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USING ROBUST STATISTICS TO IMPROVE NAA RESULTS

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ABSTRACT

Neutron Activation Analysis (NAA) is an analytical technique where an unknown sample is submitted to a neutron flux in a nuclear reactor, and its elemental composition is calculated by measuring the induced activity produced. By using the relative NAA method, one or more well-characterized samples (usually certified reference materials - CRMs) are irradiated together with the unknown ones, and the concentration of each element is then calculated by comparing the areas of the gamma ray peaks related to that element. When two or more CRMs are used as reference, the concentration of each element can be determined by several different ways, either using more than one gamma ray peak for that element (when available), or using the results obtained in the comparison with each CRM. Therefore, determining the best estimate for the concentration of each element in the sample can be a delicate issue.

In this work, samples from three CRMs were irradiated together and the elemental concentration in one of them was calculated using the other two as reference. Two sets of peaks were analyzed for each element: a smaller set containing only the literature-recommended gamma-ray peaks and a larger one containing all peaks related to that element that could be quantified in the gamma-ray spectra; the most recommended transition was also used as a benchmark. The resulting data for each element was then reduced using up to five different statistical approaches: the usual (and not robust) unweighted and weighted means, together with three robust means: the Limitation of Relative Statistical Weight (LRSW), Normalized Residuals (NR) and Rajeval (RT). The resulting concentration values were then compared to the certified value for each element, allowing for discussion on both the performance of each statistical tool and on the best choice of peaks for each element.

1. INTRODUCTION

In the process of analyzing the quantitative results of an experiment where a certain variable has been determined more than once, the determination of the most reliable value for this variable, with the lowest realistic uncertainty, is often an issue. The most common techniques for obtaining this estimate are the unweighted average, the σ^{-2}-weighted average, or even the choice of the "best" measurement (as judged by the experimentalist), and either of them have their favorable points and weaknesses. Above all, the two common averages can't take into account the possibility that one value might have been influenced by unexpected factors and resulted way off the expected value – these *oulier* values may influence both common averages and result in a distorted final value. Several techniques have been proposed to the task of identifying outliers [1]; others have suggested averaging procedures that intend to

identify and deal with these outlier values, also called *robust averages*, that should lead to more reliable estimates of the measured magnitude [2].

In the case of Instrumental Neutron Activation Analysis (INAA), an analytical technique where the elemental concentration of a sample is determined by measuring the gamma-ray activity induced in it after irradiation in a neutron field and comparing it to the activity induced in one (or, usually, more) well-known standards, one can frequently determine a given element's concentration by more than one gamma-ray transition and/or by comparison with more than one standard, thus leading to several estimates for the same magnitude, i.e., the concentration of that particular element. The determination of the single, final estimate for the concentration of that element in the sample (and its uncertainty) is, then, a typical case of the process described in the previous paragraph and could profit from a more refined data analysis.

2. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Neutron Activation Analysis (NAA) is a widely used analytical technique where a sample is irradiated with neutrons, and the induced gamma-ray activity is measured and used to determine the original sample's elemental composition. Mathematically, if a given mass of some element (m_e) is subjected to a thermal neutron flux ϕ_{th} for a period of time (t_i), the activity of a specific gamma transition induced in the sample due to the irradiation of this element is [3]:

$$Activity = \frac{A_p}{\varepsilon(E_\gamma)} = \frac{m_e \cdot N_A \cdot \phi_{th} \cdot \sigma \cdot I_\gamma \cdot F_I \cdot \left(1 - e^{-\lambda \cdot t_i}\right) \cdot \left(1 - e^{-\lambda \cdot t_c}\right) \cdot e^{-\lambda \cdot t_e}}{M_A \cdot \lambda} \quad (1)$$

where σ is the target isotope's thermal neutron cross section, $\varepsilon(E\gamma)$ the detector efficiency for the energy of that gamma-ray, A_p is the observed area of the peak related to the gamma transition, N_A is Avogadro's constant, $I\gamma$ is the absolute intensity of the gamma ray in that decay, F_I is the isotopic fraction of the target isotope, M_A is its atomic mass, λ is the decay constant of the radioisotope produced and t_e and t_c are the waiting and counting times, respectively.

