Typical uncertainties in alpha-particle spectrometry

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Abstract

Alpha-particle spectrometry is routinely performed with the aim of measuring absolute activities, activity ratios between different alpha-emitting nuclides or decay data such as branching factors, alpha emission probabilities and relative half-lives. It is most commonly performed with ion-implanted silicon detectors. Strong features of the technique are the low background levels that can be achieved due to low sensitivity to other types of radiation, the intrinsic efficiency close to 1 which reduces the efficiency calculations to a geometrical problem and the uniqueness of the energy spectra for each \( \alpha \)-decaying nuclide. The main challenge is the limitation to the attainable energy resolution, even with thin and homogenous sources, which causes alpha energy peaks to be partially unresolved due to their width and low-energy tailing. The spectral deconvolution often requires fitting of analytical functions to each peak in the alpha spectrum. True coincidence effects between alpha particles and subsequently emitted conversion electrons cause distortions of the alpha spectra which lead to significant changes in the apparent peak area ratios. Optimum energy resolution can only be achieved on very thin sources, which puts constraints on the source preparation techniques. Radiochemical separations may be needed to extract the alpha emitters from voluminous matrices and efficiency tracing is performed by adding in another isotope by known amounts. Typical uncertainty components are discussed by means of some hypothetical examples.

Keywords: alpha-particle spectrometry, alpha-emission probabilities, maximum likelihood, least-squares fit, uncertainty

(Some figures may appear in colour only in the online journal)
Their main advantages are better energy resolution, lower peak tailing and an intrinsic counting efficiency close to unity. The entrance window is <50nm equivalent Si, which reduces the particle energy loss and results in better energy resolution and lower tailing. The resolution depends also on the detector size, as does the size of the tailing. Whereas small detectors of 50mm² render the best resolution, somewhat less tailing may be achieved with larger detectors and a diaphragm [1, 3, 4].

In spite of the technical improvements, the best attainable resolution with a silicon detector is about 8keV, close to the physical limit due to the finite number of electron–hole pairs that is produced in the Si lattice [5]. The interference of neighboring alpha peaks therefore necessitates spectral deconvolution, which complicates the uncertainty analysis. Moreover, the optimum resolution is only achievable with homogeneously thin sources prepared by vacuum sublimation, electrodeposition or other suited techniques [3, 6–8]. Significantly better resolution can be established with cryogenic detectors [9, 10], which should be advantageous for improving emission probabilities in complex spectra. However, these sophisticated techniques are difficult to run for long periods and can handle only limited count rates, so that up to now measured spectra are scarce and their statistical accuracy is poor (see also [4]).

Alpha spectrometry with silicon detectors is also imperfect with respect to linearity between pulse height and particle energy [11]. Underlying reasons are that energy loss in dead layers varies with the particle’s energy and the required energy for creating an electron–hole pair depends on the stopping power [12]. Cryogenic detectors may in the future be an alternative, but by far the best information up to now was obtained from an ‘absolute’ magnetic alpha spectrograph [13]. Using extremely thin sources, a line width of (2–4)keV could be established [14] and absolute emission energies were measured with uncertainties of the order of 0.1 keV. Additional alpha-particle energies are usually measured relative to reference nuclides. Nevertheless, there are inconsistencies among data sets and therefore it is of importance that the community agrees on one consistent list of evaluated reference energies [15].

Background rates are usually extremely low in alpha spectrometry, which allows us to reach low detection limits on the basis of a few counts. The most extreme low-background examples are alpha emissivity measurements at ultra-low levels <5 \times 10^{-7} \text{s}^{-1} \text{cm}^{-2} with dedicated gas-filled counters. They are used by manufacturers in the semiconductor industry to determine the suitability of materials for use in devices and to estimate a device’s soft error rate [16]. The determination of contamination levels in such materials is complicated with respect to background subtraction, as small geometrical changes and simplistic data analysis may lead to negative numbers. Devices that employ pulse discrimination algorithms instead of background subtraction, risk being biased towards high values by an amount that may be inversely proportional to the atmospheric overburden [16].

