

HOMOGENEITY STUDY ON BIOLOGICAL CANDIDATE REFERENCE MATERIALS: THE ROLE OF NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Instrumental Neutron activation Analysis (INAA) is a mature nuclear analytical technique able to accurately determine chemical elements without the need of sample digestion and, hence, without the associated problems of analyte loss or contamination. This feature, along with its potentiality use as a primary method of analysis, makes it an important tool for the characterization of new references materials and in the assessment of their homogeneity status. In this study, the ability of the comparative method of INAA for the within-bottle homogeneity of K, Mg, Mn and V in a mussel reference material was investigated. Method parameters, such as irradiation time, sample decay time and distance from sample to the detector were varied in order to allow element determination in subsamples of different sample masses in duplicate. Sample masses were in the range of 1 to 250 mg and the limitations of the detection limit for small sample masses and dead time distortions for large sample masses were investigated.

1. INTRODUCTION

The use of reference materials (RM) and, when possible, certified reference materials (CRM) are essential so that the laboratory can provide the results of analytical measurements with an acceptable level of reliability [1, 2]. Although there is a wide number of CRMs produced by multiple producers, features such as high price, difficulty in purchasing and absence of national CRMs, still preclude its use by national laboratories into their routine. In this context, it is of great interest new studies related to CRMs and their homogeneity test in order to contribute to the national laboratories in the certified reference material production process.

According to ISO Guide 2006, the study of homogeneity is used to verify whether the differences observed between different vials of bulk material, i.e., the residual heterogeneity is significant compared to the uncertainty of the material characterization. The evaluation of the homogeneity can be carried out with the study of homogeneity of bottles, what is used to ensure that there is no variation in the properties of interest along the batch material bottles. Also, through the homogeneity of the study within the vial, which is characterized using different masses in a single sample, it is possible to estimate the minimum mass of the sample required for a particular application, our case [3, 4].

The Instrumental Neutron Activation Analysis (INAA) is an analytical technique often used for determining the concentration of elements in various matrices. The use of a small amount of the sample mass does not need any dissolution. Consequently, there is little concern with blank problems, contamination, loss or yields, making the INAA a reliable reference technique for evaluating the degree of RMs homogeneity [5, 6].

However, there are some limitations to this technique that should be considered by the analyst. Detection limit (LD) for lower masses and problems with dead time (DT) for higher masses, are examples of limitations of this method. Such limitations were observed by Moreira in his doctoral study at IPEN - CNEN/SP, on a mussel RM. A decrease in concentration values with the increase of mass for various elements analyzed by the INAA were observed, particularly for elements with shorter half lives, like Na. Thus, a trend was seen in the results depending on the sample mass, ranging between 50 and 500 mg [7].

In the present study, the INAA was used to study the within bottle homogeneity of K, Mg, Mn, Na and V, elements with short lived radionuclides in order to determine the minimum sample mass of a mussel reference material, prepared previously at IPEN - CNEN/SP. The tendency of the results was verified as a function of the mass ranging between 1 and 250 mg. This study is important to assess the homogeneity status of reference materials at small sample masses.

2. EXPERIMENTAL

2.1 Sample and elemental standard preparation

For the study of homogeneity in one vial, the mussel RM vial selected was number 91, and then, 10 subsamples of the mussel reference material were weighed inside polyethylene bags properly cleaned using a calibrated Shimadzu analytical balance Libror AEL - 40SM. Sample masses were 1, 5, 10, 15, 20, 25, 30, 50, 150 and 250 mg of the same bottle. Standards of the elements of interest were prepared by pipetting Spex standard solutions on Whatmann filter paper sheets, using pipettes (Eppendorf) with varied volumes. For some elements, dilutions were carried out in a volumetric flask from the original solution, before pipetting. After drying, the filter papers were maintained in polyethylene vials, with the same geometry as for the samples.

2.2 Irradiation and determination of elements

Subsamples were simultaneously irradiated with standards of K, Mg, Mn, Na and V elements, in the pneumatic station of the IEA-R1 reactor of IPEN - CNEN/SP, for 20 seconds, under the flux of 10^{12} n cm s⁻¹ thermal neutrons. Immediately after irradiation, measurements of gamma activities for Mg and V were carried out, for 300 s, on different distances sample-detector (shelves 0, 1, 2 and 3, being shelf 0 the closest to the detector).

