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# TRACE ELEMENT DETERMINATION IN A MUSSEL REFERENCE MATERIAL USING SHORT IRRADIATION INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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## ABSTRACT

The production of certified reference materials in Brazil, and the consequent availability to national end users, is an important task for the enhancement of Metrology in Chemistry status in the country, as these materials are used for method validation, equipment calibration and for establishing metrological traceability links. In this study, Instrumental Neutron Activation Analysis (INAA) was applied to the determination of magnesium, manganese and vanadium in a mussel reference material produced at IPEN-CNEN/SP. For the determination of these elements via the comparative INAA method, the respective analytical radionuclides, $^{27}$Mg, $^{56}$Mn, and $^{52}$V, are short lived and then, short irradiations are used. The main advantage over longer irradiation methods is the faster output of analytical results. Six subsamples from two bottles of the *Perna perna* mussel reference material were analyzed. Each subsample was simultaneously irradiated with elemental standards for 10 s at the IEA - R1 research nuclear reactor through a pneumatic transfer system. After suitable decay periods, gamma radioactivity measurements were carried out, using a hyperpure germanium detector. The accuracy of the method was checked by using the NIST SRM 1566b – "Oyster Tissue" certified reference material. The comparison of the obtained results to the robust mean of the interlaboratorial collaborative trial used for the characterization of the mussel reference material showed that the short irradiation INAA method is suitable for the characterization of new reference materials.

## 1. INTRODUCTION

Certified reference materials (CRM) play an important role in the quality assurance of measurement results as they are used for method validation, equipment calibration and for establishing metrological traceability links of measurement results [1]. A CRM is defined as a reference material, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability [2]. In the context of trace elements in the environment, the specified properties are the mass fractions of trace elements in the reference material.

The production of certified reference materials in Brazil, and the consequent availability to national end users, is an important task for the enhancement of Metrology in Chemistry

status in the country and the interest in this issue is growing fast in the national scientific community.

In this study, the application of Instrumental Neutron Activation Analysis (INAA) to the determination of magnesium, manganese and vanadium in a *Perna perna* mussel reference material produced at IPEN-CNEN/SP was investigated. The production of this material was planned as mussels tend to bioaccumulate contaminants from the surrounding waters and are used in biomonitoring programs [3-6].

For the determination of these elements via the comparative INAA method, the respective analytical radionuclides, $^{27}$Mg, $^{56}$Mn, and $^{52}$V, are short lived and then, short irradiations are used. The main advantage over longer irradiation methods is the faster output of analytical results.

## 2. EXPERIMENTAL

### 2.1. Sample and Elemental Standards Preparation

Six subsamples of approximately 0.180 g from bottles number 54 and 129 of the mussel candidate reference material and of NIST SRM 1566b – "Oyster Tissue" certified reference material were weighed in properly cleaned polyethylene vials using a Shimadzu AEM-5200 analytical balance. The mussel reference material bottles were selected at random, one for each half of the batch. Elemental standards were prepared by pipetting Spex standard element solutions onto Whatman paper filters, using variable volume pipettes (Eppendorf or Jencons). After drying, paper filters were kept in polyethylene vials with the same geometry as for the samples.

### 2.2. Irradiation and Element Determination

Subsamples of the mussel reference material, certified reference material and elemental standards were simultaneously irradiated for 10 s at 6.6 x $10^{12}$ n cm$^{-2}$ s$^{-1}$ thermal neutron flux at the IEA-R1 Nuclear Research Reactor from IPEN-CNEN/SP through a pneumatic transfer system. Immediately after irradiation, $^{27}$Mg and $^{52}$V radionuclides were measured for 200 s. After a 1.5-h decay period, $^{56}$Mn radionuclide was measured for 600 s. Gamma ray measurements were performed using a GC2018 Canberra hyperpure germanium detector coupled to a Canberra DSA-1000 multichannel analyzer. Gamma ray spectra were collected and processed using a Canberra Genie 2000 version 3.1 spectroscopy software. Element content calculations were carried out using a Microsoft Excel spreadsheet.

Table 1 presents radionuclides, their corresponding gamma ray photopeak energies and half lives that were used in the two measurement steps of the INAA short irradiation procedure [7].

**Table 1 Radionuclides used in the short irradiation INAA [7]**

| Measurement | Radionuclide | Half life | Energy, keV |
|---|---|---|---|
| 1st (200 s) | $^{27}$Mg | 9.46 min | 843.8 |
| | $^{52}$V | 3.75 min | 1434.08 |
| 2nd (600 s) | $^{56}$Mn | 2.58 h | 846.8 |

## 3. RESULTS AND DISCUSSION

As the gamma ray energies for Mg and Mn radionuclides are very close (Table 1), it was necessary to let the sample to decay for 1.5 h in order to avoid the spectral interference of $^{27}$Mg in the determination of $^{56}$Mn.

Table 2 presents the short irradiation INAA results obtained for the mussel candidate reference material as well as for the NIST SRM 1566b certified reference material. Coincident results were obtained for the two bottles of the candidate reference material if the confidence intervals are considered. This reflects the good homogenization procedure employed during the preparation of the material [4].