Significant background count rates occurring in routine alpha spectrometry are usually due to recoil or volatilization of atoms from alpha-emitting sources introduced into the chamber [17]. Emission of an alpha particle results in recoil of the residual nucleus in the opposite direction, thus conserving total momentum. A 5MeV alpha emission produces about 2% recoil energy, i.e. 100keV, in a residual atom of mass 200. This recoil energy may suffice for atoms to detach from the source surface, move freely in the vacuum chamber and attach to the inner walls and detector surface. The corresponding contamination spectrum mainly shows alpha emissions by short-lived daughter nuclides from the parent decay series. Their alpha energy peaks are typically shifted upwards compared to those of the source because of the lower self-absorption and the additional signal from recoil atoms trapped inside the silicon [18]. These peaks interfere with the spectrum of the source, not only by complicating the spectral shape but by altering relative peak size between parent and daughter nuclides [1, 19].

Recoil contamination of the detector surface can be reduced by leaving enough air in the counting chamber to produce 12μg cm⁻² of absorber between the source and detector, and by applying a ~6V negative potential to the source plate [17].

It was noticed early that the recoil mechanism can be used beneficially as a radiochemical separation method. Recoil atoms from an open source can be collected on a flat surface which then constitutes a thin source of daughter products suitable for high-resolution alpha spectrometry. This is particularly useful in the study of decay series of short-lived alpha emitters suitable for alpha immunotherapy, such as for example the ²¹⁰P and ²²⁵Ac decay progeny [19, 20]. The recoil atoms may, in fact, even be collected on the detector surface itself, which helps to achieve good counting efficiency and energy resolution. For example, the energy determination of the ²¹¹Bi alpha emission peaks could be significantly improved by perfect recoil separation from the parent ²²⁵Ac and its interfering peaks [20].

The performance of alpha spectrometry with respect to detection limit and selectivity can be improved by sample preparation techniques. Radiochemical and chemical manipulations may be applied to extract the alpha emitters of interest from voluminous matrices, while excluding interfering nuclides [21]. In order to keep track of the absolute activity concentration of the extracted radionuclide, the bulk is first spiked with a quantified amount of a reference radionuclide, which should preferably not occur in appreciable quantities in the sample material but have a similar chemical behavior as the nuclide of interest and emit activity that can be easily detected and distinguished. The task is then reduced to a relative activity measurement, which relies on decay data, detection efficiency calibrations and chemical yields.

Alpha spectrometry is also performed with gridded ionisation chambers or silicon detectors on ‘thick’ sources, far from optimal energy resolution and with difficult conversion from count rate to activity [22–24]. Rapid alpha radionuclide identification can be performed on large area sources and applied for monitoring of the environment, bioassay, safeguards, security and emergency response [23, 24]. Gross alpha counting is often used as a quick but crude screening technique, even though its adequacy may be questioned in view of disappointing results in proficiency tests [25]. Monitoring of radon decay is a research field on its own [26] because of health issues, but also because of applications, e.g. as an earthquake
precursor [27]. Alpha spectrometry also has applications related to nuclear safety, reprocessing, waste, etc [28]. In radionuclide metrology, alpha–gamma coincidence measurements are used for a better unravelling of complex decay schemes.

Obviously, the uncertainty analysis of such a wide variety of measurements cannot be discussed in a single paper. In this work, typical uncertainty components in alpha spectrometry are addressed by means of a few case studies which are transposable to other applications. The first case is a typical example of an activity ratio determination in a plutonium mixture. The second is the determination of natural activity in water using a tracer method. In the third case, the measurement of alpha-emission probabilities by means of high-resolution spectrometry is addressed.