For determining K, Mn and Na, the decay time of the subsamples were 1.5 h and such measurements were performed on the same shelves described previously. For this procedure, a high-purity Ge detector, coupled to a Camberra DAS-1000 multi canal analyzer was used. Gamma ray spectra were collected and the data were processed in the Genie 2000 3.1

version, spectroscopy software. The calculation of element mass fractions was achieved using a Microsoft Excel spreadsheet.

3. RESULTS AND DISCUSSION

The graphs represented in Figures 1 to 5 show the results of the analyzed element concentration, in relation to the sample mass and in different distances from the detector.

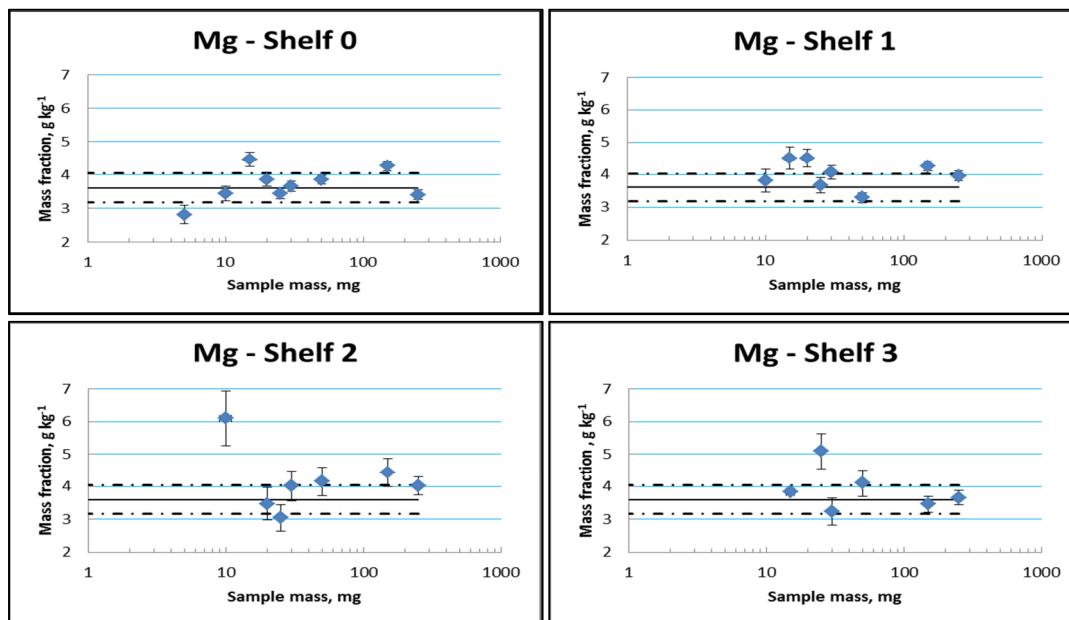


Figure 1: Mg mass fraction obtained at various sample masses in the mussel reference material at different sample-detector distances.

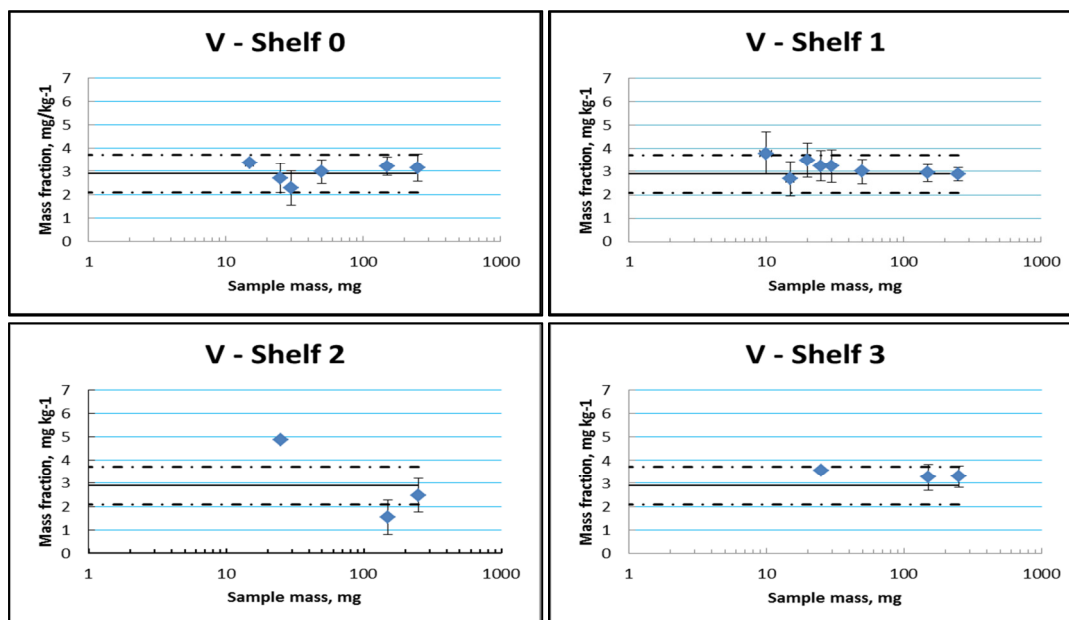


Figure 2: V mass fraction obtained at various sample masses in the mussel reference material at different sample-detector distances.

