elemental content. With large samples, inhomogeneity can be a major concern both during irradiation and during the counting of the irradiated intact object. Consider the extreme case of an inert cylinder in which one half is plated with cadmium and the other half is not; the irradiation geometry and the counting geometry must be carefully considered if the results are to be meaningful. Interpreting measurement data and reporting analysis results from inhomogeneous objects may demand entirely new approaches, as well as close communication with end-users. Indeed, the majority of the challenges with using large sample methods arise directly from the fact that geometry considerations are usually imposed for large samples and not for small samples.

Methods to mitigate and understand the geometry effects are the subject of this Section, and are certainly a part of the consideration whether large sample analysis techniques should be used for a particular object or class of objects. Objects that have large cross sections for neutrons (for example samples that contain large amounts of hydrogen or boron) or samples that efficiently shield gamma rays (for example lead bricks) are probably not candidates for accurate large sample analysis or, at best, should be viewed with care.

Along with the obvious strengths of using large sample methods, there are limitations in this method that are perhaps not as obvious. Because the large sample counting geometry will be not be as efficient as a point geometry, the overall induced activities for large samples will have to be larger than in the normal small samples to maintain the same level of precision (counting statistics). As samples can approach and even surpass kilogram quantities, even moderate activation can therefore lead to larger doses to experimenters and technicians during handling of the (large) samples than in normal NAA.

One important criterion in the selection of the LSNAA technique is the ability to manage, control, and ultimately dispose of potentially greater amounts of activated material than is normal for traditional NAA. Even though the specific activity (Bq/g) may be much lower than in disposed samples of normal NAA (as the induced activity is slightly higher but the mass considerably higher), the total mass of remaining activated material should be estimated well in advance.

LSNAA is a unique tool for analysing objects of archaeological or cultural origin without sub-sampling — and thus without visible destruction. However, a few constraints have to be mentioned. The presence of large amounts of strong neutron absorbing elements such as boron, cadmium or gadolinium may result in local temperature increase during the irradiation. High radiation doses by gamma rays (as occurring in the direct vicinity of the reactor core) may lead to colouring of glasses. In any doubt, test irradiations should be done.

Finally, insurance issues and related security requirements for cultural objects may come at stake, but in principle these can be solved.

3.2. TECHNICAL ASPECTS OF LSNAA

3.2.1. Overview

The neutron irradiation conditions and gamma counting configuration for LSNAA are optimized on the basis of the sample type and size. Typically, for LSNAA on masses varying from a few tens of grams to the kilogram range, a neutron fluence rate in the range of 10^8-10^{10} $cm^{-2}s^{-1}$ is required (see section 3.2.2)[2]. Such a neutron fluence rate is usually found at many low power nuclear research reactors (i.e., < 100 kW). Although there are some distinct advantages associated with the use of a well moderated neutron field such as is encountered in the thermal neutron column of a nuclear research reactor (see section 3.2.2), if a thermal neutron column is not available, large sample neutron irradiation can be successfully performed by sample irradiation in the pool at a distance from the core or using an external neutron beam. After irradiation the large sample is transferred to the gamma ray spectrometry system to be counted either as a whole or using a scanning geometry counting configuration. Data evaluation should consider the self-shielding of activating neutrons, self-absorption of gamma rays, heterogeneity of the sample and the geometric factor during gamma counting. Several LSNAA calibration techniques have been developed including the absolute, relative, k_0 and internal standard methods. Gamma ray transmission measurements are performed to

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[2] For LSPGA the required neutron flux in the beam may also be proportionally lower as the sample mass increases, i.e., instead of 10^7–10^9 $cm^{-2}s^{-1}$, 10^5–10^7 $cm^{-2}s^{-1}$ would make LSPGA feasible.

evaluate the effective linear attenuation coefficient of the large sample. In addition, techniques such as neutron and gamma radiography, X ray imaging and Computerized X ray Tomography are used for the detection of inhomogeneities within the large sample and correction of the results for their effect.

In this section an overview of the irradiation facilities, counting systems of different configurations, calibration methods and data evaluation techniques used by the participants under this CRP is provided.

3.2.2. Irradiation facilities

3.2.2.1. Irradiation sources and facilities

A wide range of neutron sources can be used for LSNAA [22]. These sources include small to higher power nuclear research reactors, reactor neutron beams, neutron generators and radionuclide neutron sources.

The type and strength of the neutron source and the neutron energy spectrum characteristics play an important role in any type of NAA including LSNAA, as the radioactivity produced is directly proportional to neutron flux, energy dependent neutron absorption cross section and the number of target atoms. Besides these, counting rates depend on the sample counting geometry, i.e. sample to detector distance. The preferable neutron source strength requirement is that the induced activity within a large sample would result in a count rate equivalent to that obtained in conventional small sample NAA. Therefore, the product of mass, neutron flux, irradiation time and absolute detector efficiency for the large sample should be similar to that of a small sample used in conventional NAA, in which for example a 200 mg (0.2 g) test portion is used. This criterion indicates that for a test portion with mass in the order of 2 kg (2000 g), a neutron flux of approximately $5\times10^{12} \times 0.2/2000 = 5\times10^{8}$ $cm^{-2}s^{-1}$ would result in a similar level of induced radioactivity during a set irradiation time, considering all other parameters to be the same. In practice, a slightly larger (e.g. 20 % higher) neutron fluence rate will be required in LSNAA to compensate for losses by neutron self-shielding and gamma ray self-attenuation.

Such fluence rates in the order of 10^{8}-10^{10} $cm^{-2}s^{-1}$can be found at a distance from the core of small reactors (as used by the CRP participants from Ghana and Syria) as well as in medium and higher power research reactors (used by participants from Brazil, Romania, Russia, USA); in reactor beam tubes (applied by participants from Peru, Japan) and in thermal columns (available for the participants from Netherlands, India, Greece, USA, Thailand, Egypt). Nevertheless, neutron irradiation can also be performed using neutron generators (as demonstrated by the participant from China) and isotopic neutron sources (applied by the participant from Malaysia).

The irradiation facilities used by the different participants under this CRP are given in Table 4 with the relevant details.

3.2.2.2. Irradiation requirements for LSNAA and LSPGA

The advantage of reactor thermal neutron columns above e.g. pool side facilities is that the longitudinal neutron flux gradient (i.e. horizontally away from the reactor core) over the sample is much less steep due to the multiple neutron scattering in the graphite inside the thermal column, as can also be derived from the differences in thermal neutron diffusion length in carbon and water, viz., 64.2 cm and 2.76 cm, respectively. Moreover, the very high thermal to epithermal flux ratio encountered in a thermal column (see Table 4) simplifies the activation calculations since moderation in the large sample itself (see below, paragraph 3.2.2.3) is not significant anymore and the use of the k_0 constants for LSNAA is facilitated. However, in some cases neutron self-attenuation combined with the neutron flux gradient may result in a significant lower activation of the central part of the large sample compared to its periphery. This effect depends on the sample size and neutron attenuation properties. In such a case, the measured gamma rays originate mainly from the periphery of the sample and the analysis result will apply mostly to the outermost layers of the sample rather than reflecting the bulk composition.

External neutron beams with neutron fluence rates of 10^5-10^8 $cm^{-2}s^{-1}$ are also suitable for both in-beam activation of large samples and LSPGA. An advantage associated with external neutron beams is the flexibility in the size and shape of the object to be irradiated as there is no dependency of a fixed geometry irradiation container. However, one should be careful in increasing the test portion mass when using external neutron beams as it might adversely affect the measurements since the background radiation is also sample dependent due to scattering effects. A large sample neutron beam activation facility is in use in Peru [14]. LSPGA facilities have been realized in Japan [23, 24] and Hungary [8]. In LSPGA a complication may arise in the cases where high mass fractions of nuclides that emit intense prompt gamma rays (such as hydrogen, boron and cadmium) are present in the large test portion [25].