2. Case study I: activity ratio

Figure 1 shows a measured alpha energy spectrum of a plutonium mixture of 238,239,240Pu [29]. The aim is to determine the activity ratio of 238Pu versus 239 + 240Pu. The energy resolution is insufficient to separate the 239Pu and 240Pu peaks and the low-energy tailing of the 238Pu peak partly interferes with the 239 + 240Pu peaks. For convenience, two regions of interest have been defined in the spectrum: $P_1$ represents the count integral in the first region, mainly 239 + 240Pu events and a part of the 238Pu peak tailing, $P_2$ is the count integral in the fraction of the 238Pu peak that does not interfere with the 239 + 240Pu peaks and $T_2$ is the estimated number of counts of the 238Pu tail included in $P_1$. The activity ratio is obtained from the ratio of both count integrals, after subtracting $T_2$ from $P_1$ and adding it to $P_2$:

$$R = \frac{A_1}{A_2} = \frac{P_1 - T_2}{P_2 + T_2}$$

(1)

The tailing, estimated from a least-squares fit of a functional shape to the peaks, is a crucial factor because of the anti-correlation ($\rho = -1$) between numerator $A_1 = P_1 - T_2$ and denominator $A_2 = P_2 + T_2$. The uncertainty on $A_1$ and $A_2$ propagates to $R$ via

$$\frac{\sigma^2(R)}{R^2} = \frac{\sigma^2(A_1)}{A_1^2} + \frac{\sigma^2(A_2)}{A_2^2} - \frac{2\sigma(A_1)\sigma(A_2)}{A_1 A_2}$$

$$\approx \frac{\sigma^2(A_1)}{A_1^2} + \frac{\sigma^2(A_2)}{A_2^2} + \frac{4\sigma^2(T_2)}{A_1 A_2}$$

(2)

Applying Poisson statistics, $\sigma(A) = P + T$, the counting uncertainties in both peaks and in the tail ($A_1 = 635,381$, $A_2 = 1,357,194$, $T_2 = 111,428$) are 0.15% and 0.09% and 0.3%, respectively. There is an additional uncertainty associated with the hypothetical nature of the functional shape used, which was estimated to be about 4% of $T_2$. The fitting software cannot take such potential errors into account, as the residuals are always assumed to be stochastic, ergo the functional shape is assumed to represent reality to perfection. The choice of the energy intervals in the spectra also affects the relative amounts, but the effect on the ratio was 0.3% at most. The total uncertainty on the ratio was 1%, and the resulting activity ratio was confirmed by mass spectrometry as being correct within 0.2% [29].

3. Case study II: actinides in water

Alpha-particle spectrometry is the most frequently used technique for the activity determination of alpha emitters, such as radium, uranium, plutonium, americium and thorium in environmental samples [30]. This case study pertains to a typical alpha-particle spectrometry measurement of the 226Ra and 234,238U activity concentration in drinking water [31, 32]. The set-up used is a common alpha-spectrometry system for environmental samples consisting of alpha spectrometer chambers and PIPS® (passivated implanted planar silicon) detectors with a 450 mm$^2$ sensitive area. Further in the same decay chain, there are other nuclides of interest, such as the long-lived 210Pb and 210Po, which are widespread as 222Rn progeny and play an important role in human radiation exposure. The 210Po activity level in water is easily determined by alpha spectrometry after spontaneous deposition on a silver disk. The reader is referred to literature for...
a discussion [33–35]. The uncertainty on the half-life of the frequently used 210Pb tracer is a potential source of error [36]. Also the chemistry presents problems, since polonium easily adsorbs on the walls of the sample container [33] and sublimes from its source support in a vacuum [3, 17]. To avoid contamination, the source can be covered by a thin film.

3.1. Sample preparation and chemical recovery

Extensive chemical separation of 226Ra is performed to remove interferences from other alpha emitters. A co-precipitation procedure is used for the preparation of the radium sources, using BaSO4 as a carrier. As a tracer, 133Ba is added for the determination of the chemical yield of the radiochemical procedure and its activity concentration in the sample is determined by gamma-ray spectrometry with a high-purity germanium detector (HPGe) [31].

