

# MASS FRACTION DETERMINATION OF TOTAL As IN GEOLOGICAL MATRIX SAMPLE BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS: A STUDY OF METHOD VALIDATION

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## Abstract

In this study the method validation of total As mass fraction in geological matrix samples by Instrumental Neutron Activation Analysis was carried out, according to ISO/IEC 17025:2005 and recommendations of INMETRO DOQ-CGCRE-008. Accuracy, robustness, selectivity, linearity, detection limit, quantification limit and uncertainties were outlined in a marine sediment certified reference material.

Keywords: method validation, As, sediment, INAA

## 1. INTRODUCTION

The Neutron Activation Analysis Laboratory (LAN) is a subdivision of the Research Reactor Centre (CRPq) at IPEN - CNEN/SP. Since 2010's, a new Quality policy has been implemented aiming to obtain full compliance with the requirements of NBR ISO/IEC 17025:2005. The implementation of this new quality management system is absolutely essential to LAN, aiming to produce reference materials for environmental studies. In the context, the validation of measurement methods is essential for suitability of the laboratory in this quality system.

ISO/IEC 17025:2005 specifies the general requirements for the competence to carry out tests and/or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods [1]. The method validation is defined as “*the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled*”. The validation process shall be as extensive as is necessary to meet the needs of the given application or field of application. The laboratory shall record the results obtained, the procedure used for the validation, and a statement as to whether the method is fit for the intended use.

The most important activity in LAN is Neutron Activation Analysis, especially the Instrumental Neutron Activation Analysis technique (INAA). INAA is a multielemental technique relatively free from the matrix effects, which has a non destructive character and do not require digestion procedures [2, 3]. This makes the technique attractive for several applications in geochemistry, environmental monitoring, biomonitoring, reference material characterization and related sciences [4-7].

INAA is employed for determination of several elements, based on the conversion of a non radioactive nuclide, in a radioactive nuclide (radionuclide). This process occur through neutron bombardment in the material to be analyzed resulting in nuclear reactions characteristics of each element. In INAA, the reaction product to be measured is the gamma radiation arising from the radionuclide obtained by the neutron bombardment process. Gamma-ray decay presents best characteristics for identification (selectivity) and simultaneous detection of different radionuclides [2].

In the procedure, sample and standard (containing know concentration of measurand) with the same geometry are simultaneously irradiated in a nuclear reactor. The determination of measurand content in the sample is obtained comparing the photopeak area of the radionuclide at gamma-ray spectrum of the sample with that of the standard (comparator method). According to the Comité Consultatif pour la Quantité de Matière (CCQM) INAA comparator method has potential to be considered a primary method of measurement [2].

Accuracy (trueness and precision), robustness, linearity, detection limit, quantification limit and uncertainties budget were outlined in marine sediment certified reference material. This study is one among many others developed aiming the suitability of LAN according to NBR ISO/IEC 17025:2005.

## 2. OBJECTIVE

The main objective of this study was to carry out the method validation of INAA for mass fraction determination of total-As in geological matrix sample, according to ISO/IEC 17025:2005 Standard and recommendations of INMETRO DOQ-CGCRE-008.

## 3. METHODS AND MATERIALS

### 3.1. Instrumental Neutron Activation Analysis

The INAA comparative method was performed for the mass fraction determination of total-As in geological matrix samples. Samples and multielemental standards were simultaneously irradiated for 8 h under  $0.5$  to  $1.0 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$  thermal neutron flux at IEA-R1 Nuclear Research Reactor.  $^{76}\text{As}$  radionuclide was quantified by gamma-ray spectrometry, using a GC2018 Canberra HPGe detector coupled to a DSA 1000 multichannel analyzer. Genie 2000 – Gamma Acquisition & Analysis 3.1 software was used to perform the processing of the gamma-ray spectrum. The analytical photopeak used to mass fraction determination of total-As was 559.10 keV. Mass fraction calculations were carried out using a Microsoft Excel spreadsheet, according to Equation 1 [8].

$$C = \frac{A * wst * Cst * e^{(t-tst)}}{Ast * w} \quad (1)$$

where:

$C$  is the sample element concentration ( $\text{mg kg}^{-1}$ );

$Cst$  is the standard element concentration ( $\text{mg kg}^{-1}$ );

$A$  is the activity of the element in the sample (cps);

$Ast$  is the activity of the element in the standard (cps);

$w$  is the sample mass (mg);

$wst$  is the mass of As in element standard (mg);

$\lambda$  is the radionuclide decay constant ( $\lambda = \ln(2)/t_{1/2}$ ) ( $\text{s}^{-1}$ );

and  $(t - tst)$  is the time difference between sample and element standard measurements.