It has been shown that external neutron beams of isotopic neutron sources and neutron generators can in principle be used for both LSNAA (activation) and LSPGA, though the energy definition becomes a tedious problem in the unknown sample. ^{252}Cf is probably the most attractive isotopic neutron source from a neutron spectrum shape point-of-view and ease of moderation [26]. However, the short half-life (2.64 y) of ^{252}Cf may be seen as an economic disadvantage. Other isotopic neutron sources have relatively harder neutron spectra but much longer half-lives (for example the mean neutron energy of ^{241}Am-Be source is 4.5 MeV and the half-life is 433 y) [27].

Significant technological improvements have been performed in the recent years and D-D and D-T neutron generators with high neutron output are commercially available [28, 29]. Since the neutron energy is above the threshold for neutron reactions, generators may enable fast neutron activation also to be performed. An additional advantage of LSNAA with D-D and D-T generators as compared to reactors is that the sample may be quickly removed from its irradiation position upon shutting down the accelerator, facilitating the measurement of radionuclides with short half-lives as well. However, the main advantage of isotopic neutron sources and neutron generators is that they enable realization of field analysis methods [5, 6, 7]. Nevertheless, the applicability of neutron sources and neutron generators is limited so far to the measurement of major components in the sample.

A neutron generator based LSNAA facility has been realized in China [31], isotopic neutron source based LSPGA facilities are in use in some places (for example Malaysia [36]).

TABLE 4. IRRADIATION FACILITIES

Country	Neutron Source	Irradiation System	Fluence Rate (cm^{-2} s^{-1})	Thermal to epi-thermal	Sample Size(max)	Ref.
Brazil	IPR-R1 100 kW	In-pool	6.3E+11	25	1.2 cm D, 4.0 cm H	[30]
China	Generator					[31]
Egypt	ETTR-2 22 MW	Thermal column	1.3E+12	120	9.6 cm D, 25.7 cm H	[32]
Ghana	GHARR-1, MNSR 30 kW	Irradiation channel in graphite reflector	3.5E+10		15 cm D, 30 cm H	[33]
Greece	GRR-1 5 MW	Thermal column	1E+08	300	15 cm D, 40 cm H	[34]
India	APSARA, 400 kW	Thermal column	1E+08	1000>	30 cm × 60 cm × 100 cm	[35]
	AHWR, 0 W	Irradiation channel in graphite reflector	2E+07	300	12.5 cm × 12.5 cm × 150 cm	
Japan	JRR-3, 20 MW	Beam	1E+06 to 1E+07	Cold	2 cm × 3 cm	[23]
Malaysia	252-Cf, 0.5 µg	Beam				[36]
Netherlands	HOR, 2 MW	Thermal column	3E+08	> 3000	14 cm D, 100 cm H 5 cm D, 7 cm H	[1]
		In-pool	3E+13	15		
Peru	PNRR 10 MW	Beam	3.9E+10		18 cm × 23 cm	[14]
Romania	ACPR, 14 MW	Dry channel	1E+13	2.5	14 cm D, 28 cm H	[37]
Russian Federation	WWR-M, 16 MW	Dry Channel	1E+08 to 1E+09		35 cm × 40 cm × 70 cm	[38]
Syrian Arab Republic	MNSR, 30 kW	Thermal column	1E+09			[39]
Thailand	TRR-1/M1, 1.2 MW	Thermal column	1E+09		14 cm D, 14 cm H	[40]
		In-Pool	5.6E+10		2 cm D, 8 cm H	
USA	Texas A&M Triga MI, 1 MW	In-Pool	7E12	3		[41]
		Thermal column	1E8	>3000		
		Dry cell	1E9	various		

3.2.2.3. Design considerations

There are various design aspects to be taken into account for irradiation facilities for LSNAA:

a) A large volume facility near the core of a nuclear reactor creates a void in the reactor's reflector, whereas loading and unloading may cause unwanted fluctuations in the core's reactivity. Moreover, a high amount of ^{41}Ar can be produced from activation of air in the container and in the irradiation tube.

b) The thermal neutron fluence rate gradient in the water reflector of a light water moderated reactor is quite steep; typically a factor of 3 for each 3 cm of water from the core is observed, what is due to the neutron diffusion length (2.76 cm) in water. Such a gradient would also create an unwanted flux variation over the large sample. This may be partly corrected for by rotating the sample during counting [42] or by mixing the sample after irradiation [43] or by the use of *in-situ* relative efficiency method [2]. In mixing, however, information about inhomogeneities is lost and cannot be applied for analysis of precious samples that need to be intact.

c) Large hydrogen mass fractions may result in neutron spectrum changes over the sample volume due to neutron moderation in the sample. The extent of this effect depends, of course, on the neutron spectrum shape and the fractions of epithermal and fast neutrons compared to the thermal neutrons. This effect may be reduced by characterizing well the neutron spectrum at the irradiation facility and applying an appropriate neutron moderation correction. In this respect, well-thermalized neutron irradiation facilities have an advantage since such corrections are not required. In particular, in thermal column facilities, the ratio of thermal over non-thermal neutrons may be much larger than a factor of 1000, eliminating the significance of neutron self-moderation. The user of the irradiation facility should be acquainted with this phenomenon, and *a priori* information must always be collected about the sample composition so as to estimate the extent of these effects and to decide if empirical correction factors can be applied or if additional in-situ monitoring is needed.

d) Large sample activation facilities using neutron beams must be designed in such a way that adequate shielding is ensured against neutrons scattered from the large sample and the prompt gammas both from the core and from the sample. In principle, the relatively small area of neutron exposure facilitates scanning the object, particularly for PGA

e) Transferring test portions to the irradiation position of the neutron source is usually done with pneumatic or hydraulic transfer facilities and/or manually or automatic loading facilities. Most existing rabbits (i.e. pneumatic facilities) are designed to handle volumes up to a few tenths of ml; however, it may be possible that large rabbits can be obtained with the required specifications (quality of the rabbit materials, purity and radiation/mechanical resistance) for application in LSNAA.

3.2.2.4. Sample containers

The relatively low neutron and gamma ray dose encountered in LSNAA does not impose restrictions on the choice of materials used for sample containers and therefore the use of almost any packaging material is possible (e.g. plastic or quartz aluminium containers) [22].

The large sample container itself may be of almost any shape and type. A wide-neck bottle is easy to fill when coarse material has to be analysed [42]. Since the ratio of sample to packaging material mass is large, as compared to conventional NAA, a container of inexpensive plastic may be preferred, as the impurities in the plastic itself (blank contribution) may be neglected at a particular sample size [22]. If the contribution from the sample holder is substantial, irradiated large samples may also easily be transferred after irradiation into non-irradiated containers and possible small losses during transfer can be neglected in view of the large test portion mass. As such, Marinelli beaker geometry or a multi-sample container [44] may have certain advantages, depending on the application, although they are not applicable for those objects that need to be intact.

3.2.2.5. Neutron fluence monitoring

Neutron fluence rate monitoring is carried out preferably non-invasively, with the flux monitors positioned outside the sample [22]. The neutron flux outside the large sample is used to estimate the neutron flux distribution within the sample [34]. During the irradiation, the sample is monitored by flux monitors at any desired height around the sample. The neutron flux on the surface of the sample, coupled with information on the flux depression within the sample as estimated by analytical [45] or Monte Carlo [46] calculations, can provide the flux correction factor. However, for a few samples (e.g. soil and ore) neutron monitors can be positioned within the sample to provide direct information on the flux distribution [47–49]. In addition, neutron monitors such as Self Powered Neutron Detectors (SPND) placed at the core margin can be used for monitoring the neutron flux during irradiation and provide the scaling factor for the computations [37]. Rotation of the sample during activation may help alleviate some of these flux gradient problems.