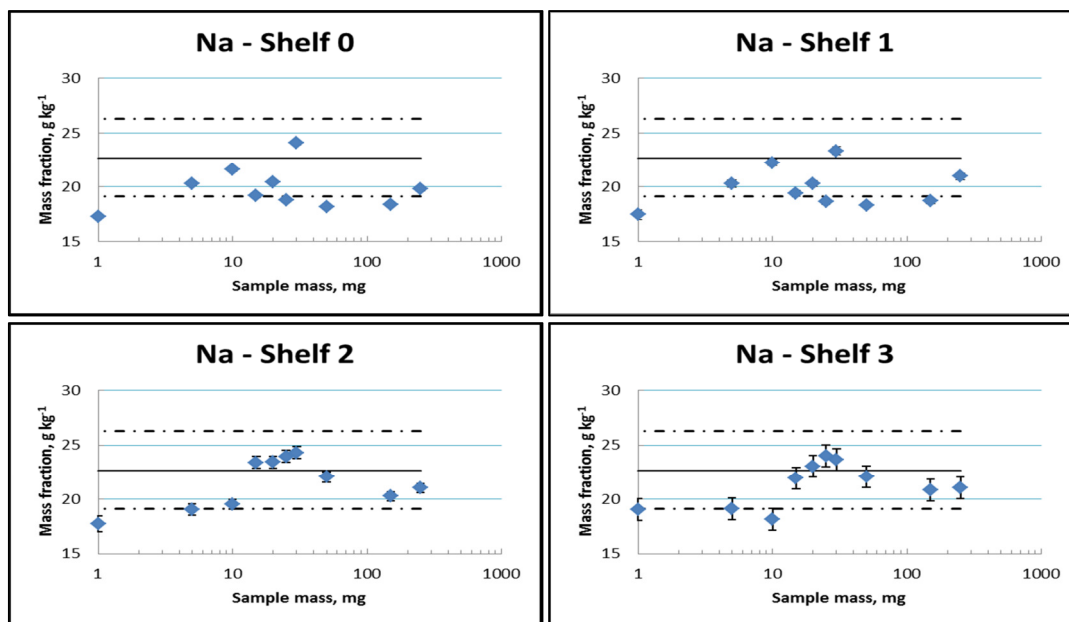


Figure 3: Na mass fraction obtained at various sample masses in the mussel reference material at different sample-detector distances.

