

UNCERTAINTY ANALYSIS IN COMPARATIVE NAA APPLIED TO GEOLOGICAL AND BIOLOGICAL MATRICES

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ABSTRACT

Comparative nuclear activation analysis is a multielemental primary analytical technique that may be used in a rather broad spectrum of matrices with minimal-to-none sample preprocessing. Although the total activation of a chemical element in a sample depends on a rather large set of parameters, when the sample is irradiated together with a well-known comparator, most of these parameters are crossed out and the concentration of that element can be determined simply by using the activities and masses of the comparator and the sample, the concentration of this chemical element in the sample, the half-life of the formed radionuclide and the time between counting the sample and the comparator.

This simplification greatly reduces not only the calculations required, but also the uncertainty associated with the measurement; nevertheless, a cautious analysis must be carried out in order to make sure all relevant uncertainties are properly treated, so that the final result can be as representative of the measurand as possible.

In this work, this analysis was performed for geological matrices, where concentrations of the interest nuclides are rather high, but so is the density and average atomic number of the sample, as well as for a biological matrix, in order to allow for a comparison. The results show that the largest part of the uncertainty comes from the activity measurements and from the concentration of the comparator, and that while the influence of time-related terms in the final uncertainty can be safely neglected, the uncertainty in the masses may be relevant under specific circumstances.

1. INTRODUCTION

In the last years, the precise determination of the uncertainties related to experimental measurements have been of great concern. The *Guide to the Expression of Uncertainty in Measurement*, for instance, states that “When reporting the result of a measurement of a physical quantity, it is obligatory that some quantitative indication of the quality of the result be given so that those who use it can assess its reliability.” [1]. It is important, also, to have a good understanding of all the individual uncertainties that contribute to the final value, as well as to know which parameters have a stronger contribution to the final uncertainty. This knowledge may help in assessing which uncertainties really need to be taken into account, as well in determining which parameters might be tweaked for an optimum result.

1.1. Neutron Activation Analysis

Neutron Activation Analysis (NAA) is a nuclear analytical technique that relies on nuclear reactions to determine, both qualitatively and quantitatively, the composition of a sample. It is based on very well-understood physical principles, thus allowing for a very reliable uncertainty determination. Moreover, in the instrumental variation of NAA, solid samples don't require any previous chemical treatment (unlike techniques such as AAS and ICP-MS), which further reduces the possibility of unwanted influences in the results and renders the uncertainty estimation even more precise and reliable [2]. It must be noted, though, that depending on the gamma transition set chosen and on the choice of comparators, comparative NAA may deliver more than one result for some chemical elements in a given sample; although some type of average can be applied to produce a more robust final result [3], this treatment will remove the direct relation between the final uncertainty and the individual parameter contributions, and therefore such a treatment was not performed in this work.

If a sample with N nuclei of a given species is irradiated in a thermal neutron flux ϕ , and this nuclide has an absorption cross section σ for a reaction leading to a radioactive nuclide, the probability of creation of this nuclide is:

$$\frac{dN}{dt} = N \cdot \phi \cdot \sigma \quad (1)$$

Solving this equation, and considering that the radioactive nuclide produced has a decay constant λ , that the sample was irradiated for a time t_i , at the end of the irradiation the number of radioactive nuclides produced will be:

$$N'(t = t_i) = \frac{N_0 \cdot \phi \cdot \sigma}{\lambda} \cdot (1 - e^{-\lambda t_i}) \quad (2)$$

where N_0 is the number of nuclei of the original nuclide in the sample. Using the definition of molar mass and considering that the sample may be composed of other chemical elements and isotopes, we have that:

$$N_0 = \frac{m_s \cdot C_i \cdot N_A \cdot F_I}{M_i} \quad (3)$$

where N_A is Avogadro's constant, m_s is the total mass of the sample, C_i the concentration of the chemical element in the sample, M_i the atomic mass of that element, and F_I the isotopic fraction of the nuclide.

