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APPLICATION OF INAA COMPLEMENTARY GAMMA RAY PHOTOPEAKS TO HOMOGENEITY STUDY OF CANDIDATE REFERENCE MATERIALS

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ABSTRACT

Characterization and certification of reference materials, RMs, is a complex task involving many steps. One of them is the homogeneity testing to assure that key property values will not present variation among RM bottles. Good precision is the most important figure of merit of an analytical technique to allow it to be used in the homogeneity testing of candidate RMs. Due to its inherent characteristics, Instrumental Neutron Activation Analysis, INAA, is an analytical technique of choice for homogeneity testing. Problems with sample digestion and contamination from reagents are not an issue in INAA, as solid samples are analyzed directly. For element determination via INAA, the activity of a suitable gamma ray decay photopeak for an element is chosen and it is compared to the activity of a standard of the element. An interesting possibility is the use of complementary gamma ray photopeaks (for the elements that present them) to confirm the homogeneity test results for an element. In this study, an investigation of the use of the complementary gamma ray photopeaks of ^{110m}Ag, ^{82}Br, ^{60}Co, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{140}La, ^{233}Pa (for Th determination), ^{46}Sc and ^{75}Se radionuclides was undertaken in the between bottle homogeneity study of a mussel candidate RM under preparation at IPEN - CNEN/SP. Although some photopeaks led to biased element content results, the use of complementary gamma ray photopeaks proved to be helpful in supporting homogeneity study conclusions of new RMs.

1. INTRODUCTION

Characterization and certification of reference materials, RMs, of biological and environmental origin is a complex task involving many steps, such as: sampling site selection, sampling layout, material preparation and cleaning, freeze-drying, grinding and sieving, water content control, homogenization, bottling, sterilization, definition of storage conditions and chemical characterization [1].

One important part in the characterization step is the homogeneity testing which purpose is to assure that the property values of interest will not present variation among the bottles of the RM, more than allowed by its intend use. In other words, the homogenization of the bulk RM must be done in such a way that any residual inhomogeneity of the material will not be significant when the uncertainty of the analytical method in which the RM is used is concerned [2].

Good precision is the most important figure of merit of an analytical technique to allow it to be used in the homogeneity testing of candidate RMs. Due to its inherent characteristics, Instrumental Neutron Activation Analysis, INAA, is an analytical technique of choice for homogeneity testing [3].

With the use of appropriate INAA measurement schemes it is possible to obtain precise measurement results simultaneously for a large number of elements. Another advantage is the fact that solid samples are analyzed directly and, hence, problems in sample digestion and contamination from reagents are not an issue for the technique. INAA also allows the use of different sample weights, which is usually used in the definition of the minimum sample intake in homogeneity studies.

For element determination by the comparative method of INAA, the activity of a suitable gamma ray decay photopeak, the analytical photopeak, is compared to the same photopeak of a standard of the element. The analytical photopeak is chosen according to resolution (measured by the full width at half-maximum, FHWM), intensity (good counting statistics) and freedom of interferences. INAA handbooks present the recommended analytical photopeaks [4].

An interesting possibility is the use of complementary gamma ray photopeaks, for the radionuclides that present them, to confirm the INAA results obtained using the analytical photopeaks. In the context of homogeneity assessment, precision is more important that trueness and the use of complementary gamma rays for element determination may be used to corroborate conclusions about the homogeneity of the reference material, although in some cases the results might present bias.

In this study, the application of the complementary gamma ray photopeaks of ^{110m}Ag, ^{82}Br, ^{60}Co, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{140}La, ^{233}Pa (for Th determination), ^{46}Sc and ^{75}Se radionuclides was investigated in the between bottle homogeneity study of a mussel candidate RM under preparation at IPEN - CNEN/SP.

Box-plots were used for visual inspection of element content obtained using different gamma ray photopeaks. An analysis of variance approach, ANOVA, was performed to assess the homogeneity among the bottles, considering the result obtained with different gamma ray photopeaks [5, 6].

2. EXPERIMENTAL

2.1. Homogeneity Testing Layout

With the purpose of obtaining a representative sampling of the batch of the mussel candidate RM, a random stratified scheme was applied for the selection of six bottles used in this study (bottles number 19, 40, 75, 112, 143 and 156). The HISTO software, provided by the International Atomic Energy Agency, IAEA, was used in the selection of the bottles [7]. For each bottle, eight subsamples were taken for analysis. The HISTO software was also used for randomization of all subsamples, prior to irradiation and gamma ray measurement. This procedure was necessary in order to avoid interferences from any possible trends that might arise in the results during the measurement campaign.

2.2. Sample and Elemental Standards preparation

Subsamples of approximately 0.150 g were weighed in properly cleaned polyethylene bags using a Shimadzu AEM-5200 analytical balance. Elemental standards were prepared by pipetting Spex standard element solutions onto Whatman paper filters, using variable volume pipettes (Eppendorf or Jencons). For some elements, the original solution was diluted in volumetric flasks prior to pipetting. After drying, paper filters were kept in polyethylene vials with the same geometry as for the samples. Eight subsamples were taken from each bottle for analysis.