For the comparison of INAA results obtained for the NIST SRM 1566b certified reference material with the certified values [8], $E_n$ scores were calculated as described on Equation 1. From the obtained scores it was concluded that the short irradiation INAA method used is accurate to the analysis of Mg, Mn and V in biological materials as $|E_n| \leq 1$ [9].

$$En = \frac{w_{lab} - w_{ref}}{\sqrt{(u_{lab}{}^2 + u_{ref}{}^2}} \quad (1)$$

Where $w_{lab}$ is the mass fraction value obtained by the laboratory with combined standard uncertainty $u_{lab}$, and $w_{ref}$ is the reference mass fraction value with combined standard uncertainty $u_{ref}$.

**Table 2. Element mass fraction obtained by INAA for the candidate mussel reference material and for the oyster tissue certified reference material[1]**

| Element | Mussel reference material | | NIST SRM 1566b | | |
|---|---|---|---|---|---|
| | Bottle 54 | Bottle 129 | INAA | Certified value[2] | $E_n$ score |
| Mg, % | 0.361 ± 0.022 | 0.341 ± 0.030 | 0.1104 ± 0.0051 | 0.1085 ± 0.0023 | 0.34 |
| Mn, mg kg$^{-1}$ | 20.5 ± 1.1 | 21.9 ± 1.2 | 18.63 ± 0.36 | 18.5 ± 0.2 | 0.33 |
| V, mg kg$^{-1}$ | 2.60 ± 0.20 | 2.74 ± 0.31 | 0.566 ± 0.032 | 0.577 ± 0.023 | -0.32 |

[1] mean values and confidence interval at 95 % for $n = 6$;
[2] uncertainties are expanded uncertainties informed by the producer;

Figure 1 presents the graphical representation of the obtained results in comparison to the robust mean and corresponding expanded uncertainty obtained during the collaborative program used in the characterization of the mussel candidate reference material.

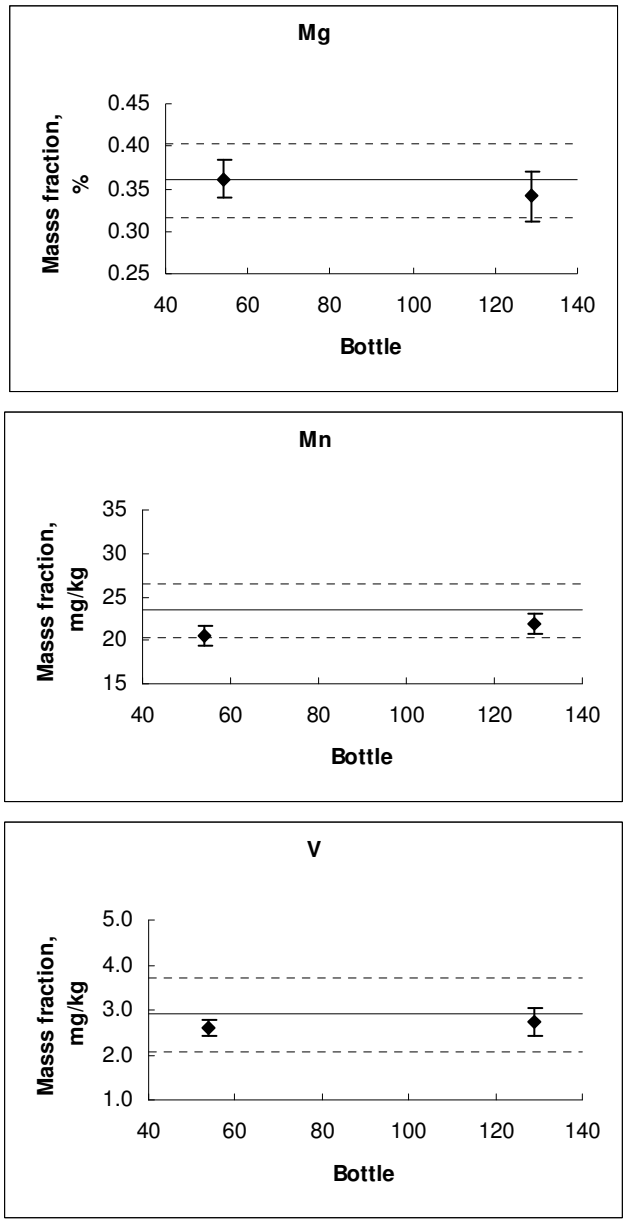


**Figure 1. Graphical representation of the results obtained by INAA for the mussel reference material (mean value and confidence interval, 95 %) compared to the collaborative program results (robust mean (————) and expanded uncertainty, $k = 2$ (- - - - - - - - -)).**

According to the certification criteria adopted in the comparative program, assigned values obtained for Mg and Mn were considered certified values while the V value was considered a reference value, as there was less metrological confidence on the comparative program results for this element [4]. It was observed that INAA results overlap the uncertainty interval proposed for the collaborative program, confirming the suitability of the INAA short irradiation method proposed.

## 4. CONCLUSIONS

In this study a short irradiation Instrumental Neutron Activation Analysis method was applied for the determination of magnesium, manganese and vanadium in two bottles of a *Perna perna* mussel reference material produced at IPEN – CNEN/SP. The accuracy of the method was checked by using the NIST SRM 1566b – "Oyster Tissue" certified reference material and was considered adequate. The comparison of the obtained results to the robust mean of the interlaboratorial collaborative trial used for the characterization of the mussel reference material showed that the short irradiation INAA method is suitable for the characterization of new reference materials.

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