Finally, if the decay of the radioactive nuclide produced emits a given γ -ray with an intensity I_γ , and the sample is counted in a detector with an absolute efficiency ε to this

γ -ray, the total number of counts recorded in the peak associated with this γ -ray after a counting time t_c is:

$$A = \frac{\varepsilon \cdot m_s \cdot C_i \cdot N_A \cdot \phi \cdot \sigma \cdot I_\gamma \cdot F_I \cdot (1 - e^{-\lambda t_i}) \cdot (1 - e^{-\lambda t_c}) \cdot e^{-\lambda t_e}}{M_i \cdot \lambda} \quad (4)$$

where t_e is the time it took from the end of the irradiation to the start of the counting.

1.1.1. Comparative Neutron Activation Analysis

Although the concentration of a given chemical element may be determined by equation 4, the excess of parameters imply that there are too many sources of uncertainty, so that the final result often has a quite large uncertainty. A way to overcome that limitation is to irradiate the sample together with a comparator with a known concentration of the chemical element under study, and count that comparator for the same time in the same detector as the sample. This way, the concentration of a chemical element in the sample can be determined using only the peak areas in the sample (A_s) and in the comparator (A_c), the masses of the sample (m_s) and comparator (m_c), the concentration of the element in the comparator (C_c) and the difference between the beginning of the counting of the comparator and sample ($\Delta t = t_e(c) - t_e(s)$):

$$C_s = \frac{A_s \cdot m_c \cdot C_c}{A_c \cdot m_s} \cdot e^{-\lambda \Delta t} \quad (5)$$

It must be noted, though, that while the physical constants (σ , F_I , M_i , N_A , λ , and I_γ) and the irradiation time (t_i) are absolutely identical and can be safely crossed out from the equation, the neutron flux (ϕ), the detection efficiency (ε) and the counting time (t_c) are assumed to be identical, but some very small differences between the sample and the comparator might occur and, therefore, their uncertainties, while very hard to assess properly, should not be crossed out without further investigation. In this work, though, these will be assumed to be negligible, as neither of these is expected to contribute with more than 0.1% to the final value of the uncertainty, which is usually in the 1 – 10% range.

1.2. Uncertainty Propagation

The “general law of error propagation” [1] consists in expanding the equation used in the calculation of the final result (in the present case, eq. 5) in a Taylor series around the parameters used in the calculation, and then using the square of the 1st-order term of the expansion as an estimation of the combined variance (σ^2), i.e., if $f(p_1, \dots, p_i)$ is a function of the parameters $p_1 \dots p_i$ whose uncertainties are $\sigma_1 \dots \sigma_i$, then:

$$\sigma(f)^2 = \sum_{j=1}^i \left(\frac{\partial f}{\partial p_j} \cdot \sigma_j \right)^2 \quad (6)$$

In the specific case of eq. 5, and neglecting the “occult” uncertainties explained above, the final uncertainty in the concentration is, then:

$$\left(\frac{\sigma_{C_s}}{C_s} \right)^2 = \left(\frac{\sigma_{A_s}}{A_s} \right)^2 + \left(\frac{\sigma_{A_c}}{A_c} \right)^2 + \left(\frac{\sigma_{m_s}}{m_s} \right)^2 + \left(\frac{\sigma_{m_c}}{m_c} \right)^2 + \left(\frac{\sigma_{C_c}}{C_c} \right)^2 + (\lambda\sigma_{\Delta t})^2 + (\Delta t\sigma_{\lambda})^2 \quad (7)$$

where it should be noted that, while for the linear variables (mass, peak area, and concentration) the dependence is proportional to the relative uncertainty, for the time-related variables the dependence is linear. On the other hand, both the values and uncertainties for the decay constants are usually *very* small, so that the contributions to the uncertainty from both terms are usually significant only when the times considered are considerably larger than the half-life of the nuclide under investigation.

