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Monte Carlo Simulation of k_0 Instrumental Neutron Activation Analysis

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ABSTRACT

Neutron activation analysis (NAA) is a powerful set of methods for elemental composition analysis. However, the standard approach used to calculate the elemental composition from NAA measurements has many limitations. We replaced the current method of data analysis with computer simulation. By using the Geant4 particle simulation toolkit, we simulated NAA from the initial neutrons that activate the sample, to the final gamma rays hitting the high purity germanium (HPGe) detector.

To compare simulation results with measurement, we used a simple model of detector electronics, that converts energy deposition events within the detector, to the energy recorded by the electronics, by taking into account both true and random coincidence effects. NAA thus became an optimization problem - to minimize the difference between simulation output and experiment, by finding the appropriate simulation inputs, e.g. the sample composition, or HPGe detector geometry. This unified the up to now disparate parts of k_0 instrumental neutron activation analysis (k_0-INAA) - sample composition determination, detector calibration, and neutron spectrum determination all reduce to the same optimization problem. The only difference between them is which parameters are known versus unknown. This simplifies activation analysis, and improves accuracy, as far fewer approximations are made.

We tested this approach by comparing its results versus traditional k_0-INAA on certified reference materials.

1 INTRODUCTION

k_0-INAA is a versatile technique, allowing us to determine the concentration of many elements with a single measurement. However, due to its age, it makes many approximations that may no longer be necessary. This is due to the improvements made in nuclear cross-section data, particle simulation codes, and the increase in computing power enabling what were once prohibitively expensive calculations.

The underlying principle of k_0-INAA is simple [1]: A sample, whose elemental composition we wish to determine, is irradiated with neutrons in a nuclear reactor, and becomes radioactive, emitting gamma rays characteristic of each element. The gamma spectrum is measured on a HPGe detector, yielding gamma peaks that are proportional to the element concentration in the sample, and the neutron flux the sample was exposed to. To determine the latter, the sample

is co-irradiated with a comparator (typically an Al-Au foil) with a known concentration of Au, whose activity is used to determine the neutron flux.

There are further complications. Each isotope has a distinct neutron activation spectrum, which must be compensated for using the k_0 and Q_0 constants, and the neutron flux parameters f and α.

The HPGe detector efficiency also depends on the gamma energy. To correct for this, the full-energy peak efficiency ε_p is determined using absolutely calibrated gamma sources. Because of coincidence effects, ε_p can only be measured at larger sample-detector distances, where the likelihood of multiple cascade gammas hitting the detector is negligible, as the detector presents a smaller target. The efficiency transfer method is used to translate ε_p to other positions.

Coincidence effects further distort gamma spectrum measurements. Some nuclides emit multiple gamma rays in a rapid cascade. If multiple hit the detector simultaneously, its electronics will register them as a single event at the sum of the deposited energies. ε_p is not sufficient to correct for this, as a gamma can deposit only part of its energy and still cause interference, meaning the total efficiency ε_t is required, which is determined using coincidence-free sources.

Finally, there is peak fitting. Once we have a gamma spectrum, the peak sizes are determined manually. This is a laborious and subjective task, especially in cases where multiple peaks are close together. A further weakness is that each peak is evaluated individually, despite our knowledge on how it must diminish given known nuclide half-lives.

These weaknesses have motivated us to seek a more holistic and objective method, utilizing the Geant4 particle simulation toolkit [2].

2 THEORY

While at first glance replicating the experiment in a Monte-Carlo simulation seems simple, a number of complications arise, many related to computational efficiency, necessitating multiple variance reduction techniques.

2.1 Element concentrations

The first task is to determine the activation reactions per unit of density of each element. The problem is that naively simulating a sample with a best-guess composition will produce widely differing number of activations for each element, due to differences in concentrations and cross-sections. To overcome this, each activation event is converted into a collection of statistically-weighted activation events, one for each element. The weight ω_i of element i with microscopic cross-section $\sigma_{act,i}$, density ρ_i, and macroscopic cross-section $\Sigma_{act,i} = \rho_i \sigma_{act,i}$, is determined by the ratio of cross-sections at the activating neutron energy

$$w_i = \frac{\Sigma_{act,i}}{\Sigma_{act}} = \frac{\rho_i \sigma_{act,i}}{\Sigma_{act}} \tag{1}$$

By adjusting the weights, we can change element concentrations without re-running the simulation, with the caveat that this does not update the self-shielding factor. Meaning that if the determined concentrations greatly differ from the initial guess, the simulation should be iteratively re-ran.