### 3.2. Samples and Elemental Standard Preparation

Subsamples of Marine Sediment CRM [9] of  $150 \pm 10$  mg were weighed in polyethylene packaging previously cleaned, using a Shimadzu AEM-5200 analytical balance. The standard working solution was prepared by dilution of As Spex CRM element solution in volumetric flask. Elemental standards were prepared by pipetting of the As working solution onto Whatman paper filters using Eppendorf micropipette. After drying, the paper filters were folded, placed and sealed in polyethylene packaging with the same sample geometry (10 mm x 8 mm x 1 mm).

### 3.3. Measurement method

Depending on the characteristics of the measurement method, different configurations may generate more or less favorable results. Thus, in a validation process is necessary to make the definition of the measurement method characteristics, taking into account prior knowledge about the technical and measurands. Table 1 present the configurations of measurement method for determination of total-As mass fraction in geological matrix samples by INAA on the comparative method.

Method name	Geo-Total-As
Technique	INAA
Detection	Gamma-ray spectrometry
Measurand	Total-As
Matrix sample	Geological
Measurement linear range	3.0 mg kg <sup>-1</sup> to 50 mg kg <sup>-1</sup>
Sample mass	150 ± 10 mg
As-standard mass	2.475 ± 0.027 µg
As-peak energy	559.10 keV
Sample/As-standard geometry	10 mm x 8 mm x 1 mm
Irradiation time	8 hours
Thermal neutron flux	0.5 to 1.0 x 10 <sup>13</sup> cm <sup>-2</sup> s <sup>-1</sup>
Sample/As-standard decay time to measurement	7 days
Sample measurement time	60 minutes
As-standard measurement time	20 minutes
Sample/As-standard distance to detector	33 mm

**Table 1. Geo-Total-As measurement method characteristics**

## 4. RESULTS AND DISCUSSION

### 4.1. Method performance characteristics

Geo-Total-As method performance characteristics were outlined according to INMETRO DOQ-CGCRE-008 recommendations. The performance parameters investigated during the method validation procedure were: accuracy (trueness and precision), detection limit, quantification limit, robustness and measurement uncertainty.

Table 2 present the results obtained for repeatability limit (r), intermediate precision condition (IPC), reproducibility limit (R), trueness, detection limit (LOD) and quantification limit (LOQ) for the analysis of Marine sediment CRM by INAA on the comparative method.

Method	r <sup>a</sup>	IPC <sup>a</sup>	R <sup>a</sup>	z-score <sup>b</sup>	LOD <sup>a</sup>	LOQ <sup>a</sup>
Geo-Total-As	0.72	1.3	3.6	-1.1 to 1.5 (0.08)	0.59	1.8
a Results in mg kg <sup>-1</sup> ;						
b Z-score range for all analyses; in parenthesis (z-score average)						

**Table 2. Method performance characteristics for the measurement of total-As in geological matrix samples by INAA on the comparative method**

According to the results, the minimum natural deviation expected for two or more independent results for the measurement of total-As in geological matrix samples is 0.72 mg kg<sup>-1</sup> (r) and the maximum variation expected for two or more independent results obtained at LAN (IPEN – CNEN/SP) is 1.3 mg kg<sup>-1</sup> (IPC).

The evaluation of the IPC, i.e., the natural variability of the results within LAN, was performed considering four main factors: irradiation processes, the use of different gamma-ray spectrometers, different operating days and different analysts. Aiming to evaluate the significance of the factors, a *t*-test was performed for mean results obtained to each condition at the 5 % significance. Results did not present any significant factors for *t*-test analyses.