3.2.3. Induced activity measurement

Neutron activated small samples are often placed on the face of the detector or on a stand located a few centimetres away from the detector face. This is practised as small samples may, to some extent, be still considered as ‘point sources’. Samples in LSNAA cannot be represented anymore as ‘point-type’ sources. As such, the sample to detector geometry has to be considered, particularly if irregularly shaped or asymmetric objects that must be preserved intact have to be analysed. Depending on sample size and shape, various counting methods and counting facilities have been developed. In Table 5 some salient features of the counting facilities used by the participants under the CRP are given.

It should be noted that the gamma ray spectrum due to the natural radioactivity of the sample material has also to be measured in large sample analysis, prior to the activation. These ‘sample background’ peaks in the gamma ray spectrum should be separately treated later on in the neutron and gamma ray self-attenuation corrections.

3.2.3.1. Counting facilities

Germanium detectors of relative efficiencies in the range of 25-100 % were used during the CRP for LSNAA (see Table 5). Large volume detectors are preferred to maintain adequate sensitivity in NAA if the large samples are counted on larger distances to the detector than commonly is done for normal small sample [22]. Larger distances ease the photopeak efficiency calculation for the voluminous source, whereas corrections for coincidence effects are not significant. Side-looking detectors (‘horizontal dipstick’) have the advantage that cylindrical samples, positioned perpendicular to the detector axis, can easily be rotated around the sample axis to reduce geometrical effects. Vertical dipstick detectors have the advantage to measure large samples in Marinelli beaker geometry. Well-type Ge detectors can handle test portion volumes up to approximately 8 mL, and thus are not suitable for larger volume samples, but it is well-known that coincidence effects are highest with such detectors, setting specific requirements for calibration. For specific applications, for example when the acquired gamma ray spectra are simple and do not require high energy resolution for the analysis of the spectral peaks, large scintillation detectors could also be considered.

Automatic sample changing can be realized, if necessary, for selected applications. Adequate shielding of the samples during transfer and storage remains, of course, a prerequisite.

TABLE 5. COUNTING FACILITIES AND METHODS

Facility	Detector (rel. efficiency)	Configuration	Efficiency Correction	Calibration Method	Additional techniques
Brazil	Ge 25%	V	Efficiency transfer, ANGLE	k_0	X ray diffraction
China	Ge	H	-	-	EDXRF
Egypt	Ge 100%	H, rotation	Efficiency transfer, MCNP	k_0	
Ghana	Ge	V	Efficiencty transfer, MCNP		Gamma transmission
Greece	Ge 85%	H, rotation & collimated scanning	Efficiency transfer, MCNP	Absolute	Gamma transmission, CT
India	Ge 40% with Compton shield	H, rotation&collimated scanning	In situ relative	k_0 & Internal mono-standard	
Japan	8 clover Ge 120% with BGO Compton shield	H		Internal mono-standard	
Malaysia	n-type Ge	H			XRF
Netherlands	Ge 95%	H, rotation&collimated scanning	Analytical	k_0	Gamma tranmission
Peru	Ge 70%	V		Relative	
Romania	Ge 40%	H, rotation&collimated scanning	Efficiency transfer, MCNP	k_0	Gamma transmission
Russian Federation	planar Ge 20% at 121.8 keV 15% Ge	Collimated Scanning			
Thailand	Ge	V	Efficiency transfer MCNP	k_0	
USA	Ge 30%	H and V	Efficiency Transfer	Absolute	Gamma transmission, neutron radiography, CT

Advanced spectrometer systems have been designed in which two or more Ge detectors surround the large sample to approach a 4π geometry [23]. The individual spectra can be added to obtain a composite spectrum with better counting statistics.

3.2.3.2. Gamma ray self-attenuation

The gamma ray self-attenuation correction can be estimated when the effective linear attenuation coefficients are available, either by measurement or by calculation from the approximate (or known) elemental composition. A multi-gamma ray emitting source, having gamma ray energies over the entire range of interest (like ^{152}Eu) can be used for the measurement approach, i.e. by measuring the transmission of the gamma ray emitted by the sources. A narrow beam geometry can be created by locating this source behind a cylindrical collimator, and the gamma ray transmission can be measured at several heights along the sample. This forms the basis for the estimation of the effective linear gamma ray attenuation coefficient of the large sample [1, 34, 37, 50].

Moreover, some of the participants of the CRP used gamma scanning detection configurations in order to evaluate local inhomogeneities in the sample. Such a set-up will allow, in principle, for gamma ray emission tomography of the sample [51, 52].

3.2.3.3. Voluminous full energy photopeak efficiency

Different detector calibration approaches are needed to take into account large sample photo peak efficiency, gamma ray self-attenuation and, if applicable, coincidence summing corrections. The large sample photo-peak efficiency can be evaluated semi-empirically, by e.g. Monte Carlo methods [53], but this requires precise information about the inner geometry of the detector configuration (including the dead layer thickness). In situ relative detection efficiency in a large sample can be determined using the multi gamma emitters produced in the sample and are adequate to calculate mass ratios with respect to a reference object [54].

Several commercially available software codes exist to compute the geometry effects such as ANGLE3, Canberra Genie LabSOCS and others, or, if necessary, Monte Carlo codes such as GEANT or MCNP can be used. All these assume that the object’s dimensions are known, that gamma self-shielding is negligible or densities are known through, e.g., a Computerized Tomography (CT) scan, and other conditions.

Estimating the voluminous efficiency becomes considerably more complicated if the sample is asymmetric and has an irregular shape. In such a case, the approach followed by the CRP participant from Peru to circumvent the problem, is rendering a pragmatic solution [14].

For some samples, rotating the sample during counting can help to alleviate non-symmetry effects. Even then, thought must be given to whether rotation during counting will help for a particular sample or not. Rotating a large “L” shaped sample while counting in the same plane as the “L” may make analysis even more difficult. Collimated vertical scans were done for large activated samples as the samples were rotated [51]. For certain classes of samples, this would alleviate many symmetry problems

Several CRP participants calculated the Ge detector full energy photo-peak efficiency for large samples using the efficiency transfer method on the basis of the full energy peak efficiency measured for a reference point source [4, 30, 32, 37, 40, 41]. This factor provides the ratio of the actual detector response for a given gamma ray energy over the detector response if the large sample would have been a point source located in a reference point without gamma attenuation and scattering. The advantage of the efficiency transfer method is that many inaccuracies in the detector model can be expected to cancel out to a large degree in the calculated ratio, making it possible to work directly with non-optimized detector data supplied by the manufacturer. Therefore, the full energy peak efficiency transfer method increases greatly the degree of accuracy of the results of quantitative analysis by gamma spectrometry and avoids time consuming calibration sequences [55].

3.2.3.3. Inhomogeneities correction

Combination of correction algorithms for neutron and gamma ray self-attenuation, and for the volumetric photo-peak efficiency yields an 'overall correction factor', which reflects the difference between the actual detector response for a given gamma energy and the theoretical detector response if the sample would have been a mass-less point source located in the large sample's centre, without any neutron and gamma attenuation [56].

In these corrections, it is assumed implicitly that both trace elements and major (matrix) elements in the sample are homogeneously distributed on a macroscopic scale. If this condition is not met, there is a large probability that due to inhomogeneities, the mass fractions determined will not be correct. These deviations have been studied via computer simulations [57, 58] and also experimentally. Inhomogeneities may influence the results of the irradiation as well as of the measurement; therefore, both have to be treated separately. The results of these studies demonstrated that false mass fractions may be obtained if inhomogeneities are not accounted for in the interpretation step of large sample NAA. The smallest errors may occur for matrix inhomogeneities; the most pronounced effects can be expected when the trace element of interest is distributed either on the outside or on the axis of the cylindrical sample and the consequences for the inaccuracy of the results rather indicate "worst case" conditions.