2.2 Decay time convolution

The second difficulty is that only a small fraction of gamma decays occur during measurement. E.g. the half-life of ^{198}Au is 2.697 days [3], but typically we only measure it for 5

minutes. If we naively simulated decay times, the vast majority of gammas would be wasted. Instead, we sample decays only inside the measurement interval $[a, b]$, adjusting the weight of the event with

$$w_{decayt} = \int_a^b p(t)dt \tag{2}$$

where $p(t) = \lambda e^{-\lambda t}$ is the unbiased decay probability.

To deal with the case of multiple decay, where there is no single λ, we introduce the concept of node *populations*. A node is simply one element of a particle track, with a time (measured from the previous node), position, particle species (e.g. neutron, gamma, heavy nuclide, positron,..), zero or more child node (events caused by this node. e.g. the children of an active nuclide could be multiple gammas and a decay nuclide) and possibly a half-life.

Because one particle track in the simulation does not necessarily correspond to one physical track (typical neutron flux in the TRIGA IC-40 irradiation channel is on the order of $10^{12}\ cm^{-2}s^{-1}$ [4], so 1-to-1 correspondence is computationally infeasible), we use population as the ratio of physical tracks to simulated tracks.

The population of a node grows due to its parent node acting as a source (e.g. by decaying into it), and diminishes due to its own decay. If the parent node has population $p_p(t)$ and a decay constant λ_p, then it feeds the child node with rate $f(t) = \lambda_p p_p(t)$. In case the parent node is an incident irradiation neutron, then it feeds it with an arbitrary rate $f(t) = r(t)$, defined by the neutron spectrum and flux time-profile. The child node decays with λ_c, so the proportion of population from time 0, that still remains at time t, is $g(t) = e^{-\lambda t}H(t)$. $H(t)$ is the Heaviside step function, and is used to limit the population to being affected only by past events. In other words, it follows from the definition of $g(t)$, that $g(t < 0)$ must be 0. If the child node did not decay, its population would simply be the accumulation of its source up to time t:

$$p_c(t) = \int_{-\infty}^{t} f(x)dx \tag{3}$$

Because the child node is subject to radioactive decay, its population must be adjusted to

$$p_c(t) = \int_{-\infty}^{t} f(x)g(t-x)dx \tag{4}$$

The integration range can be expanded to $(-\infty, \infty)$ because $g(t - x) = 0$ for $t < x$. This simplifies to a convolution of f and g:

$$p_c(t) = \int_{-\infty}^{\infty} f(x)g(t-x)dx \tag{5}$$

$$= (f * g)(t) \tag{6}$$

This covers the case where the parent and child nodes both have durations determined by radioactive decay. The other possibility is that a node has a constant duration (e.g. the time between two scattering events). In that case, the duration is used to offset $f(t)$ until encountering a decay node, at which point the convolution result can be applied.

This approach supports an arbitrary, time-dependent neutron flux, so it can simulate phenomena such as reactor flux changes during sample irradiation [5].

With this result, we can calculate the population of every node with an unstable nuclide at the start of measurement, and efficiently sample their decay times during the measurement interval. Their decay products, that may be unstable themselves, are sampled using the full

exponential distribution, without limiting it to the measurement interval. This yields the full cascade of energy deposition events, that is used to simulate coincidence effects.

Note that even if the decay times of the child particles are much longer than the measurement time, there is no cause for concern from the point of view of computational efficiency. This is because the child particles have also had their population at the start of measurement calculated, and the same sampling of decay within measurement interval will be applied to them.

2.3 Gamma direction biasing

To avoid wasting time on gammas that do not hit the detector, we rotate gamma decay events towards the detector, adjusting their weight proportionally to the solid angle towards which they are biased. We apply the same rotation to all the child nodes as well, so that angular correlations, if any, are preserved.

Additionally, we also orient some decay gammas *away* from the detector. This is to keep the simulation mathematically correct. The statistical weight of an event is

$$w = \frac{p_{true}}{p_{sim}} \tag{7}$$

Where p_{true} is its true probability, and p_{sim} is the probability in our simulation, after variance reduction. p_{true} of a gamma being emitted away from a detector is > 0. If we neglected to simulate any such gammas, that would make $p_{sim} = 0$, and the weight of such a particle would diverge. There is a chance, however unlikely, that a gamma emitted away from the detector scatters towards the detector. In that case, the variance of our result would be infinite. To avoid this, we keep some such gammas, and use Russian Roulette to reduce their numbers.