R was estimated by means of the results obtained for IPC, as it was not possible to perform interlaboratory studies for evaluation of method performance in another measurement laboratories. Thus, the IPC result was multiplied by 2.8, resulting in the R value estimation (3.6 mg kg<sup>-1</sup>).

By means of the r/IPC ratio is possible to make an interpretation about the percentage corresponding to the natural variation of the results for the method, that is, how much of the IPC value can be explained by the natural variability of the results (r). According to r/IPC ratio 56 % of the variability of the results for IPC can be explained by the natural variability of the results. In this context, the interpretation is how the higher value found for r/IPC ratio, greater robustness of the measurement method.

Trueness results ranged from -1.1 and 1.5 according to z-score calculations and were considered suitable results. For all measurements, the z-score average was 0.08.

The evaluation of the robustness status of the method as well as the measurement uncertainty estimation are still in progress. Anyway, from preliminary results, relative expanded uncertainties below 5 % are feasible for this kind of matrix.

## 5. CONCLUSION

The sizing of the method performance characteristics and subsequent validation of methods in INAA, certainly contribute to support of the analytical quality of results at LAN. Another contribution of this work is attributed to the restructuring of the quality management system, according to NBR ISO/IEC 17025:2005 Standard.

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## REFERENCES

- [1] ISO - International Organization for Standardization, "ISO/IEC 17025:2005. General requirements for the competence of testing and calibration laboratories". International Organization for Standardization, Geneva (2005)
- [2] R.R. Greenberg, P. Bode, E.A. De Nadai Fernandes, "Neutron activation analysis: A primary method of measurement". Spectrochim Acta B (2011) 66:193-241
- [3] P. Bode, E.A.N. Fernandes, R.R. Greenberg, "Metrology for chemical measurements and the position of INAA". J Radioanal Nucl Chem (2000) 245:109-114

- [4] R.L. Franklin, F.J. Ferreira, J.E. Bevilacqua, D.I.T. Fávoro, "Assessment of metals and trace elements in sediments from Rio Grande Reservoir, Brazil, by neutron activation analysis". *J. Radioanal Nucl Chem* (2012) 291:147-153
- [5] L. Ma, L. Feng, A. Hioki, K.H. Cho, J. Vogl, A. Berger, G. Turk, S. Macleod, G. Labarraque, W.F. Tong, D. Schiel, C. Yafa, L. Valiente, L.A. Konopelko, C. Quetel, P. Vermaercke, J.V.L. Manzano, M. Linsky, E. Cortes, S. Tangpitayakul, L. Plangsangmas, L. Bergamaschi, R. Hearn, " International comparison of the determination of the mass fraction of cadmium, chromium, mercury and lead in polypropylene: the Comité Consultatif pour la Quantité de Matière pilot study CCQM-P106". *Accred Qual Assur* (2010) 15:39-44
- [6] D. Seo, M.B.A. Vasconcellos, M.G.M. Catharino, E.G. Moreira, F.C.P.M. de Sousa, M. Saiki. "Vanadium determination in *Perna perna* mussels (Linnaeus, 1758: Mollusca Bivalvia) by instrumental neutron activation analysis using the passive biomonitoring in the Santos coast, Brazil". *J Radioanal Nucl Chem* (2013) 296:459-463
- [7] Moreira E.G. " Preparo e caracterização de um material de referência de mexilhão *Perna perna* (Linnaeus, 1758)". Doctoral Tesis – Instituto de Pesquisas Energética e Nucleares, São Paulo, Brazil (2010)
- [8] W.D. Ehmann, D.E. Vance, "Radiochemistry and Nuclear Methods of Analysis". John Wiley & Sons, New York (1991)
- [9] NIST - National Institute of Standards and Technology, "Certificate of Analysis: Standard Reference Material 2702 Inorganics in Marine Sediment". (2012) [https://www-s.nist.gov/srmors/view\\_detail.cfm?srm=2702](https://www-s.nist.gov/srmors/view_detail.cfm?srm=2702). Accessed 12 Oct 2014