2. EXPERIMENTAL PROCEDURE

In the present study, the uncertainties obtained for two sets of samples were investigated, one consisting of five different soil samples from a scrapyard of impounded vehicles near to So Paulo city, Brazil, and the other consisting of five different samples of *Tillandsia usneoides* used as biomonitors for air pollution. The samples were analyzed using the comparative NAA technique. In both cases standard reference materials were used as comparators – in the case of soil samples these were IAEA-Soil-7, ANRT GS-N (Granite) and IWG BE-N (Basalt), while for the *Tillandsia* samples INCT-MPH-2 (Mixed Polish Herbs) and NIST-1547 (Peach Leaves) were used. Approximately 100mg of each sample was carefully weighted, placed into sealed polyethylene bags, and irradiated, together with a similar amount of the comparators, in the IEA-R1 reactor ($t_i \approx 8h$, $\phi \approx 10^{13} cm^{-2} s^{-1}$). Samples and comparators were then counted twice in a 25% HPGe detector (nominal resolution of 1.9 keV for the 1332 keV ^{60}Co transition) for approximately 1 hour, once 5-7 days after irradiation and again 10-15 days after irradiation. 27 chemical elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, Zn and Zr) were determined in the soil samples, and 23 (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Th, Yb and Zn) in the *Tillandsia* samples.

The concentration of each chemical element was determined individually by each of the recommended transitions [4] and by comparison with each comparator that had a certified concentration value for that element, so that occasionally more than one value was determined for it in a given sample – these results were not averaged in any way, because doing so combines the uncertainties in a rather complicated way [3] and makes the discussion on the individual contribution of the uncertainties virtually impossible.

Table 1: Maximum relative contribution of each term (in %) to the final uncertainty for each element in the soil samples; C_s is the concentration range, $\sigma(C_s)$ is the range of the 1- σ relative uncertainties, and the remaining terms are as of eq. 7.

Element	C_s $\mu\text{g} \cdot \text{g}^{-1}$ (range)	$\sigma(C_s)$ % (range)	$\sigma(C_c/C_c)$ % (max)	$\sigma(A_c/A_c)$ % (max)	$\sigma(A_s/A_s)$ % (max)	$\sigma(M_c/M_c)$ % (max)	$\sigma(M_s/M_s)$ % (max)	$t\sigma(\lambda)$ % (max)	$\lambda\sigma(t)$ % (max)
As	0.4–103	4–41	70.2	98.8	98.7	1.7	1.7	0.0	0.0
Ba	138–399	6–18	48.5	40.1	91.3	0.7	0.7	0.0	0.0
Br	1.7–5	25–28	96.2	2.8	20.3	0.0	0.0	0.0	0.0
Ca	8–40	3–17	61.5	97.5	54.0	2.2	2.2	0.0	0.0
Ce	42–138	3–5	97.3	2.1	7.8	3.1	3.2	0.0	0.0
Co	1.7–6	4–8	89.9	6.8	67.6	1.6	1.6	0.0	0.0
Cr	8–48	4–12	96.7	2.1	72.7	1.7	1.7	0.0	0.0
Cs	2.3–14	6–29	82.8	80.8	57.4	0.8	0.8	0.0	0.0
Eu	0.4–1.9	4–12	96.4	19.1	58.0	1.7	1.7	0.0	0.0
Fe	0.5–2.2	1.1–2.1	56.6	14.5	74.2	21.3	21.7	0.0	0.0
Hf	4–10	4–6	92.5	31.8	21.7	1.7	1.8	0.0	0.0
K	0.6–2.5	7–14	7.7	72.5	78.0	0.4	0.5	0.0	0.0
La	19–70	2–4	95.1	8.6	13.8	6.3	6.3	0.1	0.0
Lu	0.08–0.8	14–26	98.8	18.0	23.8	0.1	0.1	0.0	0.0
Na	0.03–0.4	1.5–5	77.9	67.8	79.7	10.1	10.3	0.1	0.2
Nd	5–99	3–33	94.6	69.7	91.4	2.5	0.2	0.0	0.0
Rb	22–190	4–13	52.3	81.5	83.0	1.7	1.8	0.0	0.0
Sb	0.09–6	7–60	91.0	78.3	95.6	0.5	0.5	0.0	0.0
Sc	7–14	6–7	98.8	0.2	0.3	0.8	0.8	0.0	0.0
Sm	1.8–15	3–10	95.6	91.0	2.4	3.7	3.8	0.0	0.0
Ta	1.1–2.4	9–19	69.1	40.9	58.4	0.3	0.3	0.0	0.0
Tb	0.01–2.0	13–32	71.4	67.1	82.6	0.1	0.1	0.0	0.0
Th	6–17	6–9	98.9	2.5	3.4	0.6	0.6	0.0	0.0
U	1.3–8	12–32	74.4	87.5	72.1	0.2	0.2	0.0	0.0
Yb	0.4–7	8–24	91.1	50.4	77.0	0.4	0.4	0.0	0.0
Zn	31–97	5–13	85.0	35.3	71.2	1.2	1.2	0.0	0.0
Zr	64–304	16–25	16.5	56.6	77.4	0.1	0.1	0.0	0.0
Max	399	60	98.9	98.8	98.7	21.3	21.7	0.1	0.2
Min	0.011	1.1	7.7	0.2	0.3	0.0	0.0	0.0	0.0