The chemical yield is determined by relative measurements based on the comparison of the measured gamma peak areas of the 133Ba tracer in the water samples (P_{Ba}) and a 133Ba standard source (P_{Ba-Std}) that was prepared in the same manner. The recovery factor of the standard (R_{Ba-Std}) was determined by measuring the activity left in the filtrate and the washing solution after the filtration of BaSO4. The chemical yield R_{chem} in the water sample is calculated from:

\[
R_{chem} = \left( \frac{P_{Ba}}{t_{Ba} \cdot m_{Ba} \cdot P_{Ba-Std}} \right) \cdot R_{Ba-Std} \tag{3}
\]

in which \(t_{Ba}\) is the counting time; \(m_{Ba}\) is the mass of added 133Ba; \(R_{Ba-Std}\) is the recovery factor of the standard source.

In evaluating the uncertainty due to the sample preparation and the chemical yield, the contributions of the weighing of the tracer, geometrical reproducibility and peak area determination have to be taken into account. Also the use of 133Ba for yield correction must be taken with caution, as one may suspect a different microscopic chemical behavior between radium and barium. In literature [37], it has been shown that the yield ratio \(Y_{Ra-226}/Y_{Ba-133}\) is slightly higher than 1 (=1.04), with a typical uncertainty of 8%. This is the major uncertainty component in the chemical procedure.

An independent, squared sum is made of the components due to the sample preparation and the chemical recovery, including uncertainty on the standard (2%), weighing (1%), counting uncertainty (1%) and yield ratio uncertainty (8%), leading to an 8% total uncertainty for the chemical yield.

Similarly, for 234,238U activity concentration measurements [32] the water is spiked with 232U and the uranium is pre-concentrated by co-precipitation with iron (III) hydroxide at pH 9–10 using an ammonia solution. The radiochemical separation is performed over a column and the source for alpha counting is prepared by micro-coprecipitation with CeF3. The yield of the radiochemical procedure is derived from the count rate in the 232U alpha peak, thus requiring no additional measurements other than alpha spectrometry of the samples. The main uncertainty components are counting statistics in 234,238U (2%) and tracer (1%) peaks (which reduce by increasing the number of samples measured), systematic effects from choosing fixed regions of interest (2%), activity (0.6%) and mass (0.5%) of the tracer and sample volume (0.1%). An additional uncertainty on the chemical yield cannot be excluded, since the uranium in the mineral water could behave differently from the tracer because of matrix effects, for example if it were encapsulated in silica grains which are not easily dissolved [32].

3.2. Detection efficiency and solid angle

In the case of 234,238U, the activity concentration measurement is calibrated directly through comparison with the 232U tracer peak in the same alpha spectrum, under the reasonable assumption that the detection efficiency for all alpha-emitters in a thin, homogenized source is equal. The situation is different with 226Ra, for which the tracer is not an alpha emitter and the absolute alpha detection efficiency needs to be determined. Assuming that none of the alpha particles are stopped by absorption in the source or detector dead layer, the detection efficiency equals the subtended solid angle.

For a point source, the relative uncertainty on the source–detector distance \(d\) and detector radius \(R_{D}\) propagate roughly by a factor 2 to the solid angle [38]. Using a 450 mm2 PIPS detector (\(R_{D} = 11.95 \pm 0.05\) mm) and positioning the source at a distance of \(d = 5.0 \pm 0.1\) mm, the propagation of the estimated uncertainties on \(R_{D}\) and \(d\) leads to 5% standard uncertainty on \(\Omega\). This uncertainty can be lowered by measuring relative to a reference source with standardised activity. Beside geometrical differences between sources (height, radius, eccentricity), the activity distribution in the source layer produces significant differences in counting efficiency [31].

Realistic sources are inhomogeneous and not as reproducible as desired. Figure 2 shows an autoradiograph of three BaSO4 co-precipitated sources, together with the corresponding radial activity distribution. The detector set-up being axially symmetric, the source can be subdivided into concentric rings with constant solid angle and the relative amount of activity in each ring used as a weighting factor to calculate the total solid angle of the source. Thus, any deviation from a homogeneous disk source is taken into account, including variations on the source radius and the eccentricity of the source material on its substrate, but not the eccentricity of the source holder. Analysis of 16 226Ra sources showed a 3% standard deviation in the solid angle, solely due to differences in activity distribution within the sources [31]. At a closer source-detector distance, the impact on the measurement may be significantly larger.