2.4 Detector response

The steps so far yield a series of energy deposition events, as produced by Geant4, given our best knowledge of the detector composition. We use a simple simulation of the HPGe electronics to convert these to counts as measured by the detector, with three main parameters: the energy needed for the electronics to register the start of a hit $E_{threshold}$, the time during which charge collection takes place t_{meas}, and the time after that when the electronics are non-responsive t_{dead}.

This reproduces coincidence and dead-time effects, but produces much sharper peaks than those measured by the detector. To reproduce peak widths, we empirically measure the full-width half-maximum (FWHM) at different energies, fit a 2nd-order polynomial to them to get the peak width at all energies, and then apply Gaussian broadening to the simulated spectrum.

A further correction we make is that of detector efficiency. We use the differences between the measurement and simulation of absolutely calibrated gamma sources to find a correction function that minimizes the root-mean-square of those differences:

$$\frac{\epsilon_{meas}}{\epsilon_{sim}} = 1.0362 - 0.058611\left(\frac{E}{MeV}\right) - 0.018678\left(\frac{E}{MeV}\right)^2 - 0.0058065\left(\frac{E}{MeV}\right)^3 \tag{8}$$

While this is not as principled as the approach taken by [6], who adjusted detector geometry in the simulation to improve the results, it is faster and simpler. Note that the correction function was chosen to minimize differrences on the entire spectrum, not only the peaks. Fig. 1 shows how the efficiency correction improves the agreement between simulation and experiment on a

section of the ^{226}Ra. spectrum. Note that empirical peak broadening is already applied to the 'simulated' spectrum. In contrast, Fig. 2 shows the failure of empirical peak broadening to correctly reproduce the 511 keV annihilation peak, that is approximately 2x wider than simulated.

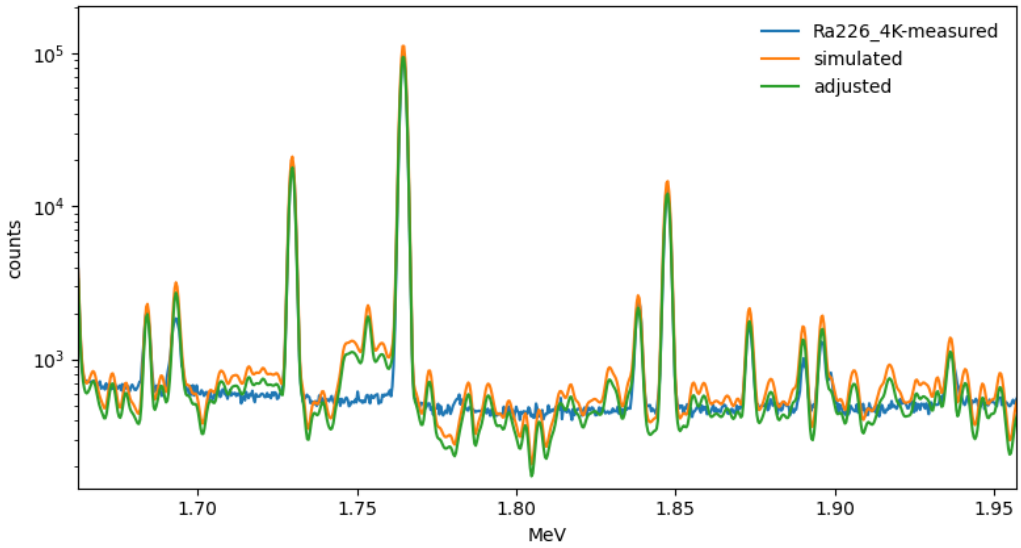

Figure 1: Comparison of measured, simulated, and adjusted spectra for ^{226}Ra. 4K refers to the measurement position with a sample-detector distance of 16.2 cm.