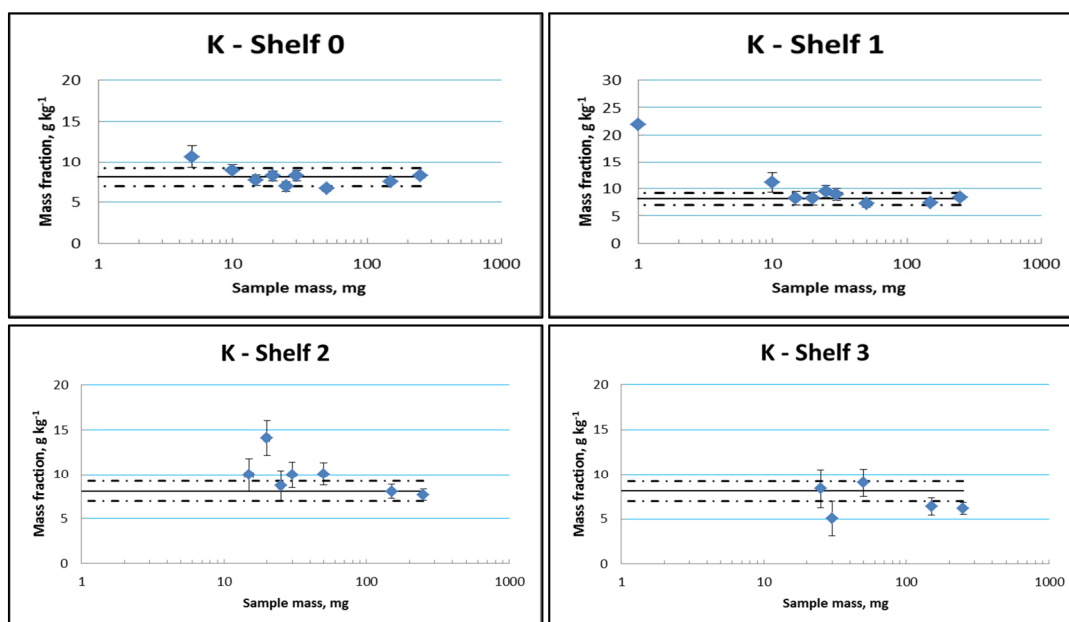


Figure 4: K mass fraction obtained at various sample masses in the mussel reference material at different sample-detector distances.

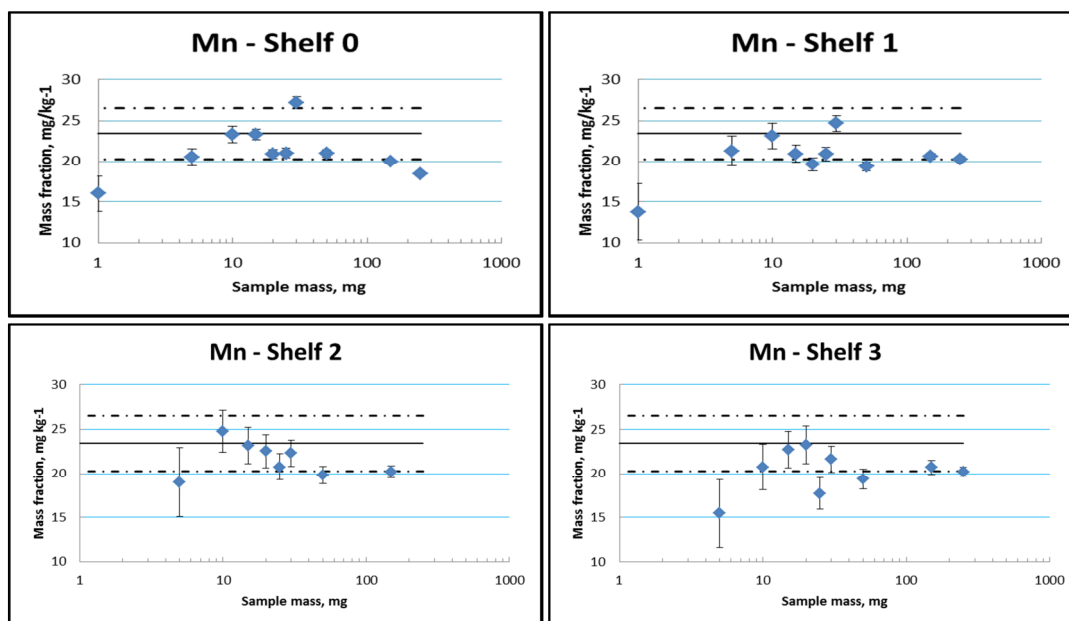


Figure 5: Mn mass fraction obtained at various sample masses in the mussel reference material at different sample-detector distances.

As general trends, Mg was determined for all the masses only for shelf 0 and smaller uncertainties were obtained for this shelf in comparison to the others. In the case of V, it was observed that at shelves 3 and 2, most of the V photo peaks were not detected in the experimental setup used due to the larger distance sample-detector and uncertainties were smaller for larger sample masses. Mg and V values overlapped the expanded uncertainty range of the reference material but for Mg, masses below 25 mg showed wider result dispersion.

Somewhat different results were obtained for the elements with longer lived radionuclides (Na, K and Mn) In the case of K, best results were obtained at shelf 0, possibly due to the lower sensibility of INAA towards this element. On the other hand, Na and Mn could be determined at all the shelves but at shelves 1 and 0 bias on the expected results were noticed, influence of the high dead times, which also was observed in a previous study [7]. High result dispersions were observed at masses below 10 mg for Na and for Mn, result bias was also enhanced at shorter distances sample-detector.

4. CONCLUSIONS

From the observed results it was concluded that the within-bottle homogeneity of the mussel reference material may be successfully evaluated at much smaller sample masses than the usual (100 mg), by using INAA. Further investigation is necessary in order to minimize the dead time influence and for detection limits in sample mass fraction results, by INAA. After the measurement procedure is optimized, replicate analyses will allow the determination of the within-bottle homogeneity of the mussel reference material.

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