The presence of extreme inhomogeneities in large samples may be considered a nuisance [22]; on the other hand large sample analysis is a unique tool for measuring these inhomogeneities without destroying the sample. To this end, sample scanning using a collimated detector has been introduced, in which it has been assumed that the sample consists of volume elements that individually may be considered as homogeneous for the amount of the element of interest. [51, 52, 59].

Since the results of the computations of the neutron self-shielding and gamma ray self-attenuation correction factors in LSNAA depend on the geometry and composition of the material of the sample (including the effects of inhomogeneities), an approximation of this composition as close as possible is required. In this respect, two laboratories have chosen to perform a Computerized Tomography (CT) scan of the large sample (Greece, USA). The obtained tomography data enabled accurate representation of the complex sample geometry in the input of the subsequent Monte Carlo simulations performed in order to derive the neutron and gamma ray correction factors [60].

3.2.4. Methods of LSNAA

Quantitative assessment of the element masses in LSNAA may be done with similar approaches as in small sample NAA, via [22]:

- the absolute method

- the comparator method
- the k_0 method
- the internal standard method

3.2.4.1. Absolute method

The absolute method for standardization in NAA is based on using known (best estimate) values for the thermal and epithermal neutron flux and related activation cross sections, derived either from previously performed measurements, from reactor physics estimations (neutron fluxes) and/or from literature data (cross sections). For many (n,γ) reactions and radionuclides, parameters such as cross section, gamma ray abundance and half-life are not known with well-defined uncertainties. The natural isotopic abundance is also not known accurately for some isotopes. Since the various parameters were often evaluated via independent methods, their individual uncertainties will add up in the calculation of the elemental amounts. This may lead to relatively large uncertainties of measurement. This method is best applicable if the composition of the sample matrix is fairly well established in advance, e.g. when dealing with pure materials; or if the degree of accuracy is of lower importance, e.g., if the results are needed for screening purposes (e.g., if the results fits in a decimal order). Participants from USA, Greece and Romania used this method for LSNAA.

3.2.4.2. Relative method

In the relative method, the test portion is co-irradiated with a calibrator containing a known amount of the element(s) of interest. The calibrator is measured under (preferably) the same conditions as the sample (sample-to-detector distance, sample size/geometry and if possible composition). The ratio of the measured count rates of the analyte in the sample and standard are used to calculate the mass of the analyte and its mass fraction. Though the relative method is simple and precise and has been proven yielding the highest degree of trueness if only one element has to be measured, prior knowledge of the elements present in the sample is necessary to prepare multi-elemental standards or use certified reference materials (CRMs) of a similar matrix. It is almost impossible to produce a multi-element standard containing known amounts of all detectable elements by NAA with sufficient degree of accuracy in a volume closely matching the size and the shape of the samples encountered in LSNAA. In dealing with large samples — gram to kilogram in mass — the use of (certified) reference materials is not practical (major differences may exist in neutron spectrum characteristics in the real sample and in the standard), not economical (reference materials are expensive and large sample analysis would imply a high consumption rate) or not warranted (certified reference materials are produced for method validation purpose, not necessarily for calibration).

Nevertheless, in-house standards can be prepared and used. This approach was successfully utilised by the participant from Peru [14]. Custom replicas of the precious object may be made with arbitrary precision from available clay of known composition to match the sample and produce a near exact reference standard.

3.2.4.3. k_0-based method

The k_0 method for standardization in NAA is based on best (experimental) estimates of a factor comprising all irradiation- and measurement independent nuclear parameters (the k_0 factor) and an experimental parameterisation of the irradiation and measurement conditions. [61, 62]. For the irradiation conditions, the ratio f between the thermal neutron flux and the epithermal neutron flux, and the ratio α between the resonance integral and the thermal activation cross section are experimentally established. This is often done ‘once and forever’ unless there are significant changes in the reactor configuration. In addition, in each irradiation one or more neutron flux monitor must be added for estimating the neutron flux gradient(s). The application of the k_0 based method is significantly simplified when the irradiations are carried out in a well moderated neutron field such as inside a reactor’s thermal neutron column. This method is very well usable for large sample analysis of e.g. liquid large samples, such as water or oil, as well as solid samples. Netherlands, Brazil, Thailand, Malaysia and Egypt used this method.

3.2.4.4. Internal mono-standard method

In the internal mono-standard method (IM-NAA) the *a priori* known amount of one of the chemical elements (from which a measurable amount of radioactive nuclides may result) in the test portion is used as the mono-standard. The rationale behind this is that the effect of neutron spectrum perturbation is the same for this parent chemical element as for all other elements in the sample. Another assumption is that the mono-standard and the other elements to be measured are in constant ratio through the matrix (homogeneity). This method utilizes an in-situ relative detection efficiency obtained using gamma rays from the activation products of the elements present in the sample to overcome the problem of gamma ray self-attenuation. The IM-NAA gives relative elemental mass fractions with respect to the internal mono-standard mass. The relative mass fraction is converted to an absolute value by using the mono-standard mass [4, 63, 64]. In special cases e.g., mostly metals and alloys where all major and minor elements are amenable to NAA, absolute mass fractions can be arrived at by mass balance and this approach is called standard-less approach of NAA [65]. India developed this method and uses it regularly to analyse various large samples. IM-NAA is beneficially used to analyse large (kg scale) and non-standard size samples, in the cases where f is in the order of 10^3-10^4, as in the case of thermal column of a nuclear reactor.

3.2.5. Quality Control and Trueness

Quality control in analytical measurements consists of an inspection to assess if, at the end of a process step, the result is fit for the intended use, based on pre-defined quantitative criteria. Measurement of the degree of trueness (or bias) is usually done by processing commutable materials with known property values of the measurement of interest. Certified reference materials may serve this purpose although the importance of commutability should not be ignored. This approach is common in neutron activation analysis but there are implicit limitations in analysing large samples.

Firstly, the processing of certified reference materials at the tens of grams scale can be quite expensive and would result in a high consumption of these valuable reference materials. Secondly, reference materials are usually bottled at amounts of 50–150 gram, and are not available at larger amounts.

Thirdly, there are no certified reference materials available of irregular shape like may occur when analysing archaeological or cultural objects. Finally, as mentioned in the above, the quality control material should be commutable to the test portion. This not only applies to the element, its amount and the gross matrix composition, but also to the degree of homogeneity of all components in that quality control material. And this latter precondition is even more difficult to satisfy.

As an alternative, laboratories may wish to prepare their own trueness control material using materials that are known to be sufficiently homogeneous for the elements of interest, and inexpensive commonly available, such as coal fly ash or ground coffee milk powder.

Demonstrating the degree of trueness is therefore a specific challenge in LSNAA [66]. Laboratories embarking on large sample analysis have to invest in method validation in which a series of test analyses is done to verify the computational part of NAA. As a start, well homogenized materials such as clay or certain granular food commodities can be used both at the normal (small) NAA mass and at the large NAA mass. Measured gamma ray intensity ratios of the same radionuclide, and calculated masses of multiple radionuclides of the same element will provide a first indication if the voluminous photopeak efficiency and/or the gamma ray self-attenuation have correctly be estimated. The neutron self-attenuation correction is more difficult the verify, but a smart use of control materials in which one of the elements may serve as internal monitor [54] may provide the necessary insight.

However, this all will not guarantee the degree of trueness if objects are analysed in which the measurand is inhomogeneously distributed. It marks one of the challenges for the future of large sample analysis.