2.3. Irradiation and Element Determination

Subsamples and elemental standards were irradiated simultaneously for 8 hours at 10^{12} n cm^{-2} s^{-1} thermal neutron flux of the IEA-R1 Nuclear Research Reactor at IPEN-CNEN/SP. ^{82}Br and ^{140}La radionuclides were measured for 1.5 hours, after a 7-day decay period, while ^{110m}Ag, ^{60}Co, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{233}Pa, ^{75}Se and ^{46}Sc radionuclides were measured for 10 hours, after a 15-day decay period. Gamma ray measurements were performed using a GC2018 Canberra HPGe 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 photopeak energies and percent abundances that were used in the INAA investigation of the between bottle homogeneity of the mussel candidate RM [8].

Table 1. Radionuclides used in the between bottle homogeneity study*

Radionuclide	Energy, keV	Abundance, %	Radionuclide	Energy, keV	Abundance, %
^{110m}Ag	657.76*	94.64	^{152}Eu	121.78	28.37
	677.62	10.35		344.29	26.58
	706.68	16.44		778.92	12.96
	763.94	22.29		964.11	14.62
	884.69	72.68		1085.89	10.16
	937.49	34.36		1408.00*	20.85
	1384.30	24.28	^{59}Fe	1099.25*	56.50
	1505.04	13.04		1291.60	43.20
^{82}Br	554.35	70.76	^{140}La	328.76	20.61
	619.11	43.44		487.02	44.27
	698.37	28.49		815.77	22.90
	776.52*	83.54		1596.21*	95.40
	827.83	24.03	^{233}Pa	300.18	6.20
	1044.08	27.23		312.01*	36.0
	1317.47	26.48	^{46}Sc	889.28*	99.98
^{60}Co	1173.24*	99.90		1120.55	99.99
	1332.50	99.98	^{75}Se	136.01	59.00
^{134}Cs	604.70	97.56		264.66*	59.20
	795.85*	85.44		279.54	25.20

* Recommended photopeak energy.

3. RESULTS AND DISCUSSION

For representative elements, Figure 1 shows the obtained box-plots for the comparison of the distributions of the element content results calculated from different photopeaks. Although there were discrepancies among the results obtained for each photopeak, mean and median values as well as interquartile ranges are at the same order of magnitude for most of the elements and photopeaks analyzed. The exceptions are the results for La, Th and Eu (displayed in Figure 1). In the case of Eu, it is clear that the 121 keV and 964 keV photopeaks are experiencing some positive interference, resulting in higher concentration values. For some radionuclides, whose photopeaks are in the same region of the spectrum and present very similar counting statistics, such as Co, Cs, Fe (displayed in Figure 1), and, Sc, the obtained results agree much better, suggesting that, at least for the mussel matrix, any of the photopeaks could be used in the element determination.