In order to simplify this calculation, as well as to reduce the sources of uncertainty, the *Instrumental* (or *comparative*) NAA variation was proposed, where one or more comparators with well-determined concentrations of the elements of interest are irradiated together with the sample, so that now the concentration of a given element in that sample is obtained by a simple comparison with the activity of that element induced in the comparator:

$$C_s = C_c \cdot \frac{A_s \cdot M_c}{A_c \cdot M_s} \cdot e^{\lambda \cdot dt} \quad (2)$$

where C, A and M are the concentration of the element, the measured peak area and the total mass of the samples (s) and comparator (c), respectively, λ is the decay constant of the radioisotope and *dt* is the delay between counting the sample and the comparator. It must be stressed that if a given element can be measured by more than one reaction (for instance, if there's more than one isotope that can be activated) or if a given decay can produce more

than one gamma-ray, either of these processes can be used to determine the element's concentration.

3. ROBUST AVERAGES

When dealing with a set of discrepant data (roughly speaking, data where a simple average leads to a large χ^2), some steps must be taken to assure that the final result, as well as its uncertainty, are a good estimate of the measured value and not influenced by unexpected outliers. There are several techniques developed specifically for this task; for instance, the evaluators of the *Nuclear Data Sheets* recommend using the *Limitation of Relative Statistical Weight* (LRSW) method [4], where steps are taken to prevent a single datapoint to have more than 50% of the total weight in a weighted average. Other, more refined, techniques are proposed in [2], the *Normalized Residuals* technique (NR) and the *Rajeval* technique (RT), which try to locate possible outlier results and prevent them from having a great influence in the calculation's outcome. All three techniques are described in detail in [2], and the next subsections will only give an outline of each.

3.1. Limitation of Relative Statistical Weight

In this technique, a σ^{-2}-weighted average is performed, but if a single point has more than 50% of the total weight its uncertainty is raised so that its weight equals 50%; the aim of this technique is just to prevent a single point from having too much influence on the final result.

3.1. Normalized Residuals

In this case, a σ^{-2}-weighted average is also performed, then the normalized residuals for each point are calculated and, for each point where this residual is larger than a critical value (determined by a 99% probability interval), the uncertainty of that point is enlarged accordingly and the average is recalculated - this procedure is repeated until no residual is larger than the critical value. The aim of this procedure is to assure that values far from the average (i.e., outliers) have little influence in the final outcome of the calculation.

3.1. Rajeval Technique

This is a more refined variant of the Normalized Residuals technique; here points are first submitted to a population test in order to reject gross outliers and the remaining points are submitted to an individual consistency test, similar to the one used in the Normalized Residuals but using a slightly different statistical approach, and the points with a large deviation have their uncertainties enlarged; this, too, is an iterative procedure, and its aim is basically identical to that of the Normalized Residuals technique.

4. EXPERIMENTAL PROCEDURE

In order to test the usefulness and assess the performance of these statistical tools, as well as to analyze the potential benefits of using a greater set of gamma transitions in the analysis of

INAA results, 100mg aliquots of three Certified Reference Materials (CRM) were irradiated together in the IEA-R1 reactor for 8 hours under a thermal neutron flux of approximately $4x10^{12}cm^{-2}s^{-1}$. These samples were then counted twice in a 20% HPGe system – the fist counting took place 7 days after the irradiation, to detect radioisotopes with half lives ranging from several hours to a few days, and the second one 15 days after irradiation, to detect longer-lived isotopes. In all cases the samples were counted for 1h and the source-detector distance was of 9cm in the first counting and of only a few mm in the second one. The spectra were then processed using the in-house developed software VISPECT, which gives the peaks found in each spectrum and the *cps* (counts per second) for each with its respective uncertainty. One of the CRMs (JB-1 Basalt) was used as an unknown sample, while the other two (GS-N Granite and BE-N Basalt) were used as comparators to determine the elemental composition of the unknown sample.

The usual procedure is to check for the recommended gamma rays for each isotope, as defined in [5]; in order to verify for the usefulness and reliability of using a larger set of gamma rays, the spectra were also checked for other gamma rays associated with the relevant radioisotopes, and two different datasets were analyzed: one with all the transitions found for each isotope and a second one using only the recommended transitions. Both datasets were submitted to the same statistical tests and the results for each element were then analyzed both in terms of the relative uncertainty and of the Z-Score, when compared to the certified values for the JB-1 material. Finally, the value with the lowest uncertainty observed using only the most recommended transition in [5] was also calculated. It must be stressed, though, that as all three robust techniques described in section 3 are meaningful only when at least 3 values are available for an isotope – the Rajeval Technique, actually, can't be applied at all to sets with less than 3 points – only the results for the isotopes where 3 or more points were available were included in the analysis.

