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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 bromine, chlorine, magnesium, manganese, potassium 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, ^{80}Br, ^{38}Cl, ^{27}Mg, ^{56}Mn, ^{42}K and ^{52}V, are short lived and then, short irradiations are used. 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 results obtained in this study to the robust mean of the interlaboratorial collaborative trial used for the characterization of the mussel reference material was performed via *z*-score tests. The comparison showed that the short irradiation INAA method is suitable for the characterization of new reference materials.

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Introduction

Certified reference materials (CRMs) 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 bromine, chlorine, magnesium, manganese, potassium 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, ^{80}Br, ^{38}Cl, ^{27}Mg, ^{56}Mn, ^{42}K and ^{52}V, are short lived and then, short irradiations were used.

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Experimental

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). After drying, paper filters were kept in polyethylene vials with the same geometry as for the samples.

Irradiation and element determination

Subsamples of the mussel reference material, certified reference material and elemental standards were simultaneously irradiated at a thermal neutron fluence of 6.6×10^{13} n cm^{-2} at the IEA-R1 Nuclear Research Reactor from IPEN-CNEN/SP through a pneumatic transfer system. Immediately after irradiation, ^{80}Br, ^{38}Cl, ^{27}Mg and ^{52}V radionuclides were measured for 200 s. After a 1.5 h decay period, ^{42}K and ^{56}Mn radionuclides were 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 the radionuclides that were used in the two measurement steps of the INAA short irradiation procedure along with their corresponding gamma ray photopeak energies and half lives [7].

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

Measurement	Radionuclide	Half life	Energy (keV)
1st (200 s)	^{80}Br	17.68 min	616.3
	^{38}Cl	37.24 min	1642.7
	^{27}Mg	9.46 min	843.8
	^{52}V	3.75 min	1434.1
2nd (600 s)	^{42}K	12.36 h	1524.6
	^{56}Mn	2.58 h	846.8

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 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 [8]. Coincident results were obtained for the two bottles of the candidate reference material considering the confidence intervals. This reflects the good homogenization procedure employed during the preparation of the material [4]. Also, from the Student's t test performed on obtained results, it was inferred that the mean values do not differ in a statistically significant manner as $t \leq t_{crit}$ for the significance level $\alpha = 0.01$ [9].

For the purpose of quality assurance, INAA results obtained for the NIST SRM 1566b certified reference material were compared to the certified values using z-scores. The z-score was originally designed for the performance assessment in interlaboratory programs and is calculated as described on Eq. 1 [9].

$$z = \frac{w_{lab} - w_{ref}}{\hat{\sigma}} \quad (1)$$

where w_{lab} is the mass fraction value obtained by the laboratory, w_{ref} is the certified mass fraction value and $\hat{\sigma}$ is the target range.

In this study, the modified Horwitz equation was used to estimate the reproducibility standard deviation of the method (s_R) which was used as the target range, according to Eq. 2 [10, 11].

$$s_R = \begin{cases} 0.22c & \text{if } c < 1.2 \times 10^{-7} \\ 0.22c^{0.895} & \text{if } 1.2 \times 10^{-7} \leq c \leq 0.138 \\ 0.01c^{0.5} & \text{if } c > 0.138 \end{cases} \quad (2)$$

where c is the certified mass fraction expressed in g g^{-1}.

From the obtained z-scores it was concluded that the short irradiation INAA method used is accurate to the analysis of Cl, K, Mg, Mn and V in biological materials and in candidate references materials in particular as $|z| \leq 2$ [10]. As there is no certified value for Br in NIST SRM 1566b, NIST SRM 2976–"Mussel Tissue" was used for this element [12]. The INAA result was 332 ± 22 mg kg^{-1} and the certified value for Br is 329 ± 15 mg kg^{-1}. From the z-score result ($z = 0.013$), Br results were also considered satisfactory.

Figure 1 presents the graphical representation of the obtained results in comparison to the robust mean and corresponding expanded uncertainty obtained during the interlaboratory program used in the characterization of the mussel candidate reference material [13].

With the exception of Cl and K, it was observed that INAA results overlap the uncertainty interval proposed for the interlaboratory program, confirming the suitability of

Table 2 Element mass fraction in mg kg^{-1}at dry mass basis obtained by INAA for the candidate mussel reference material and for the oyster tissue certified reference material

Element	Mussel reference material		NIST SRM 1566b–Oyster Tissue		
	Bottle 54	Bottle 129	This study	Certified value[a]	*z*-Score
Br	245 ± 30	230 ± 24	43.8 ± 2.6	–	–
Cl (g kg^{-1})	48.9 ± 3.4	42.0 ± 4.4	5.20 ± 0.15	5.14 ± 0.10	0.023
K (g kg^{-1})	6.40 ± 1.09	7.25 ± 0.65	6.34 ± 0.41	6.520 ± 0.090	−0.060
Mg (g kg^{-1})	3.61 ± 0.22	3.41 ± 0.30	1.104 ± 0.054	1.085 ± 0.023	0.028
Mn	20.5 ± 1.1	21.9 ± 1.2	18.63 ± 0.37	18.5 ± 0.2	0.0061
V	2.60 ± 0.20	2.74 ± 0.31	0.566 ± 0.033	0.577 ± 0.023	−0.010