3.2.6. Best measurement capability in LSNAA

The high degree of trueness in normal NAA results from decades of method development, validation and experience in the characterisation of candidate certified reference materials. All sources of error are known and uncertainties can be estimated and quantified as has been demonstrated [67]. This evidence was one of the considerations of recognizing that NAA has all the potential to meet the requirements of a primary method of measurement. NAA laboratories participating in the metrological key-comparisons organized by the Bureau International des Poids et Mesures (BIPM) have demonstrated that the degree of trueness of NAA results can be at least equivalent to what can be obtained by other analytical techniques. The Proficiency Testing by Interlaboratory Comparison of NAA laboratories mechanism implemented by the IAEA in conjunction with WEPAL [13] since 2010, has provided an opportunity for laboratories to demonstrate their proficiency, and to perform root cause analysis of deviating results, leading to overall significant improvement in analytical capability of the participating laboratories. The trend towards greater automation of all the steps involved in NAA can also enhance the quality and reliability of results by reducing human error and improving timing precision of irradiations, transfer and measurement [68].

The random and systematic errors known in normal NAA may and will occur in LSNAA as well. However, some of them — such as gamma ray self-attenuation and neutron/photon fluence rate or e.g. neutron spectrum gradients — have much larger effects. Extreme inhomogeneities are an additional phenomenon in large sample analysis with an impact on the degree of trueness. Computer simulations have provided insight in the impact of inhomogeneities to the degree of trueness. Matrices with inhomogeneous composition in major chemical elements have been modeled by composing a sample of cylinders with strongly differing neutron or gamma ray attenuation properties. Inhomogeneity for trace elements has been simulated by modeling extreme distributions of a trace element with either neutron or gamma ray attenuation properties, strongly differing from those of the main composition of the sample [57]. Both inhomogeneities in matrix composition (e.g., layered structures) as trace element inhomogeneities (e.g., ‘hot spots’) were taken into account.

These simulations clearly demonstrated that false values of mass fractions may be obtained if inhomogeneities are not accounted for in the interpretation step of LSNAA. The smallest deviations may occur if matrix inhomogeneities are encountered; the most pronounced effects can be expected when the trace element of interest is distributed either on the outside, or on the axis of the cylindrical sample. Inhomogeneities affecting the gamma ray attenuation have, in general, a stronger effect on the degree of trueness than inhomogeneities affecting the neutron absorption.

Computer tomography or neutron radiography can help to identify extreme inhomogeneities and a better estimate of their impact can be made.

4. CONSIDERATIONS FOR IMPLEMENTATION OF LSNAA

4.1. STAKEHOLDER AND USER NEEDS

Implementing LSNAA should best be done after a careful evaluation of potential stakeholders and their current and future needs including an assessment of the analytical feasibility and the associated risks. The type(s) and size of material to be analysed with the facility may set requirements and constraints to the encapsulation. Analysis of irregularly shaped objects, such as the vase described in Section 2, sets further requirements beyond those for e.g. inhomogeneous but granular or powdered material. Stakeholders dealing with e.g. sediment or rock drill cores may provide well dimensioned cylindrical objects, but future expectations on trends in the diameters of such cores should be discussed. Similar considerations apply to archaeological and cultural objects that might be provided for analysis.

In view of this all, large sample facilities using external neutron beams offer more flexibility for sample handling than pool-side facilities albeit at less flexibility regarding the neutron flux needed. Pool-side facilities may also have the potential of irradiations under Cd cover (epithermal NAA) if self-moderation is expected to be insignificant; thermal column facilities require more construction. The same applies to the counting facility. As mentioned in the above, horizontal dipstick (side-looking) detectors allow for rotation during counting of the irradiated object along its vertical axis.

Implementing LSNAA (and/or LSPGA) should be preceded by a thorough evaluation of the potential stakeholders, including their current and future needs. To some extent, such stakeholders may be part of the project implementation team for a good communication on decisions taken in the design phase.

4.2. HANDLING OF LARGE, INTACT ACTIVATED OBJECTS

Neutron activation of large, intact activated objects has also consequences for the handling of these materials once the analysis has been completed. For traditional NAA the concern is simply how to dispose of several tens of milligrams of radioactive material. For LSNAA, if the sample were given the same neutron flux, the activities could be in the GBq range depending on the mass of the sample. The total neutron fluence must be carefully rationed for some samples. For rare coins, valuable pottery, and other precious objects, the importance of assuring that the samples can be released after an agreed upon decay time cannot be overstated.

Other radiation effects should be considered for precious samples – radiation can alter the properties of organics, fade some colors, or create “hot spots” if the object contains elements such as, for instance, cadmium. For these types of objects there are other tools that can be brought to bear before irradiation with neutrons, including CT scans to discover inhomogeneity in the sample that could affect the counting efficiency, X ray fluorescence studies to see if “hot spots” could be generated by mass fractions of elements with high neutron activation cross sections, neutron radiography with relatively low fluence rates to assess the distribution of absorbing materials in the sample (along with a preliminary count with a gamma spectrometer) before full activation. While this all may sound discouraging, these cautions are for worrisome samples, and many large samples are easily accommodated — the only challenge for these samples is the interpretation of the counting results.

One further technical consideration that must be addressed early on is the degree of accuracy or trueness needed in the analysis. Is the analysis carried out for gross screening or is a high precision analysis required? Needless to say that, if there is tolerance in the trueness of the results, LSNAA can be relatively straightforward to implement. Another issue is, again, the "preciousness" of the sample. Can the analysis be done and the sample still be released to the owner at the end of the analysis?

4.3. OTHER ASPECTS OF JUSTIFYING LSNAA

The economics of LSNAA is not discussed because much depends on specific reactor capabilities, the type of sample and above all, the added value on element masses in the entire sample that could not be obtained elsewise. As an example, it could be related to a unique precious sample that can only be analysed by LSNAA; then cost may not be a factor. At the other extreme the sample might be somehow (macroscopically) homogeneous and of too low density (e.g., collected tree leaves) to be placed in a Marinelli container. Here the primary economic consideration is whether it is cheaper to prepare a representative sample or to incur costs for a calibration standard.

5. RECENT DEVELOPMENTS AND OUTLOOK

5.1. RECENT DEVELOPMENTS

The IAEA CRP on LSNAA to which this document is dedicated was concluded in the year 2012. Several LSNAA facilities have been developed during the CRP, as described in Section 3, and very strong methodological advancements were achieved.

However, one further important outcome of the CRP was to bring about an increased awareness of the capability of NAA and PGA to measure chemical elements in large objects. This has resulted in both new applications in existing facilities and in new facilities being established after the CRP ended. These will be described in this section.

An important next step in analysing large samples is the spatially resolved quantitative element measurement. Computer tomography and neutron radiography techniques already provide qualitative information about the distribution of elements. Combining this with e.g. focused neutron beams and prompt gamma analysis opens a new unique area of applications. The CRP participant from Japan published an attempt for simultaneous imaging and elemental composition measurement performed at the object, used for the laboratory intercomparison described in Section 2 [69]. Using a slit collimator (1 cm width, 7 cm height) they were able to detect inhomogeneities in the scanned layers of the vase for the elements H, B, Na and Si. Other groups are also working towards spatially resolved element measurement in large objects [70].

The absence of sample treatment makes LSNAA useful for bulk analysis of ultrapure materials for verification of specifications. In the past, this was to some extent already demonstrated by the analysis of low mass intact (thin) silicon wafers with dimensions up to 12.5 cm. Trace elements in the entire neutron activated silicon ingots (30 cm length, 5 cm diameter) were measured by Vins et al. [71], demonstrating the capability of measuring trace impurities even inside large crystals and not on the surface wafer layers only.

Menezes et al. applied the large sample technique to study the composition of dietary supplements [72]. Elias et al. measured impurities in the content of complete packages of commercially available dog food as collected from the shelf, which is a material composed of various granular components [73]. Yagob [74] demonstrated that LSNAA can be fitfully applied in dietary intake studies in which, on basis of the double portion approach, multi kilogram amounts of food is collected over 3-5 days. Analysing these amounts ‘as collected’ circumvents the homogenization and sub-sampling problems.