In summary, a 3.4% total uncertainty of the solid angle is calculated from an independent, squared sum due to the radial activity distribution (including source inhomogeneity, internal eccentricity and source radius) (3%), distance \(d\) (1.2%), detector radius and tilt (0.5%) and possible source holder eccentricity (1 mm) (1%).

3.3. Spectral analysis

The 226Ra activity is derived from the count rate in the 4.78 MeV alpha peak in the spectrum of figure 3. Whereas the commercial spectral analysis software reports an uncertainty on the fitted peak areas, one has to be cautious not to
underestimate the true uncertainty. The residuals of the fit show non-stochastic deviations and, since the fit is restricted to the $^{226}$Ra peak region (3.7–4.8) MeV, the tailing of the higher-energy daughter peaks is not properly subtracted [31].

As an alternative to the fit, one can calculate the net area ($N$) by taking the numerical integral of the number of counts in the peak region ($P$) instead and correcting for background ($B$) and subtracting the low-energy tail of the interfering peak at 5.49 MeV ($T$):

$$N = P - T - B$$

A tail-to-peak ratio (ca. $T/N \approx 0.05$) is derived from the well-isolated peak at the end of the spectrum (7.68 MeV) and this ratio is applied to subtract the tailing of the 5.49 MeV peak from the $^{226}$Ra peak. The uncertainty was calculated from the sum of the counting uncertainties (Poisson) and an additional, estimated 10% uncertainty on the tailing:

$$u(N) = \sqrt{P + B + T + (T/10)^2}$$

which is slightly higher than the uncertainty delivered by the software. A typical relative uncertainty is (1–1.5)% [31].

The spectral analysis of the $^{234,238}$U peaks versus the $^{232}$U tracer peak is relatively easy, in which counting statistics play a major role and a systematic uncertainty of 2% is assigned for the choice of the region of interest. However, analyses of many samples show a continuous increase of the activity concentration in the $^{234}$U and $^{238}$U activities, which remain proportional but are not in equilibrium. This has been attributed to inhomogeneity in the bottles, as they were taken in

Figure 2. Autoradiographs (left) and radial activity distributions (right) for $^{226}$Ra samples prepared by BaSO$_4$ co-precipitation. A perfectly homogeneous source should have a flat radial activity distribution.
sequence from the batch [32]. The uncertainties due to system dead time, counting time and decay correction (i.e. half-life) are considered to be negligible compared to the other uncertainty components (in total <0.1% of the total uncertainty). In principle, using the number of counts of Poisson distributed data as their relative weight in the least-squares fit, can lead to a small bias towards lower values [39].

4. Case study III: emission probabilities

High-resolution alpha spectrometry is performed on a single alpha-emitting radionuclide in the shape of a thin, homogenous source. The spectrum contains peaks at different emission energies, the complexity of which may vary significantly among radionuclides, from a singlet to tens of peaks. The density of peaks can be so high that individual peaks remain unresolved and gamma spectrometry is needed to determine the relative feeding of nuclear levels in the daughter nuclide [40]. The alpha-emission probabilities are calculated from the peak areas normalised to the total area. Complications are the finite energy resolution, peak tailing and true coincidence effects between alpha particles and conversion electrons or x-rays.

4.1. Peak shape representation

Spectral deconvolution is a big issue in alpha-particle spectrometry, since individual alpha emission peaks tend to partially overlap even in ideal conditions. Various mathematical models have been proposed in the past to faithfully represent the typically asymmetric peak shape induced by mono-energetic alpha particles in detectors (see [41]). One of the most successful analytical models to represent the shape of a single alpha particle is the convolution of an exponential low-energy tail with a Gaussian distribution: [42, 43]

\[ f(u - \mu; \sigma, \tau) = \frac{A}{2\tau} \exp\left(\frac{u - \mu}{\tau} + \frac{\sigma^2}{2\tau^2}\right) \times \text{erfc}\left(\frac{1}{\sqrt{2}} \left(\frac{u - \mu}{\sigma} + \frac{\sigma}{\tau}\right)\right) \]

