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COVARIANCE ANALYSIS AND FITTING OF GERMANIUM GAMMA-RAY DETECTOR EFFICIENCY CALIBRATION DATA *

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The measurement of neutron-induced reaction cross sections often requires detection of either prompt gamma rays or gamma rays emitted during the decay of radio nuclides. This paper describes the analytical procedures we use to generate calibrations for germanium gamma-ray detector full-energy-peak efficiency ϵ versus photon energy E, and to predict the associated uncertainties. Our method, which involves fitting a parameterized regression formula to measured data by the principle of least squares, is widely applicable beyond the specific problem considered here. It differs from most commonly used methods in that comprehensive use is made of available information on all known sources of random and systematic (correlated) error associated with the calibration process. This is accomplished through the formation and application of a calibration-data covariance matrix. Objective prediction of the errors in subsequently derived quantities (e.g., detector efficiencies at energies not directly represented in the calibration data) is then achieved through error propagation. Specifically, this paper discusses our experiences in fitting the particular empirical formula $\ln \epsilon = \sum_{k=1}^{m} p_k (\ln E)^{k-1}$ to measured calibration data at gamma-ray energies from just above 200 keV to several MeV. A numerical example is provided to demonstrate the utility of this approach.

1. Introduction

In experimental physics one is frequently faced with the problem of representing measured calibration data by means of a smooth curve. This happens because the experimental calibration points rarely address explicitly all the individual conditions of interest to the experiment. The most common technique is to generate this smooth curve by fitting (in some fashion) a parameterized regression formula to the calibration data. The objective of such a fitting exercise is always to determine "best values" for these few parameters. The intent is that they will provide an "adequate" description of the measured calibration data (by means of a selected functional relationship which employs them) and, furthermore, allow for interpolation (and possibly limited extrapolation) to regions where measured data are unavailable.

There are two fundamental considerations involved. The first consideration is that of selecting the form of the regression formula, i.e., the model for parameterizing the data. In practice, this may be a purely empirical exercise or it may involve a large measure of physical justification, depending upon the circumstances of the problem. In the final analysis, this choice is usually governed rather subjectively by the experience of the experimenter as to what "works well". The second consideration concerns how one goes about determining the "best" parameters for such a model, once it has been selected. This, in fact, can be posed as a very well defined mathematical problem in statistics, one for which there exists an exact solution. It is in this second aspect of the problem, namely "fitting" the formulas to the data, where most of the previously reported schemes are found to be deficient. The problem lies in the way in which the available calibration data are weighted in the fitting process, i.e., in the way the experimental data uncertainties are specified and employed in the analysis. It is quite common for important sources of error to be overlooked, and even more typical for correlations between the various errors to be neglected. The result of such oversight is inevitably the generation of estimates for the fitting parameters which do not make optimal use of the available information. In short, the fitting parameters are biased and not of minimum variance. Furthermore, most procedures do not yield error estimates for the "best-fit" parameters which they produce, and they also fail to provide methods for estimating the uncertainties associated with those calibration values which are subsequently derived from the fitted formula.

Our research program emphasizes the measurement of neutron reaction cross sections, particularly those involving detection of prompt gamma rays or gamma

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rays emitted from product radionuclides. The importance of objective error estimation in such investigations has been emphasized in a review paper on the subject [1]. In the present paper, we specifically address the matter of generating calibrations for full-energy-peak efficiencies of germanium gamma-ray detectors at energies from above 200 keV to several MeV, a region of particular relevance to our research activities. We have observed that those uncertainties in our measured cross sections which can be traced to the calibration procedure are typically in the range of 1–2%. Since the total errors in our measured cross-section results generally are in the vicinity of 5%, this calibration error component is significant. Although the focus of this paper is on the calibration of germanium gamma-ray detectors, the methods described here are widely applicable to other curve-fitting problems in experimental physics.

Germanium detectors have been used effectively as photon detectors for more than two decades. They offer excellent energy resolution, good stability and adequate efficiency for many applications. Standard single- or multiline photon sources are readily used to experimentally derive full-energy-peak photon detection efficiency calibrations for these instruments. It is not our intent to review the plethora of journal articles and reports which have been written about the various methods used in performing calibrations of this nature. Relevant papers from this journal alone amount to nearly 50 contributions since 1980. We have used the particular method described in this paper with good success for several years, in both $(n,n'\gamma)$ and (n,X) reaction activation experiments. The associated experimental details have been reported elsewhere [2–4]. It has been our experience that calibration data from such measurements can usually be represented well by the empirical formula

$$\ln \epsilon = \sum_{k=1}^{m} p_k (\ln E)^{k-1}, \qquad (1)$$

provided that the energy range spanned does not extend much below 200 keV where the efficiency function exhibits considerable curvature for most germanium detectors. Our observations are consistent with those reported by other investigators [5,6]. We shall see below that an important feature of this formula is that eq. (1) is linear in the fitting parameters p_k.