The projects in the frame of the IAEA CRP were mainly related to the application of LSNAA in research reactors. Several new applications have also been reported utilising D-T and D-D neutron generators. Ma and Mildenberger reported the development and use a method for measuring toxic elements in 200 L drums of radioactive waste, packed in concrete [75, 76] using PGA and a 14 MeV n-generator. Yang [77], Naqvi [78] and Eftekhari Zadeh [79] used this combination for measuring trace elements in cement; Gierlik et.al. used the same approach for studies of explosives [80]. Monte Carlo based modelling of the interaction of the neutrons in the sample, the neutron and gamma ray self-attenuation and the voluminous photopeak efficiency have now become common [81].

In addition, the use of neutron generators and isotopic neutron sources in belt-analysers and flow-analysers (e.g. for oil) for process control in industry continues [82]. Indeed, belt-analysers using neutron sources are in fact based on large sample analysis. The same applies to in-vivo measurement of major components in (human, animal) bone and other tissues. Both techniques (belt-analysers and in-vivo NAA/PGA) are around for decades but remarkably enough, it has taken until the 1990s before these approaches were conceived as valuable complementary assets for, e.g., reactor-based NAA/PGA.

Although much less worldwide available, photon activation analysis shares many of the advantages of NAA and PGA for the analysis of large objects. A review of this technique has been published by Segebade et.al. [83] referring to examples of the analysis of large samples by photon activation. Stamatelatos et al. [84] demonstrated the use of photon activation analysis for multi-element measurements in intact large clumps (ca. 125 g) of metallurgical slag from a copper furnace; these measurements were done for an archaeological research project to gain more insight in the metallurgical techniques applied in the early bronze age.

The scope of applications may expand further. The domain of forensic science is also an area to explore. Objects can now be directly analysed ‘as collected’, circumventing all problems on the representativeness of a small sub-sample taken for analysis. Moreover, the object is not disturbed by sub-sampling or even destructed by dissolution, and is thus preserved as evidence.

5.2 OUTLOOK AND SCIENTIFIC CHALLENGES

Large sample neutron activation analysis can be considered to be still in its formative years, when compared to normal NAA, which has more than 80 years of history. From the current status and recent developments, as described in this report, several scientific challenges can be identified as outstanding:

- As already mentioned in Section 3.2.6, neutron transmission measurement and CT scanning can provide valuable details as input for the neutron self-shielding and gamma ray self-attenuation. This will contribute to enhance the degree of trueness of the measured amounts of the elements;
- Activation using epithermal and fast neutrons for inducing specific nuclear activation reactions will require research into the modelling of the self-moderation in large (inhomogeneous) samples;
- Activation using isotopic neutron source arrays or D-D neutron generator arrays may be also an approach towards further development towards a field method of LSNAA. The use of such sources implies attention to the change of the neutron energy distribution inside the sample as the much lower neutron fluence rate will have to be compensated with sample sizes that can easily reach 10 kg or more. Whereas belt analysers for major components are applied in many industrial areas, a stand-alone field method for also minor and trace element analysis may be of interest for, e.g., the screening of mine tailings, recycled electronic parts and other bulk materials, e.g. for compliance with import requirements;
- Laboratory intercomparison studies with asymmetrically shaped objects, and objects with point or layered inhomogeneities for further underpinning the validation of the computational methods and demonstration of the degree of trueness of the results;
- Representativeness studies in areas where a sample undergoes many treatment steps before a test portion is finally available. Analysis of the original material and of sub-samples taken after processing may provide unprecedented insight in sampling errors and sample handling errors;

- A fundamental aspect that needs to be considered is the reporting of the measured data, i.e. as mass fractions or total amounts. Reporting in mass fractions indicates an assumption on the degree of homogeneity; possibly criteria may have to be developed for the acceptable homogeneity in large samples at which reporting in mass fractions is scientifically sound.

6. CONCLUSIONS

Representativeness of analytical test portions for objects to be characterised is crucial for taking sound decisions on the most appropriate technique for a given purpose. This can be sometimes accomplished by dissolution of the object — and assuming 'total' digestion — sometimes by analysis of multiple test portions taken from the object. However, there are many areas and considerations why dissolution is unwanted or not possible, and sub-sampling not allowed. Surface analysis by X ray fluorescence spectrometry may provide relevant answers but nuclear techniques such as NAA, PGA and Photon Activation Analysis provide currently the only opportunity for bulk analysis in which the object is kept intact.

Nuclear analytical techniques such as NAA and PGA have been used for many years for measuring the element content of bulk amounts, such as in well-logging, belt analysers and for in-vivo measurements. These applications are often tailored approaches for the measurement of one or a few major elements only. Since the early 1990s these capabilities have been acknowledged as a valuable add-on for routine multi-element analysis for cases where representativeness of small test portions is difficult to achieve or test portions cannot be taken at all, such as in the domain of museum and cultural artefacts.

Different methodologies, facilities and methods of calculus and data analysis have been developed and employed for large sample analysis during the IAEA CRP (F23027) 'Application of Large Sample Neutron Activation Analysis Techniques for Inhomogeneous Bulk Archaeological Samples and Large Objects'. The CRP addressed the lack of verified and validated experimental procedures required for NAA implementation in bulk sample studies. In this way, the IAEA initiated the first concerted effort to support the planning, harmonisation and implementation of Large Sample NAA, bringing the technique developers and end-users together. The CRP focused primarily on the application of LSNAA in the areas of archaeology and geology. However, the methods, facilities and trained manpower also further the utilisation of LSNAA in other areas such as industry and life sciences, as well as in basic research.

The methods developed have been tested by analysing a large, irregular shaped object of known composition in major, minor and trace elements. An intercomparison of the results obtained in different laboratories, using different procedures and protocols, has demonstrated for the first time that neutron activation analysis is capable of providing reliable results if analyses of such objects are needed. Indeed, the degree of agreement obtained was similar to what is achieved with normal NAA.

As with any new technique, there will be still a need for refinements so as to further increase the degree of trueness of the results. However, the physics of the techniques employed is fully understood and all processes during irradiation and measurement can therefore be modelled.

Scientific challenges remain with respect to method validation, trueness control and the reporting of the results, especially if the distribution of measurand is significantly inhomogeneous. This physical basis of the nuclear analytical techniques also offers an outlook for further expansion. The first results of spatially resolved measurements (3-D mapping of the element content) of large objects, based on combing the elemental analysis with imaging techniques, are already encouraging and worth further elaboration. This publication provides, besides the results of the CRP, also a summary of the developments that have taken place after the CRP, as well as of areas of current development in LSNAA and LSPGA.

As such, large sample analyses may become a valuable asset of research reactor facilities, where the expertise with the technique may be employed for the development of large sample field methods on basis of neutron generators or isotopic neutron sources.

Success will depend on stakeholder involvement in the design and use of the technique. To this end, the opportunities of LSNAA and LSPGA have now to be shared with others. Until now, examples of accomplishments have been mainly published in (analytical) nuclear science oriented journals, as can be derived from the list of references in this document. Time has come now to share this information with potential users and future stakeholders from the applied fields such as archaeology, art sciences, forensic sciences, material processing or nutrition by presentations on conferences and publications in journals typical for those fields.

This publication is intended to make the information on LSNAA generated during the CRP available to Member States and potential stakeholders of the technique. This publication serves as a reference of interest not only to the experts, research reactor personnel, and those considering this technique, but also to various stakeholders and users such as academia, industrialists, environmental and legal experts, and administrators. An international network has been established in the frame of this recent CRP that will contribute to future use of LSNAA in different research areas and innovative methodologies.

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ANNEX I: CASE STUDIES

The county reports given in Annex II give a global overview of all the accomplishments achieved by the participants during the CRP. However, in several cases common procedures were employed by several participating laboratories, constituting one general approach. In order to facilitate comparisons of the different approaches, several case studies were extracted from the country reports, converting some of their essential points in a uniform tabulation.

These case studies constitute only a collection of different approaches of LSNAA showing the versatility of the method, and do not imply superiority of any given method used in any given laboratory over other ones.