in which \( A \) is the peak area, \( u - \mu \) the distance from the peak position, \( \sigma \) the standard deviation of the Gaussian and \( \tau \) the tailing parameter. Since a single tail often does not suffice to adequately reproduce the asymmetric part of the peak shape, a combination of two or three exponential tails is routinely applied: [44]

\[ F(u) = \sum_{j=1}^{3} \eta_j f(u - \mu_j; \sigma_j, \tau_j) \]

with different tailing parameters \( \tau_1, \tau_2, \tau_3 \) and normalised weighting factors \( \eta_1 + \eta_2 + \eta_3 = 1 \). Even more elaborate modeling has recently been implemented, allowing additional convolutions, also at the high-energy side: [41]

\[ F(u) = \sum_{j=-2}^{0} \eta_j f(u - \mu_j; \sigma_j, \tau_j) + \sum_{j=1}^{10} \eta_j f(u - \mu_j; \sigma_j, \tau_j) \]

Whereas this function is one of the very best in reproducing measured spectra [41], systematic deviations still remain visible in spectra with very high statistical accuracy (see e.g. [4, 41]). Applying other fit functions gives slightly different shapes and therefore also different ratios between fitted peak areas [4]. Besides the statistical uncertainty, which may be handled by fitting software, there is unavoidably an uncertainty component to be assigned for possible misrepresentation of the actual peak shapes. Comparing fit results of different analytical functions on the same spectrum helps in evaluating the potential error on the alpha emission probabilities.

4.2. Non-linear fitting and covariance

Beside the line shape, a goodness-of-fit criterion has to be chosen and a minimization algorithm. Some of the options have been tested in the past [45], with the Levenberg–Marquardt showing fast convergence when using good initial values and Neyman’s \( \chi^2 \) being a computationally faster criterion than the maximum likelihood statistic for Poisson distributed data. The latter has in principle the advantage of not being biased, but no significant differences were observed in the test. The fitting of complex line shapes can be time consuming because it is non-linear and the parameters are highly correlated. It often needs to be pursued by alternatingly setting a different set of parameters free while keeping others fixed to advance slowly from a mediocre fit to the optimum solution. This extra effort can lead to significant differences in the end.

The statistical uncertainties on the fitted parameters, including the peak areas, can be calculated from the covariance matrix [46–48]. A minimum requirement is that the residuals are purely stochastic. Experience with complex spectra shows that results are badly defined if a spectrum can be fitted in several ways, e.g. increasing a tailing can have similar effects as adding a small additional peak, changing the peak width or energy calibration can significantly influence the areas of overlapping peaks, the area of small peaks interfered with by the tailing of a dominant peak are crucially dependent on the exact representation of the latter, not taking into account underlying peaks from impurities can change relative positions of freely fitted peaks and alter relative peak areas. Also,
scattering effects, electronic drift and coincidences between signals from alpha particles with beta particles, conversion electrons, x-rays or electronic noise give rise to a distortion of the energy spectrum that is not explicitly implemented in the analytical model.

For these reasons, the uncertainties obtained from the covariance matrix may sometimes suffice in routine measurements with low statistical accuracy, but should be interpreted with caution in reference measurements with high statistical precision in the measurement data. Comparison of fit results with different codes does reveal biases that are not under statistical control [4] and, in fact, also basic data analysis with commercial software is visibly imperfect [49].

4.3. Coincidence effects

The spectrum is particularly distorted by true coincidences between alpha particles and electrons. The obvious solution would be to measure the source at great distance from the detector, but the need for statistical accuracy is in conflict with the need for good energy resolution in the case of long-lived nuclides. For example, for 1 Bq of 238U, 81 \( \mu g \) is required while the layer thickness should not exceed about 26 \( \mu g \) cm\(^{-2}\) [50, 51], considering that the resolution deteriorates by 0.63 keV (\( \mu g/cm^2 \))\(^{-1}\) added thickness [52]. Consequently, measurements are performed relatively close to the detector and the coincidence effects are solved by applying mathematical correction formulae [4, 51, 53, 54] and/or extrapolating fit results at different solid angles towards the correct value at an infinitely small solid angle [51, 54]. Alternatively, a magnet system is introduced to deflect the electrons away from the detector [55].