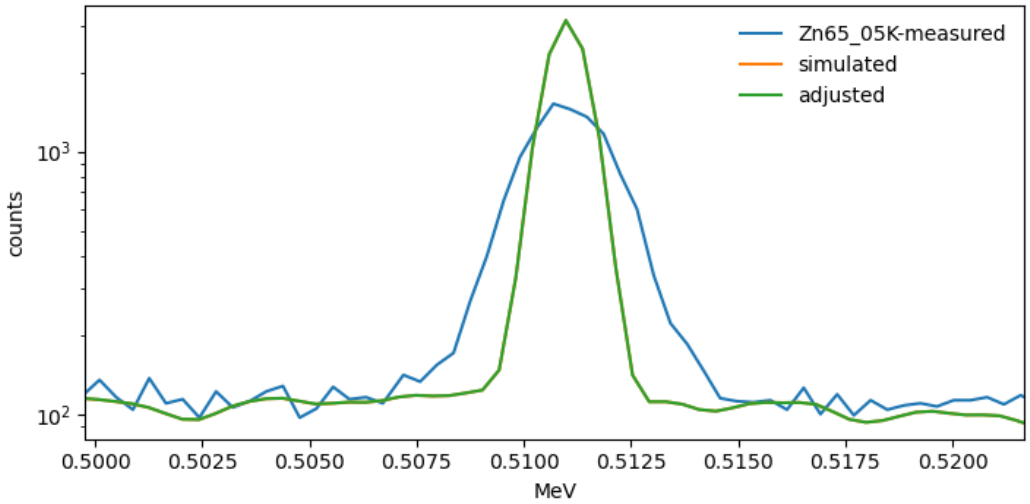

Figure 2: Annihilation peak in the ^{65}Zn spectrum. At this energy, the simulated and adjusted spectrum coincide, so they appear as a single line on the graph. 05K refers to the measurement position with a sample-detector distance of 2.2 cm.

2.5 Sample analysis

With a known neutron spectrum, detector efficiency, and peak width adjustment, we can determine the detector response per unit of neutron flux and element concentration. The neutron

flux is determined from the measurement of the Al-0.1%Au comparator co-irradiated with the sample, then the responses per unit of element concentration in the sample are determined. These responses must be simulated for each sample measurement separately, since different sample-detector distances and measuring times produce different response functions, due to differing detector efficiencies and decay times.

Fitting a weighted sum of these simulated responses to the measured spectra yields the ratios between the element concentrations used in the simulation, and that of the sample. The fitting is done consistently for all measurements. I.e. if a sample was measured multiple times, a single set of coefficients will be used to fit the responses for *all* the spectra. By iterating this step, and re-determining the response functions using element concentrations close to their true values in the simulation, we can more accurately capture random-coincidence effects as well. The results of such fitting are shown in Figs. 3 and 4.

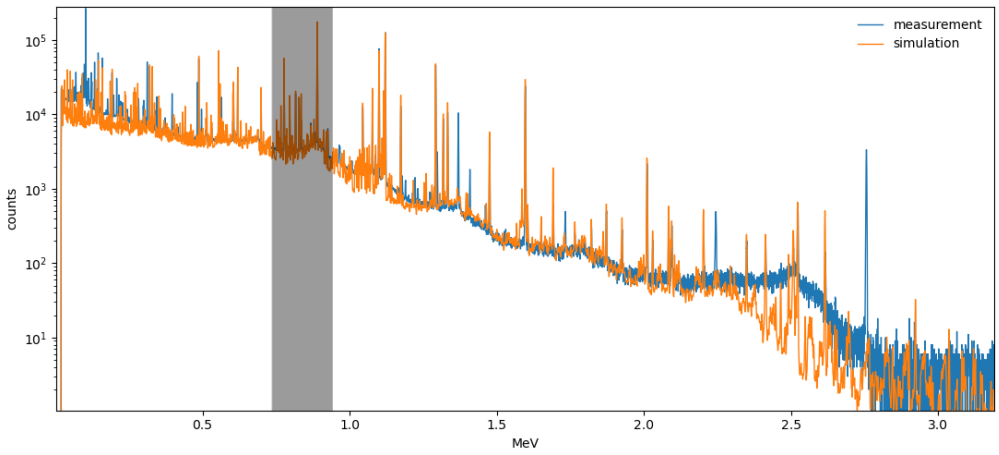

Figure 3: Simulated and measured spectrum of BCR-320R, at a sample-detector distance of 2.2 cm. The simulated spectrum is a linear sum of the spectra of individual elements.