Mean values and confidence interval at 95 % for $n = 6$

[a] Uncertainties are expanded uncertainties informed by the producer

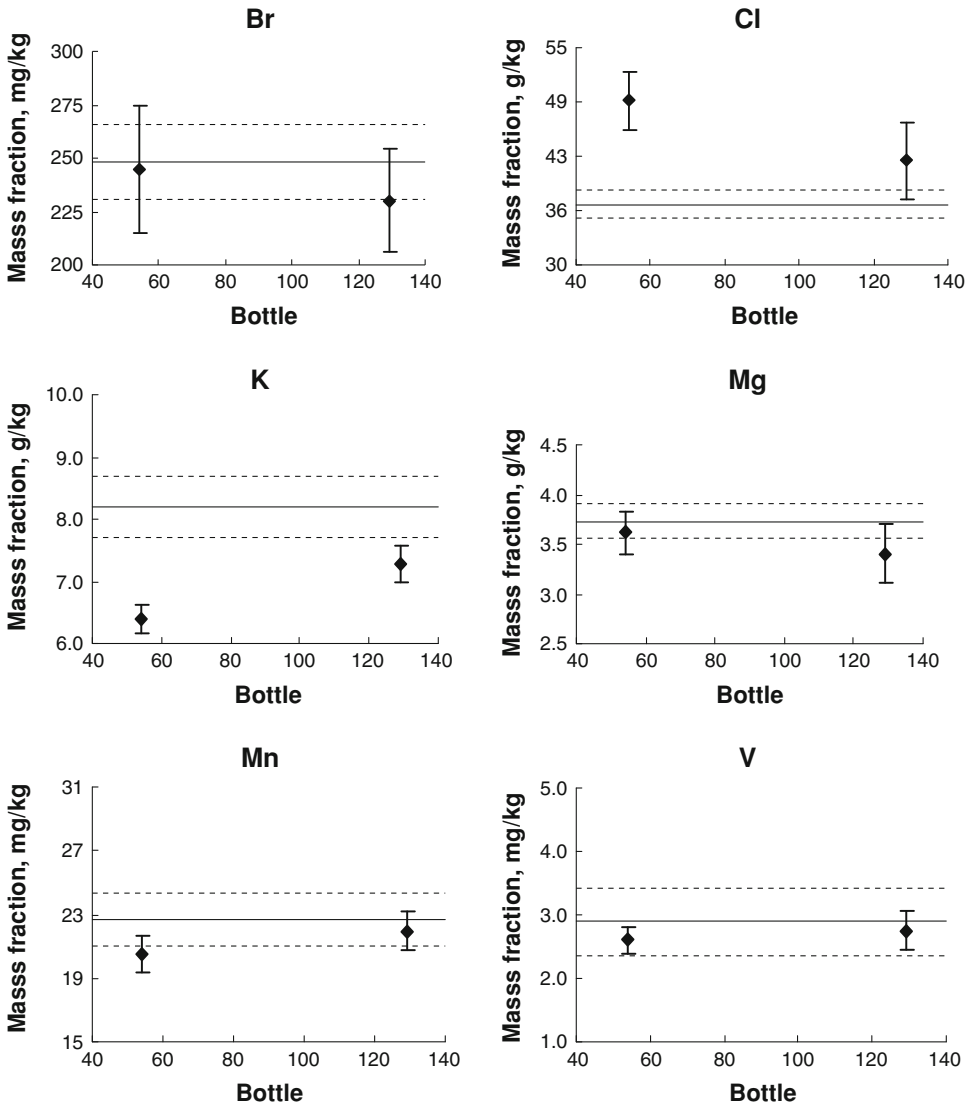

Fig. 1 Graphical representation of the results obtained by INAA for the mussel reference material (mean value and confidence interval, 95 %) compared to the collaborative program results (robust mean (*solid line*) and expanded uncertainty, $k = 2$ (*dashed line*))

the INAA short irradiation method proposed. The observed differences for Cl and K need to be better investigated as CRM results for these elements presented satisfactory *z*-scores. On the other hand, if *z*-scores are used to assess the suitability of the obtained results, using the interlaboratory comparison data on Eq. 1, the observed INAA data

may be considered satisfactory as for Cl, $z = 0.89$ and $z = 0.38$ for bottles 54 and 129, respectively and for K, $z = -0.48$ and $z = -0.25$ for bottles 54 and 129, respectively.

Conclusions

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

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