The mathematical correction consists of probability calculations for summing-in and summing-out of events in the various alpha peaks. If an alpha particle is measured in coincidence with one or more of the conversion electrons emitted in the subsequent succession of short-lived gamma transitions down to the ground level of the daughter nuclide, the added energy may suffice to move a count to a higher-energy alpha peak. Consequently, the low-energy peaks would be depopulated in favor of the high-energy peaks and the correction factors are multiplication factors by which the measured peak areas are multiplied to counteract the net count loss or gain.

Generally, the energy of the electron is lower than the energy difference between adjacent alpha peaks, due to the binding energy that was required to eject it from its orbital position. Consequently, the shifted count often ends up in the tailing of the adjacent alpha peak and metrologists have doubted if the full correction for summing effects should be applied. In the past there was a tendency to apply only one half of the calculated correction factor, as was e.g. done in the case of 235U [53]. However, more recently for 240Pu, better agreement among measurements at different solid angles was achieved by applying the full correction [4].

In general, correction factors for coincidences with x-rays have been ignored. Nevertheless, the perception was that the coincidence issue was well under control by applying the mathematical correction factors for conversion electrons if a large fraction of the applied deviation from unity is taken as uncertainty. However, recent measurements of \(^{236,238}\)U [51, 54] with and without a magnet system [55] have revealed an inadquacy of the mathematical approach, as it turned out that the correction factors compensated for only a third of the differences in the evaluated alpha emission probabilities obtained at different counting efficiencies (see figure 4). Spectral deforation was given as a tentative explanation, as the increased number of counts in the left of the high-energy peak may have caused an inflation of the fitted tailing, causing the main peak to grow even more than expected, at the expense of the adjacent low-energy peak that loses a fraction of its counts to the tailing of the main peak [54].

As a consequence, long-lived actinides previously measured in close geometries may have to be re-examined with magnet systems and in various geometries to exclude residual coincidence effects. On the other hand, cryogenic detectors measuring all emitted energy simultaneously in 4\( \pi \) configurations can be used for Q spectrometry, which may simplify identification and quantification of mixed radionuclide decay in nuclear material [56, 57].

4.4. Constraints

The area \( A_k \) of peak \( k \) is obtained directly from the fitted multiplication factor \( A \) to the normalised analytical function (equation (6)). The total number of measured alpha decays from one radionuclide is the sum of all its peak areas \( \Sigma A_k \) and the relative contribution of each peak corresponds to its alpha emission probability \( P_k = A_k / \Sigma A_k \). The sum of all relative intensities \( \Sigma P_k \) equals 100% by definition. Through normalisation, all intensities receive a degree of correlation which comes on top of the (anti-)correlation of the peak areas due to imperfect deconvolution of spectral interferences.

In the hypothetical case in which the alpha peaks are perfectly separated, i.e. their peak areas are uncorrelated, the uncertainties on the areas propagate to \( P_k \) via [54]

\[
\sigma^2(P_k) = P_k^2 (1 - P_k)^2 \left( \frac{\sigma^2(A_k)}{A_k^2} + \frac{\sigma^2(\Sigma A_k)}{(\Sigma A_k)^2} \right)
\]

which, in the absence of correlations or \( \sigma^2(\Sigma A) = \Sigma \sigma^2(A) \), is equivalent to the expression [40, 47]

\[
\frac{\sigma^2(P_k)}{P_k^2} = (1 - 2P_k) \frac{\sigma^2(A_k)}{A_k^2} + \frac{\Sigma \sigma^2(A_i)}{(\Sigma A_i)^2}
\]