Title	Absolute Neutron Activation Analysis Technique of a Large Crude Oil Sample
Authors	V. G. Zinovyev, V. V. Martynov, Yu. E. Loginov, E. M. Korotkih, G. I. Shulyak, T. M. Tukavina, P. A. Sushkov
Source	World Journal of Nuclear Science and Technology, 2013, 3, 136-142
Organization	Nuclear Physics Department, Petersburg Nuclear Physics Institute, Saint Petersburg
Country	Russia
Sample type /Mass	Crude oil / 100 g
Irradiation system	Reactor WWR-M / 18 MW Dry channel located outside the beryllium reflector Thermal neutron flux of 10^{12} $cm^{-2}s^{-1}$ Thermal to epithermal flux ratio of 45.
Counting system	15% coaxial Ge detector (FWHM 1.7 keV at 1332.5 keV) for the registration of high-energy gamma rays Thin planar Ge-detector (FWHM 0.9 keV at 122 keV) for the registration of low-energy gamma rays.
Calibration Technique(s)	Absolute and Relative
Advantage offered by LSNAA	Increased the number of determined elements and improved the detection limits
Abstract	This manuscript presents an application of calculation methods in neutron activation analysis (NAA) of a large crude oil sample. Monte-Carlo computer code was developed. The computer code calculates neutron cross sections and neutron flux density distribution in the interior large sample. ENDF/B-VII.0 data files and ENSDF BNL-NCS-51655-01/02-Rev data files were used as nuclear databases in our computer code. HPGe planar detector efficiency registration technique and the software were developed for the absolute NAA technique of the large sample. The mass fractions of Na, K, Ca, Sc, Cr, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Sr, Zr, Mo, Ag, Sb, Cs, Ba, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Tm, Yb, Lu, Hf, Ta, W, Pt, Au, Hg, Th and U in the crude oil samples of Eastern Siberia oilfield were determined using calculation and relative techniques in the mass fraction range from 10−9 to 0.5%.
Keywords	Neutron Flux; Neutron Activation Analysis; ENDF Datab

Title	Large sample NAA work at BARC: Methodology and applications
Authors	R. Acharya, K.K. Swain, K. Sudarshan, R. Tripathi, P.K. Pujari, A.V.R. Reddy
Source	Nuclear Instruments and Methods in Physics Research A622 (2010) 460–463
Organization	Bhabha Atomic Research Centre, Trombay, Mumbai
Country	India
Sample type /Mass	Clay pottery, uranium ore and stainless steel / 15 g to 55 g
Irradiation system	Reactor Apsara / 1 MW Thermal column Thermal neutron flux of 1.2 x 10^8 $cm^{-2}s^{-1}$ Thermal to epithermal flux ratio of 6000
Counting system	40% relative efficiency Ge detector
Calibration Technique(s)	k_0-based internal mono standard
Advantage offered by LSNAA	Better analytical representativeness as compared to replica subsample analysis
Abstract	Large sample neutron activation analysis (LSNAA) was carried out using thermal column facility of Apsara reactor at Bhabha Atomic Research Centre, Mumbai, India. The k_0-based internal mono-standard NAA (IM-NAA) using in-situ detection efficiency was used to analyze large and non-standard geometry samples of clay pottery, uranium ore and stainless steel. Elemental mass fraction ratios with respect to Na as a mono-standard were used in the study of pottery and ore samples. For stainless steel sample of SS 304L, the absolute mass fractions were calculated from mass fraction ratios by mass balance approach since all the major elements (Fe, Cr, Ni and Mn) were amenable to NAA. Applications of LSNAA in the above mentioned three different areas are described in this paper.
Keywords	Large sample NAA, Internal mono-standard method, In situ detection efficiency, Non-standard geometry, Pottery, Uranium ore, Stainless steel

Title	Large sample neutron activation analysis of a ceramic vase
Authors	I. E. Stamatelatos, F. Tzika, T. Vasilopoulou, M. J. J. Koster-Ammerlaan,
Source	J. Radioanal. Nucl. Chem. (2010) 283, 735–740
Organization	Institute of Nuclear and Radiological Sciences, Technology, Energy and Safety, National Centre for Scientific Research “Demokritos”, Aghia Paraskevi
Country	Greece
Sample type /Mass	Pottery / 376 g
Irradiation system	Hoger Onderwijs Reactor (Netherlands)/ 2 MW Thermal column Thermal neutron flux of 5 x 10^8 cm^{-2}s^{-1} Thermal to epithermal flux ratio of > 2500
Counting system	96 % relative efficiency coaxial Ge detector (BISNIS)
Calibration Technique(s)	Absolute
Advantage offered by LSNAA	Non-destructive multi-elemental analysis of precious object as a whole
Abstract	Large Sample Neutron Activation Analysis (LSNAA) was applied to perform non-destructive elemental analysis of a ceramic vase. Appropriate neutron self-shielding and gamma ray detection efficiency calibration factors were derived using Monte Carlo code MCNP5. The results of LSNAA were compared against traditional Neutron Activation Analysis (NAA) results and a satisfactory agreement between the two methods was observed. The ratio of derived mass fractions between the two methods was within 0.7 and 1.3. Estimation of the activity level decay with time showed that the vase could be released from regulatory control at about 3 months post irradiation. This study provided an analytical procedure for bulk sample analysis of precious and archaeological objects that need to be preserved intact and cannot b damaged for sampling purposes.
Keywords	Neutron activation analysis, Large sample, Gamma spectrometry

Title	Irradiation and measurement devices and methods development for LSNAA applications at the TRIGA-ACPR core
Authors	C. Roth, D. Barbos, D. Gugiu, A. Datcu, D. Dobrea, M. Preda, M. Gligor, M.B. Mweetwa
Source	J. Radioanal. Nucl. Chem. (2012) 291, 461–466
Organization	Institute for Nuclear Research, Pitesti, Arges, Romania
Country	Romania
Sample type /Mass	Neolithic pottery / 100g
Irradiation system	Annular Core Pulsed Reactor Central irradiation channel / irradiation device with polyethylene moderator Integrated flux of 2 x 10^{12} $cm^{-2}s^{-1}$ at 100 kW Thermal flux 1.2 x 10^{11} $cm^{-2}s^{-1}$ Thermal to epithermal flux ratio 2.5
Counting system	40% efficiency Ge detector Scanning device enabling rotation and vertical shift
Calibration Technique(s)	Absolute
Advantage offered by LSNAA	Non-destructive multi-element analysis of precious samples
Abstract	A Large Sample Neutron Activation Analysis (LSNAA) facility has been developed at the TRIGA Annular Core Pulsed Reactor (ACPR) operated by the Institute for Nuclear Research in Pitesti. The central irradiation cavity of ACPR can accommodate a large irradiation device. The ACPR neutron flux characteristics are well known and spectrum adjustment techniques have been successfully applied to enhance the thermal component of the neutron flux in the central irradiation cavity. An analysis methodology was developed by employing the MCNP (a general Monte Carlo N-particle transport code) code in order to estimate counting efficiency and correction factors for the major perturbing phenomena. The paper presents the development of the experimental device, the results of the neutron flux-spectrum characterization, and preliminary steps to validate the analysis methodology.
Keywords	Neutron Activation, Large sample, Flux, Spectrum