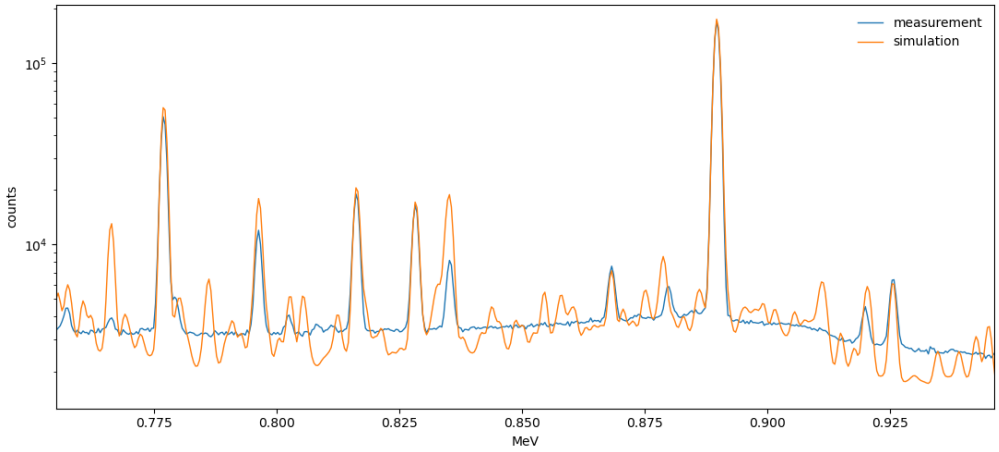

Figure 4: Detailed view of the shaded section of the spectrum from Fig. 3.

3 RESULTS AND DISCUSSION

We applied this method to measurements of the BCR-320R Channel Sediment certified reference material, conducted in the scope of calibration of the CA5 HPGe detector at IJS in 2015 [7]. Our simulations used the same detector geometry and neutron spectral parametes ($f = 27.11$, $\alpha = -0.0042$) as the k_0-INAA conducted in the scope of that calibration, that we compare our preliminary results with in Table 1.

Table 1: Preliminary analysis results comparison for the BCR-320R certified reference sample.

	Traditional k_0-INAA [7]	Certified value	Our method
Element	Concentration (mg/kg)*	Concentration (mg/kg)**	Concentration (mg/kg)
As	23.3 ± 0.8	21.7 ± 2.0	26.2
Co	10.1 ± 0.4	9.7 ± 0.6	13.5
Cr	59.7 ± 2.1	59 ± 4	75.7
Fe	26106 ± 914	25700 ± 1300	28690
Hg	0.884 ± 0.044	0.85 ± 0.09	1.031
Sc	5.45 ± 0.19	5.2 ± 0.4	5.67
Th	5.42 ± 0.19	5.3 ± 0.4	5.33
U	1.57 ± 0.06	1.56 ± 0.20	1.84
Zn	330 ± 12	319 ± 20	400

* Uncertainty with a coverage factor of $k = 1$ according to [8]
** Expanded uncertainty with a coverage factor of $k = 2$, corresponding to approximately 95% confidence.

We see this method does not yet outperform traditional k_0-INAA, and in fact gives results outside the certified confidence limits. While uncertainty quantification for our method has not yet been done, in principle the sources of uncertainty, and hence the magnitude, are very similar as for k_0-INAA. Therefore the confidence range of our results is unlikely to overlap with the certified values, suggesting the presence of one or more systematic errors.

A possible candidate for the source of this error is the separate code used to determine the neutron flux and the element detector response. Though the two code paths are theoretically equivalent, programmer error has not yet been excluded. A further source of error is the response fitting method used. Currently it is a naive least-means-square, minimizing the squared error over the entire spectrum. However, k_0-INAA is more discriminating, preferring to fit only on gamma peaks, and among the gamma peaks, only those with well-known intensities. There is also the possibility that the integral k_0 constants are more accurate than the differential cross-sections used by Geant4. Since the k_0 constants were meaured specifically for use in k_0-INAA, that possibility is likely. Finally there is the way in which spectrum fitting is done. As a linear sum of responses for individual elements, it does not account for random coincidence by different elements.

On the other hand, despite its inaccuracy, the method already exhibits several benefits. Except for data entry it is in principle entirely automatic, without the laborious peak-fitting of k_0-INAA. It partly includes random coincidence effects, and supports arbitrary sample geometry and neutron flux temporal variability. Finally, the spectrum fitting is more consistent, utilizing the full benefit of known half-lives and peak sizes consistently for multiple measurements of the same sample.

In sum, while still immature, this method is promising, with room for improvement by including various corrections to put it on par with traditional k_0-INAA.

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