If the uncertainties on the peak areas are purely statistical, the variance due to Poisson statistics is well approximated by the number of counts; \( \sigma^2(A) = A \). For a hypothetical spectrum of two well-separated peaks with areas \( A_1 = 10000 \) and \( A_2 = 100 \), the variances on \( P_1 = 99.0% \) and \( P_2 = 1.0% \) are
The uncertainties on both emission probabilities \( P_1 \) and \( P_2 \) are equal, since they are fully anti-correlated through the normalisation \( (P_2 = 1 - P_1) \). The same equations (9) and (10) can be used to propagate the interference of an impurity that affects part of the spectrum, hence also the normalisation factor. If in the example above the main peak is interfered with by an impurity peak with an estimated area of 500 counts and an additional uncertainty of 10% (or 50 counts) due to unknowns in the deconvolution, the propagated uncertainty is

\[
\sigma^2(P_1) = \sigma^2(P_2) = (99\%)^2 \left( 1\% \right)^2 \left( \frac{1}{10\,000} + \frac{1}{10\,100} \right) = (0.1\%)^2
\]

or equivalently:

\[
\frac{\sigma^2(P_1)}{(99\%)^2} = \frac{1}{10\,000} (1 - 2 \times 99\%) + \frac{1}{10\,100} = (0.1\%)^2
\]

Equation (11) is applicable in any situation in which adding an amount \( \Delta(A_k) \) to peak \( k \) implies the subtraction of the same amount from the rest of the spectrum, so that the total area \( \Sigma A \) remains invariable and the corresponding emission probability changes to \( P_k = (A_k + \Delta(A_k))/\Sigma A \). This situation occurs in the fit of an unresolved doublet in which two adjacent peaks compete for a share of the area, which makes the uncertainty of the sum of both interfering peaks smaller than the sum of the uncertainties of the individual peaks. More generally, it applies to every peak which interferes with the tailing of a higher-energy peak and vice versa. Also, the uncertainties assigned to mathematical corrections for summing-in and summing-out effects should be propagated by equation (11).

For a peak resting on the low-energy tail of another peak, there is an uncertainty associated with subtracting the tailing from the peak due to statistical variations and possible functional misrepresentations. Consider the hypothetical case that the small peak with area \( A_2 = 100 \) lies on top of the tailing of the big peak, which has an area of about 200 counts in the central region of peak 2. Taking into account twice the statistical variance and an additional 5% uncertainty (i.e. 10 counts) on the modeling of the tailing function amounts to

\[
\sigma^2(P_1) = \sigma^2(P_2) = \left( \frac{2 \times 200 + 10^2}{10\,100^2} \right) = (0.02\%)^2
\]

To a lesser extent, positively correlated uncertainties may also appear for which the propagation factor is smaller than in equations (9)–(11). If the relative deviation is the same for all peaks, there is no change in the emission probabilities. Equation (9) gives an upper limit for the propagated uncertainty. An example is the subtraction of a long tailing from high-energy peaks of other radionuclides interfering with the spectrum of interest. Also, a mismatch between fit and measured spectrum should be included in the uncertainty budget,

**Figure 4.** Extrapolation (lines) of alpha emission probabilities derived from \(^{236}\text{U}\) alpha spectra taken at different solid angles with (circles) and without magnet, the latter with (triangles) and without (rectangles) mathematical correction for coincidence effects.
e.g. by summing non-stochastic residuals near each peak separately and over the whole spectrum [54].

5. Conclusions

The applications of alpha spectrometry and the related uncertainties are too diverse to be discussed in full. Typical uncertainty components have been addressed in three case studies: the determination of the activity ratio of two alpha emitters, the absolute activity measurement of actinides in water using tracers and the determination of alpha emission probabilities from fitted peaks in high-resolution spectra. One of the common themes is spectral interference due to the limited energy resolution and the associated uncertainty correlations. The uncertainties derived from the covariance matrix in least-squares fitting routines may be incomplete, e.g. because the functional model is not rigorously defined and the system can be underdetermined. A full uncertainty budget of alpha-emission probability can be calculated by propagating uncorrelated uncertainties of the peak areas via equation (9) or (10) and anti-correlated uncertainties via equation (11).

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