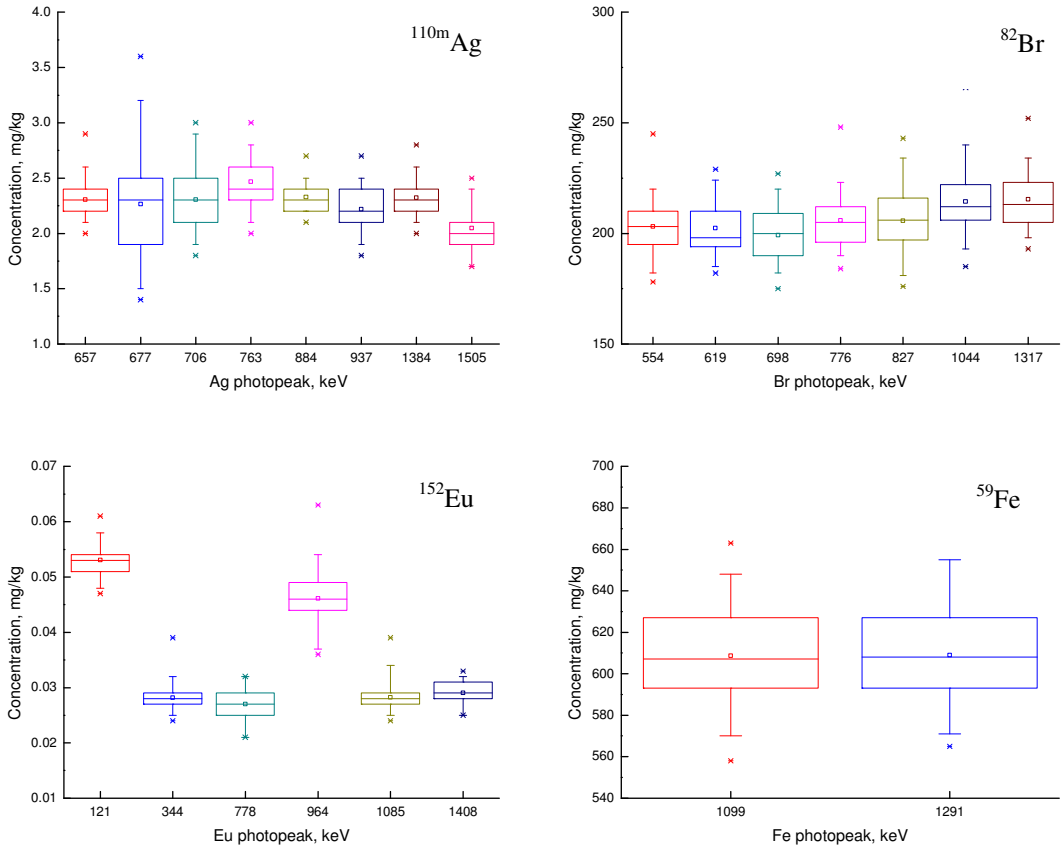

Figure 1. Box-plots for the results obtained for selected elements (eight subsamples), using different photopeak energies.

Table 2 summarizes ANOVA test output results obtained for the mean concentration of eight subsamples from six bottles. The ANOVA test was performed for the results obtained for each radionuclide gamma ray photopeaks.

Table 2. ANOVA output for the between bottle homogeneity study

Nuclide	Energy, keV	F	p-value	Fc	Nuclide	Energy, keV	F	p-value	Fc*
^{110m}Ag	657.76	3.391	0.012	2.438	^{152}Eu	121.78	0.793	0.561	2.438
	677.62	1.068	0.392	2.438		344.29	0.838	0.530	2.438
	706,68	0.894	0.494	2.438		778.92	3.616	0.008	2.438
	763.94	0.845	0.526	2.438		964.11	1.303	0.281	2.438
	884.69	0.586	0.711	2.438		1085.89	0.968	0.449	2.438
	937.49	1.978	0.102	2.438		1408.00	0.416	0.835	2.438
	1384.30	0.323	0.896	2.438	^{59}Fe	1099.25	1.210	0.321	2.438
	1505.40	1.843	0.125	2.438		1291.50	1.982	0.101	2.438
^{82}Br	554.35	1.366	0.257	2.438	^{140}La	328.76	2.811	0.028	2.438
	619.11	1.547	0.196	2.438		487.02	0.968	0.449	2.438
	698.37	2.172	0.075	2.438		815.77	1.548	0.196	2.438
	776.52	1.414	0.239	2.438		1596.21	0.639	0.671	2.438
	827.83	0.700	0.627	2.438	^{233}Pa	300.18	1.391	0.247	2.438
	1044.08	1.300	0.282	2.438		312.01	0.345	0.883	2.438
	1317.47	0.552	0.736	2.438	^{46}Sc	889.28	1.925	0.110	2.438
^{60}Co	1173.24	0.732	0.604	2.438		1220.55	1.094	0.378	2.438
	1332.50	0.504	0.771	2.438	^{75}Se	136.01	0.389	0.853	2.438
^{134}Cs	604.70	1.007	0.426	2.438		264.66	1.138	0.355	2.438
	795.85	0.565	0.726	2.438		279.54	3.371	0.012	2.438

* F_c for $\alpha = 0.05$; $\nu_1 = 5$; $\nu_2 = 42$.

The null hypothesis of the ANOVA test, H_0, is that there is no difference among the mean concentration of the vials, or in other words, sample results come from populations with the same mean. If F, the calculated statistic of the test, is lower than the critical F_c value, there is no evidence to reject H_0. Hence, the reference material may be considered stable for the test conditions.

Except for ^{110m}Ag, it was observed that $F < F_c$ for the recommended photopeaks, indicating that the candidate reference material may be considered homogeneous for the investigated elements. However, for the other ^{110m}Ag photopeaks, $F < F_c$, an indication that the candidate RM may also be considered homogeneous for this element. This is an illustration of the utility of using alternative energies in homogeneity studies. If a 99 % confidence level is considered, the results for 657 keV of ^{110m}Ag (the recommended photopeak) may be considered equal, as at this less restrictive level $F < F_c$ ($F_c = 3.488$).

For the 328 keV (^{140}La) and 778 keV (^{152}Eu) photopeaks, it was observed that $F > F_c$, indicating non homogeneity. However, for these photopeaks very low counting rates were obtained and in some subsamples the elements were not detected in the spectra. For this reason, ANOVA results for these photopeaks should not be considered accurate.

4. CONCLUSIONS

In this study, the application of the complementary gamma ray photopeaks of ^{110m}Ag, ^{82}Br, ^{60}Co, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{140}La, ^{233}Pa (for Th determination), ^{46}Sc, and ^{75}Se radionuclides was investigated in the between bottle homogeneity study of a mussel candidate reference material under preparation at IPEN - CNEN/SP. Although some photopeaks led to biased element content results, the use of the complementary gamma ray photopeaks proved to be helpful in supporting homogeneity study conclusions of this study and may be extended to other new reference materials.

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