The uncertainties were used as 1- σ , and propagated as of eq. 7; the uncertainty in the masses was admitted to be the nominal uncertainty of the analytical balance (0.0005 g); the uncertainty in the time difference was assumed to be of 60 s, as the counting times are all rounded up to the closest minute; the uncertainties in the CRMs concentrations were taken from the certificates; and the uncertainties in the decay constant were taken from [5].

3. RESULTS AND DISCUSSION

The relative contribution of each uncertainty term was determined for each of the separate measurements as a percentage of the total uncertainty of that particular measurement. The maximum relative contribution observed for each of the considered terms for the 27 chemical elements analyzed in the soil samples are shown in Table 1. These results show that the most important contributions to the final uncertainty come from the propagation of the counting statistics of the comparator (A_c) and sample (A_s) and from the propagation of the uncertainty in the concentration of the element in the comparator (C_c) – each of these uncertainties may contribute, in individual measurements, with up to more than 98% of the total uncertainty and, when considered together, are always responsible for most part of the total uncertainty. The uncertainty in the concentration of the elements in the comparator, in fact, is frequently the responsible for a large part of the uncertainties, with the exception of a few elements. The contribution of the uncertainties in each of the

Table 2: Maximum relative contribution of each term (in %) to the final uncertainty for each element in the *Tillandsia usneoides* samples; C_s is the concentration range, $\sigma(C_s)$ is the range of the 1- σ relative uncertainties, and the remaining terms are as of eq. 7.