Section 2 of this paper describes our basic procedure, step by step. In order to avoid sacrificing readability, most of the relevant mathematical details are relegated to appendix A, which is provided for the convenience of readers who wish to acquire a more thorough understanding of the statistical foundations of this method. A detailed numerical example, involving actual detector calibration data, is presented in section 3 in order to demonstrate how the method is applied in practice. Finally, the content and significance of the present work are summarized in section 4.

2. Description of the method

We now proceed to offer the reader a step-by-step prescription for the application of this method. The related mathematical details are discussed further in appendix A and in the literature (e.g., refs. [13–25]). The procedure itself is demonstrated with a numerical example in section 3.

2.1. Tabulation of measured efficiencies and their uncertainties

We suppose that n distinct measurements have been made of the absolute full-energy-peak efficiency ϵ for a particular detector. The experimental values are denoted by ϵ_i, corresponding to gamma-ray energies E_i $(i = 1, \cdots, n)$. These energies need not be distinct, e.g., there might be several measurements at the same gamma-ray energy, corresponding to various sources of the same radioactive species or repeated measurements with one source. It is entirely up to the discretion of the investigator as to how the set of pairs of experimental calibration values for the efficiency, (E_i, ϵ_i), is to be generated in his experiment. The details will certainly be strongly influenced by the experimental setup, the available calibration sources, etc.

The degree of attention which must be paid to specifying the uncertainties in the measured efficiencies may be unfamiliar to the reader. This task can be broken down into two well-defined steps. The first step involves establishing all the distinct error sources in the measurement process. What we mean here by "distinct" is that the considered error sources be uncorrelated. Examples of such distinct error sources are statistical errors, errors in absolute source strengths, geometric errors, etc. Ultimately, each experimenter must decide for himself which constitute the distinct error sources in his particular calibration experiment. Each individual error source is tagged with a subscript l. We shall assume that a total of L such error sources has to be considered. The second step involves tabulating the actual error components. Consider a particular error source l. The experimenter must estimate the corresponding magnitude of the error component $e_{\epsilon,il}$, in units of absolute efficiency, for each value of measured efficiency ϵ_i. He should then specify the correlations between these partial errors $e_{\epsilon,il}$ $(i = 1, \cdots, n)$ for this particular l. This collection of microcorrelations forms an $n \times n$ matrix $\mathbf{S}_{\epsilon,l}$. Since the various error sources considered are treated as distinct, no correlations are presumed to exist between any two partial errors involving different values of l. This procedure, when applied

for all $l = 1, \cdots, L$, yields a complete array of values $e_{\epsilon il}$, of dimension $n \times L$, as well as a set of L microcorrelation matrices $\mathbf{S}_{\epsilon l}$ ($l = 1, \cdots, L$).

This information on the partial errors and their correlations provides a basis for constructing the covariance matrix $\mathbf{V}_\epsilon$, which completely represents the uncertainties in the measured efficiencies. The elements of this matrix can be computed explicitly using the formula

$$V_{\epsilon ij} = \sum_{l=1}^{L} S_{\epsilon ijl} e_{\epsilon il} e_{\epsilon jl}, \tag{2}$$

and the total errors in the measured efficiencies are related to the variances through the formula $\sigma_{\epsilon i} = (V_{\epsilon ii})^{1/2}$.

2.2. Conversion to a logarithmic representation

It is clear from eq. (1) that the fitting analysis involves natural logarithms of efficiencies rather than direct efficiencies. Therefore, the next step in the method is to convert the measured efficiencies ϵ_i to equivalent natural logarithms, i.e., $z_i = \ln \epsilon_i$. This is simple. Conversion of the covariance matrix $\mathbf{V}_\epsilon$ to $\mathbf{V}_z$ is a bit more complicated. Nevertheless, it can be accomplished in a straightforward manner using the error propagation formula. Thus,

$$\mathbf{V}_z = \mathbf{T}^+ \mathbf{V}_\epsilon \mathbf{T}. \tag{3}$$

The symbol "+", as a superscript, denotes matrix transposition and individual elements of the matrix $\mathbf{T}$ are given by the formula

$$T_{ij} = \delta_{ij}(\partial z_i/\partial \epsilon_i) = \delta_{ij}[\partial(\ln \epsilon_i)/\partial \epsilon_i] = \delta_{ij}(1/\epsilon_i), \tag{4}$$

where $\delta_{ij} = 1$ if $i = j$ and 0 if $i \neq j$ (the Kronecker delta function). Therefore, the elements of $\mathbf{V}_z$ assume the form

$$V_{zij} = V_{\epsilon ij}/(\epsilon_i \epsilon_j). \tag{5}$$

Eq. (5) tells us that the covariance matrix for the logarithmic parameters z_i equals the relative covariance matrix for the corresponding efficiencies ϵ_i.