5. RESULTS AND DISCUSSION

The results for the concentrations obtained for the 11 isotopes where 3 or more different datapoints were available are presented in Table 1, together with the concentration value from the certificate (C), for both the larger set of transitions, the recommended set of transitions and the single recommended transition (ST); N is the number of datapoints used in each group, and UM and WM are the regular unweighted and weighted means, respectively. Table 2 shows relative uncertainties and Table 3 shows the Z-Scores obtained.

Table 1. Concentration results obtained using each of the proposed methods, either using all transitions found in the spectra or just the transitions recommended in [5], compared to the result obtained using only the most recommended transition (ST) and to the certified value (C) – all values are in mg/kg.

		ALL TRANSITIONS						RECOMMENDED TRANSITIONS						
	C	N	UM	WM	LRSW	NR	RT	N	UM	WM	LRSW	NR	RT	ST
Co	38 (5)	*	*	*	*	*	*	4	37,1 (4)	37,4 (4)	37,4 (4)	37,4 (4)	37,4 (4)	37,4 (7)
Eu	1,49 (15)	10	1,49 (6)	1,347 (16)	1,5 (4)	1,46 (4)	1,476 (22)	6	1,58 (6)	1,500 (24)	1,500 (24)	1,500 (24)	1,492 (25)	1,44 (6)
Fe	6,29 (11)	8	6,07 (11)	6,183 (16)	6,18 (4)	6,19 (3)	6,178 (17)	4	6,23 (4)	6,192 (17)	6,19 (4)	6,19 (3)	6,171 (19)	6,173 (27)
Hf	3,3 (6)	*	*	*	*	*	*	4	3,36 (4)	3,37 (5)	3,37 (5)	3,37 (5)	3,37 (5)	3,33 (11)
La	39 (4)	12	38,3 (4)	38,47 (19)	38,47 (19)	38,47 (19)	38,54 (20)	8	38,89 (28)	38,57 (20)	38,57 (20)	38,57 (20)	38,70 (21)	38,2 (4)
Lu	0,310 (29)	*	*	*	*	*	*	4	0,278 (9)	0,275 (12)	0,275 (12)	0,275 (12)	0,275 (12)	0,262 (22)
Sc	27,5 (20)	*	*	*	*	*	*	4	27,3 (5)	27,4 (4)	27,4 (4)	27,4 (4)	27,3 (5)	28,4 (8)
Sm	5,1 (5)	10	4,5 (10)	1,502 (17)	5 (4)	5,13 (11)	1,95 (13)	4	4,3 (9)	3,44 (3)	3,4 (17)	5,14 (9)	5,14 (9)	1,73 (3)
Tb	0,82 (19)	10	0,63 (15)	0,223 (7)	0,6 (4)	0,205 (20)	0,194 (7)	4	0,64 (7)	0,61 (6)	0,61 (6)	0,61 (6)	0,60 (6)	0,57 (10)
U	1,7 (3)	*	*	*	*	*	*	6	2,00 (15)	1,79 (9)	1,79 (9)	1,79 (9)	1,75 (9)	2,1 (4)
Yb	2,13 (26)	30	1,93 (8)	1,57 (3)	1,9 (10)	1,73 (6)	1,79 (4)	19	2,04 (8)	1,87 (5)	1,9 (5)	1,91 (8)	1,98 (6)	2,02 (27)

* All transitions observed were recommended by [5].

Table 2. Relative uncertainties (in %) obtained with each method, either using all transitions found in the spectra, just the transitions recommended in [5], or the result obtained using only the most recommended transition (ST).