Title	Neutron activation analysis of bulk samples from Chinese ancient porcelain to provenance research
Authors	Zhu, J., Solbrekken, G., Hao, W., Li, Y., Zhen, J. , Zhen, T., Glascock, M.D.
Source	J. Radioanal. Nucl. Chem. (2013) 298:237–242
Organization	Chinese Academy of Sciences
Country	China
Sample type /Mass	Proto-porcelain / 0.5 g
Irradiation system	Missouri University Research Reactor / 10 MW
Counting system	Normal coaxial Ge detectors
Calibration Technique(s)	Comparator using NIST SRMs and NIST RMs
Advantage offered by LSNAA	LSNAA results are less dependent on the state of the porcelain sample. Bulk samples could be measured directly without the need of grinding procedure, thus reducing the cost and contaminated risks of precious artifacts and decreasing the workload for sample preparation.
Abstract	Neutron activation analysis (NAA) is an important technique to determine the provenance of ancient ceramics. The most common technique used for preparing ancient samples for NAA is to grind them into a powder and then encapsulate them before neutron irradiation. Unfortunately, ceramic materials are typically very hard making it a challenge to grind them into a powder. In this study we utilize bulk porcelain samples cut from ancient shards. The bulk samples are irradiated by neutrons alongside samples that have been conventionally ground into a powder. The NAA for both the bulk samples and powders are compared and shown to provide equivalent information regarding their chemical composition. Also, the multivariate statistical has been employed to the analysis data for check the consistency. The findings suggest that NAA results are less dependent on the state of the porcelain sample, and thus bulk samples cut from shard may be used to effectively determine their provenance.
Keywords	Neutron activation analysis, Proto-porcelain, Provenance

Title	Non-destructive elemental analysis of large meteorite samples by prompt gamma ray neutron activation analysis with the internal monostandard method
Authors	Latif, S.A., Oura, Y., Ebihara, M., Nakahara, H.
Source	Analytical and Bioanalytical Chemistry (2013), 8749-8759
Organization	Tokyo Metropolitan University, Hachioji, Tokyo
Country	Japan
Sample type /Mass	Irregularly shaped meteorites / 0.2 g to 325 g
Irradiation system	Thermal neutron beam Thermal flux of 2.4×10^{7} cm^{-2} s^{-1}
Counting system	20% relative efficiency Ge with BGO Compton suppression system
Calibration Technique(s)	internal mono-standard method
Advantage offered by LSNAA	Non-destructive analysis of precious specimens
Abstract	Prompt gamma ray neutron activation analysis (PGNAA) using the internal mono-standard method was tested for its applicability to analyzing large solid samples including irregularly shaped meteorite samples. For evaluating the accuracy and precision of the method, large quantities of the Geological Survey of Japan standardized rock powders (JB-1a, JG-1a, and JP-1) were analyzed and 12 elements (B, Na, Mg, Al, Cl, K, Ca, Ti, Mn, Fe, Sm, and Gd) were determined by using Si as an internal standard element. Analytical results were mostly in agreement with literature values within 10 %. The precision of the method was also shown to be within 10 % (1σ) for most of these elements. The analytical procedure was then applied to four stony meteorites (Allende, Kimble County, Leedey, Lake Labyrinth) and four iron meteorites (Canyon Diablo, Toluca (Mexico), Toluca (Xiquipilco), Squaw Creek) consisting of large chunks or single slabs. For stony meteorites, major elements (Mg, Al, Si, S, Ca, and Ni), minor elements (Na and Mn) and trace element (B, Cl, K, Ti, Co, and Sm) were determined with adequate accuracy. For iron meteorites, results for the Co and Ni mass fractions determined are all consistent with corresponding literature values. After the analysis, it was confirmed that the residual radioactivity remaining in the sample after PGNAA was very low and decreased down to the background level. This study shows that PGNAA with the internal mono-standard method is highly practical for determining the elemental composition of large, irregularly shaped solid samples including meteorites.
Keywords	Prompt gamma ray neutron activation analysis (PGNAA). Large samples. Meteorites. Internal mono-standard method. Neutron activation analysis

ANNEX II: CONTENTS OF CD-ROM

List of individual paper contributors. All contributions are available on the attached CD-ROM.

Author	Affiliation	Title of the paper
Menezes, M.A.B.C.	Nuclear Technology Development Center, Brazilian Commission for Nuclear Energy, Brazil	Contribution of analytical nuclear techniques in the reconstruction of the Brazilian prehistory analysing archaeological ceramics of tupiguarani tradition
Soliman, M.	Atomic Energy Authority, ETRR-2, Cairo, Egypt	Large-Sample Neutron Activation Analysis at ETRR-2
Nyarko, B.J.B.	National Nuclear Research Institute, Ghana Atomic Energy Commission, Ghana	Large Sample Neutron Activation Analysis (LSNAA) using a low power research reactor
Stamatelatos, I. E.	Institute of Nuclear and Radiological Sciences, Energy, Technology and Safety NCSR Demokritos, Greece	Large Sample Neutron Activation Analysis of heterogeneous samples
Ebihara, M.	Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan	Report on Inter-comparison Tests of an Archaeological Pottery Sample
Abdullah, J.	Malaysian Nuclear Agency, Bangi, 43000 Kajang, Malaysia	In-Situ Compositional Analysis and Provenance Study of the Historic Terengganu Stone (the Inscribed Stone “Batu Bersurat”) using Neutron-Induced Prompt Gamma ray Techniques (NIPGAT)
Bode, P.	Delft University of Technology, Reactor Institute Delft, Netherlands	Validation of intermediate Large Sample Analysis (with sizes up to 100 g) and associated facility improvement
Bedregal, P.	Peru	Neutron Activation Analysis of archaeological pottery samples of large size, including pieces of low symmetry shape: how to get accurate analytical results in a practical way
Roth, C.	Institute for Nuclear Research Pitesti, Romania	Large Sample NAA facility and methodology development
Zinovev, V. and Martynov, V.	Saint-Petersburg Nuclear Physics Institute. Gatchina, Russia	Neutron Activation Analysis of large crude oil samples

Haddad, K. and Alsomel, N.	Atomic Energy Commission of Syria, Damascus, Syria	Large Sample Neutron Activation Analysis of sewage using shutdown MNSR photoneutrons
Haddad, K. and Noush, M.	Atomic Energy Commission of Syria, Damascus, Syria	Validation of MCNP efficiency calculation for gamma spectrometric assay of large samples
Tippayakul, C.	Thailand Institute of Nuclear Technology, Thailand	Development of large sample neutron activation technique for new applications in Thailand

ABBREVIATIONS

BIPM	International Bureau of Weights and Measurement
CDTN	Centro de Desenvolvimento da Tecnologia Nuclear
CRM	Certified reference material
CRP	Coordinated Research Project
CT	Computerized tomography
EDXRF	Energy dispersive X ray fluorescence
FWHM	Full width at half maximum
HPGe	High purity Germanium
IM-NAA	Neutron activation analysis with the internal mono-standard method
IPEN	Peruvian Institute of Nuclear Energy
JSI	Jožef Stefan Institute
k_0-NAA	Neutron activation analysis with the k_0 method
LSNAA	Large sample neutron activation analysis
LSPGA	Large sample prompt gamma analysis
NAA	Neutron activation analysis
PGA	Prompt gamma analysis
QA/QC	Quality assurance and quality control
SD	Standard deviation
SPND	Self-powered neutron detector
WEPAL	Wageningen Evaluating Programs for Analytical Laboratories
XRF	X ray fluorescence

CONTRIBUTORS TO DRAFTING AND REVIEW

Barradas, N.P.	International Atomic Energy Agency
Bode, P.	Delft University of Technology, Netherlands, currently NUQAM Consultancy, Netherlands
Montoya, R. E. H.	InstitutoPeruano de Energía Nuclear, Peru
Ramamoorthy, N.	International Atomic Energy Agency
Reddy, A.V.R.	Bhabha Atomic Research Centre, Trombay, India
Reece, W.D.	Department of Nuclear Engineering, Texas A&M University, United States of America
Ridikas, D.	International Atomic Energy Agency
Salame, P.	International Atomic Energy Agency
Stamatelatos, I. E.	Institute of Nuclear and Radiological Sciences, Energy, Technology, Safety, Greece
Yunikova, A.	ROSATOM CICE&T, Obninsk, Russian Federation
Zeman, A.	International Atomic Energy Agency

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