Element	C_s $\mu\text{g} \cdot \text{g}^{-1}$ (range)	$\sigma(C_s)$ % (range)	$\sigma(C_c/C_c)$ % (max)	$\sigma(A_c/A_c)$ % (max)	$\sigma(A_s/A_s)$ % (max)	$\sigma(M_c/M_c)$ % (max)	$\sigma(M_s/M_s)$ % (max)	$t\sigma(\lambda)$ % (max)	$\lambda\sigma(t)$ % (max)
As	0.16–4	11–14	28.2	68.8	35.6	0.1	0.1	0.0	0.0
Ba	19–178	4–11	21.8	66.3	85.1	0.7	0.6	0.0	0.0
Br	4–12	4–4	96.0	2.2	2.9	0.6	0.6	0.0	0.0
Ca	0.3–3	4–10	27.2	45.7	88.6	0.7	0.5	0.0	0.0
Ce	1.4–13	9–9	25.5	73.8	8.0	0.1	0.1	0.0	0.0
Co	0.7–3	7–8	63.5	40.7	6.8	0.2	0.2	0.0	0.0
Cr	12–81	7–7	29.6	69.8	2.0	0.2	0.2	0.0	0.0
Cs	0.13–0.4	13–15	12.1	80.5	26.7	0.1	0.1	0.0	0.0
Eu	0.02–0.19	17–21	11.0	90.7	30.1	0.0	0.0	0.0	0.0
Fe	525–7498	5–6	47.8	60.9	11.9	0.6	0.5	0.0	0.0
Hf	0.05–1.1	6–11	49.7	44.3	72.5	0.3	0.3	0.0	0.0
K	0.4–0.9	1.7–5	76.1	21.8	91.2	4.2	3.5	0.0	0.3
La	0.8–7	4–5	89.1	28.9	7.8	0.6	0.6	0.0	0.0
Lu	0.005–0.06	17–24	24.2	73.2	51.4	0.0	0.0	0.0	0.0
Na	0.03–0.06	5–5	75.8	23.1	0.7	0.5	0.5	0.0	0.0
Nd	0.15–3	20–61	25.4	78.9	78.0	0.0	0.0	0.0	0.0
Rb	15–35	5–6	48.2	43.3	34.7	0.5	0.4	0.0	0.0
Sb	0.4–11	9–9	56.3	43.4	1.7	0.1	0.1	0.0	0.0
Sc	0.09–1.1	4–4	88.5	9.5	10.1	0.7	0.7	0.0	0.0
Sm	0.09–0.9	5–5	89.5	9.3	1.7	0.5	0.5	0.0	0.0
Th	0.12–1.7	7–8	33.2	64.9	24.1	0.2	0.2	0.0	0.0
Yb	0.02–0.3	11–17	34.3	61.7	62.7	0.1	0.1	0.0	0.0
Zn	51–547	3–4	75.5	77.2	15.2	1.8	1.5	0.0	0.0
Max	7498	61	96.0	90.7	91.2	4.2	3.5	0.0	0.3
Min	0.005	1.7	11.0	2.2	0.7	0.0	0.0	0.0	0.0

masses is usually well below 5% of the total, but may add up to up to 20-21% of the total uncertainty for Fe and 10-11% for Na, in both cases due to very low uncertainties in the peak areas and in the comparator's concentrations. As for the time-related terms that come from the exponential, the contributions never exceed 0.2% of the total uncertainty and can thus be safely neglected.

In the *Tillandsia usneoides* samples (Table 2), the results are rather similar, with the counting statistics in the comparator (A_c) and sample (A_s) and the uncertainty in the comparator's concentration (C_c) being responsible for more than 90% of the uncertainty in at least one element and, together, adding to more than 92% of the total uncertainty in every element. In this case, as these uncertainties are quite larger than for soil samples, the uncertainties in the masses contribute to less than 10% of the total uncertainty. As for the soil samples, the time-related terms never contribute with more than 0.3% of the final uncertainty and can be neglected.

4. CONCLUSIONS

The analysis of the individual contribution of the uncertainties in each parameter considered in a comparative NAA analysis of samples from two types of matrices (geological and biological) show that the largest part of the uncertainties come from the concentration of the chemical elements in the comparator, and from the counting statistics in both the sample and the comparator – these contributions, together, are responsible for a minimum of 57% of the total uncertainty in the geological samples (where concentrations are usually higher, so counting statistics are better, and the CRMs have lower uncertainties

for most elements) and for 92% of the total uncertainty in the *Tillandsia* samples. The masses contribute with a maximum of 20-21% of the total uncertainty each for the soil samples, and much less than that in the *Tillandsia* samples. As for the time related terms of the uncertainty ($\Delta t\sigma_\lambda$ and $\lambda\sigma_{\Delta t}$), in these measurements they proved to be absolutely irrelevant, never adding up to 0.5% to the final uncertainty of the measurement.

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