	ALL TRANSITIONS					RECOMMENDED TRANSITIONS					
	UM	WM	LRSW	NR	RT	UM	WM	LRSW	NR	RT	ST
Co	*	*	*	*	*	1,1	1,1	1,1	1,1	1,1	1,9
Eu	4,1	1,2	24,2	2,4	1,5	4,0	1,6	1,6	1,6	1,7	4,2
Fe	1,8	0,3	0,7	0,4	0,3	0,6	0,3	0,7	0,5	0,3	0,4
Hf	*	*	*	*	*	1,2	1,6	1,6	1,6	1,6	3,3
La	0,9	0,5	0,5	0,5	0,5	0,7	0,5	0,5	0,5	0,5	1,0
Lu	*	*	*	*	*	3,2	4,2	4,2	4,2	4,2	8,4
Sc	*	*	*	*	*	1,9	1,5	1,5	1,5	1,6	2,8
Sm	22,1	1,1	95,6	2,1	6,7	20,1	1,0	49,7	1,8	1,7	1,7
Tb	24,5	3,2	69,8	9,8	3,6	10,4	9,1	9,1	9,1	9,4	17,5
U	*	*	*	*	*	7,5	4,7	4,7	4,7	5,0	19,0
Yb	4,1	1,9	50,8	3,6	2,1	3,9	2,5	25,1	4,1	2,8	13,4

* All transitions observed were recommended by [5].

Table 3. Z-Scores observed using each method, either using all transitions found in the spectra, just the transitions recommended in [5], or the result obtained using only the most recommended transition (ST).

	ALL TRANSITIONS					RECOMMENDED TRANSITIONS					
	UM	**WM**	**LRSW**	**NR**	**RT**	**UM**	**WM**	**LRSW**	**NR**	**RT**	**ST**
Co	*	*	*	*	*	-0,2	-0,2	-0,2	-0,2	-0,1	-0,1
Eu	0,0	-0,9	0,0	-0,2	-0,1	0,6	0,1	0,1	0,1	0,0	0,0
Fe	-1,4	-0,9	-0,9	-0,8	-1,0	-0,5	-0,8	-0,8	-0,8	-1,0	-0,3
Hf	*	*	*	*	*	0,1	0,1	0,1	0,1	0,1	0,0
La	-0,1	0,0	0,0	0,0	0,0	0,1	0,0	0,0	0,0	0,0	-0,1
Lu	*	*	*	*	*	-1,1	-1,1	-1,1	-1,1	-1,1	0,0
Sc	*	*	*	*	*	-0,1	-0,1	-0,1	-0,1	-0,1	0,3
Sm	-0,6	-7,3	-0,1	0,0	-6,2	-0,9	-3,4	-0,9	0,0	0,0	-1,9
Tb	-0,8	-3,1	-0,4	-3,2	-3,3	-0,9	-1,1	-1,1	-1,1	-1,1	0,0
U	*	*	*	*	*	1,0	0,4	0,4	0,4	0,3	0,0
Yb	-0,7	-2,2	-0,2	-1,5	-1,3	-0,3	-1,0	-0,5	-0,8	-0,5	0,0

* All transitions observed were recommended by [5].

The comparison between the statistical tools tested show that the Limitation of Relative Statistical Weight and unweighted mean techniques were the only ones for which all values were in agreement with the certified ones within a 99.5% interval (i.e., -3 < Z-Score < 3), but at the cost of uncertainties that sometimes are of the same magnitude as the values themselves. The Normalized Residuals technique reached the best overall compromise between precision and accuracy, failing only for Tb when the complete dataset was used; its uncertainties were slightly larger than the ones obtained using a regular weighted mean, but the results obtained with it always led to lower Z-Scores; the Rajeval Technique also gave good results.

Regarding the choice of a transition set, these results show that the use of a single transition leads to larger uncertainties and to results that are somehow less reliable than other methods (in the present experiment it was the case for Sm); on the other hand, the use of a larger dataset usually led to smaller uncertainties, but also to less reliable results – for Sm and Tb, for example, the results obtained using all available transitions were mostly far from the expected value, with Z-Scores over 3 (the dataset for these two elements were the worst ones, so they are presented in Figs. 1 and 2, together with the certified values and their 1-σ interval). Finally, the use of the recommended set of transitions together with a good statistical tool (i.e., either the Rajeval or Normalized Residuals techniques) led to very good results, with Z-Scores between -1.1 and 0.4 and relative uncertainties below 5% for all elements except Tb – and, even in this case, the relative uncertainty was still below 10%.

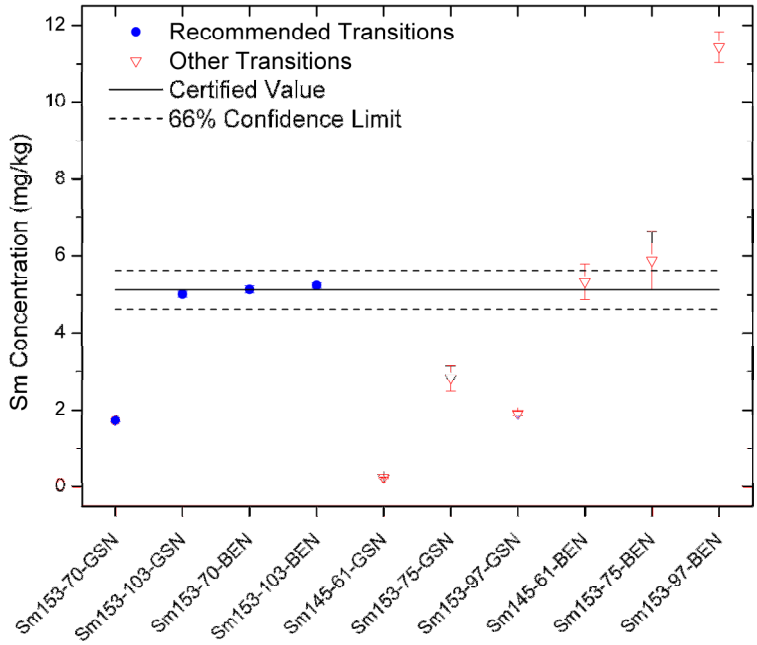

Figure 1. Results for the concentration of Sm – the data labels include the isotope (^{145}Sm or ^{153}Sm), the transition energy (61, 70, 75, 97, 103 or 145keV) and the CRM used as reference (GS-N or BE-N).

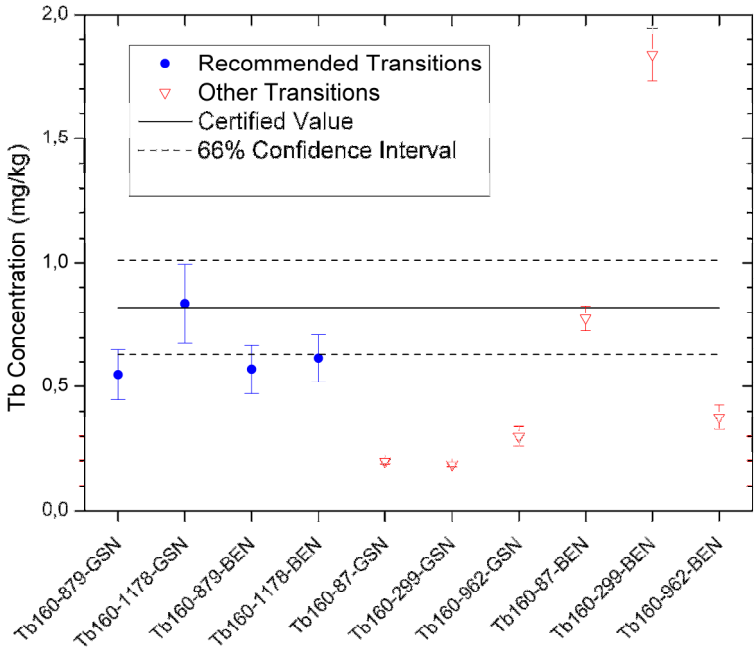

Figure 2. Results for the concentration of Tb – the data labels include the isotope (^{160}Tb), the transition energy (87, 299, 879, 962 or 1178keV) and the CRM used as reference (GS-N or BE-N).

3. CONCLUSIONS

From this test it was clear that, at least for the elements analyzed, the best choice of transitions is the transition set recommended in [5], which leads to more reliable results without increasing too much the uncertainty; on the other hand, the use of a single transition led to larger uncertainties and, in one case, to a result which didn't completely agree to the certified value. Also, regarding the statistical tools proposed, the *Normalized Residuals* technique led to the best results in all cases; when using only the recommended gamma-ray set, though, the *Rajeval* technique also led to reliable results, in some cases with a slightly smaller uncertainty.

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