2.3. Estimation of the fitting parameters and their uncertainties

At this point in the analysis we possess all the information required to generate best estimates for the parameters p_k of the fitting function given in eq. (1). For convenience we denote the complete set of these parameters by the vector $\boldsymbol{p}$. Since $z_i = \ln \epsilon_i$, we can represent eq. (1), reproduced for each calibration data point as labelled with index i, by the compact matrix expression

$$\mathbf{z} \approx \mathbf{A}\boldsymbol{p}, \tag{6}$$

where $\mathbf{A}$ is an $n \times m$ matrix whose elements are $A_{ik} = (\ln \epsilon_i)^{k-1}$. The reason why $\mathbf{z}$ is related to $\boldsymbol{p}$ through an approximate equality in eq. (6) is that even with the best possible choice of $\boldsymbol{p}$, it will never be possible to reproduce (i.e., "fit") the measured data perfectly. The least-squares condition states that the best estimate for $\boldsymbol{p}$ is the one which minimizes the statistic χ^2 given by the quadratic form

$$\chi^2 = (\mathbf{z} - \mathbf{A}\boldsymbol{p})^+ \mathbf{V}_z^{-1} (\mathbf{z} - \mathbf{A}\boldsymbol{p}), \tag{7}$$

where "-1", as a superscript, denotes matrix inversion. The solution $\boldsymbol{p}$, can be extracted from the normal equations, $\partial(\chi^2)/\partial p_k = 0$ ($k = 1, \cdots, m$). It is given by the formulas

$$\boldsymbol{p} = \mathbf{V}_p \mathbf{A}^+ \mathbf{V}_z^{-1} \mathbf{z}, \tag{8}$$

$$\mathbf{V}_p = (\mathbf{A}^+ \mathbf{V}_z^{-1} \mathbf{A})^{-1}. \tag{9}$$

$\mathbf{V}_p$ is the covariance matrix for the solution parameters $\boldsymbol{p}$.

2.4. Testing the quality of fit and consistency of the data

Substitution of the solution for $\boldsymbol{p}$ into eq. (7) yields a specific value for χ^2, thereby providing a means to test the quality of the fit. This statistic is governed approximately by a χ^2 distribution with $(n - m)$ degrees of freedom, so its expected value is $(n - m)$. In physical terms, the value of χ^2 indicates not only the quality of fit, but also tests the consistency of the measured efficiency data through its sensitivity to the degree of scatter in the experimental efficiencies about the fitted curve. A value of χ^2 about equal to $(n - m)$ indicates an optimal situation, namely a good fit and scatter of the data around the fitted curve which is consistent with the data errors. Values of χ^2 significantly less then $(n - m)$ are fortuitous and therefore without consequence. However, occurrence of a χ^2 which is substantially larger than $(n - m)$ signals the presence of a problem. There are several possibilities which the investigator will need to explore. One possibility is that the errors assigned to the data are too small. A second possibility is that one (or possibly more) of the measured efficiencies is in error (a "wild" data point) and may need to be corrected. A third possibility is that the parameter estimates are distorted by computer round-off errors and need to be recalculated using higher-precision arithmetic. A fourth possibility is that the choice of fitting function is inappropriate to represent the measured data (perhaps either fewer or more parameters p_k are required). Whenever excessively large values of χ^2 are obtained, it is the responsibility of the investigator to trace the origin(s) of the discrepancy, remedy the problem(s), and then refit the data to obtain a more reasonable χ^2 value.

2.5. Derived efficiencies and their uncertainties

The true power of this method is the opportunity which it provides to not only compute efficiencies at energies other than those represented in the set, E_i, but also to predict the uncertainties in these derived efficiencies in a statistically rigorous fashion. Let us suppose that we wish to compute the efficiencies $\epsilon_{c\nu}$ for several arbitrarily selected gamma-ray energies E_ν ($\nu = 1, \cdots, N$), within the range of applicability of the fitted formula. The subscript c indicates that these efficiencies are to be calculated using eq. (1) and the best-fit parameter set $\boldsymbol{p}$. It is obvious how the efficiencies themselves should be calculated, but how are the corresponding uncertainties to be determined? In fact, with this formalism this task is quite straightforward. It is accomplished by again employing the error propagation formula mentioned above, namely

$$\mathbf{V}_{zc} = \mathbf{A}_c^{+} \mathbf{V}_p \mathbf{A}_c, \tag{10}$$

with the elements of $\mathbf{A}_c$ given by the formula $A_{ck\nu} = (\ln E_\nu)^{k-1}$. However, our requirement is for the covariance matrix, $\mathbf{V}_{\epsilon c}$, corresponding to the calculated efficiencies, $\epsilon_{c\nu}$. From the discussion following eq. (5) we will recall that the covariance matrix for the logarithms of the efficiencies is just the relative covariance matrix for the efficiencies themselves. Thus, we conclude that the elements of $\mathbf{V}_{\epsilon c}$ can be obtained using the formula

$$V_{\epsilon c \nu\lambda} = \epsilon_\nu V_{zc\nu\lambda} \epsilon_\lambda \quad (\nu, \lambda = 1, \cdots, N), \tag{11}$$

and the total errors in the calculated efficiencies are related to the variances through the formula $\sigma_{\epsilon\nu} = (V_{\epsilon c \nu\nu})^{1/2}$.

Although the procedure described in this section involves a number of matrix multiplications and two matrix inversion operations, this should not be a very formidable task for most calibration applications so long as the experimenter has access to a small computer.

3. A numerical example

To illustrate the method discussed in section 2, we now describe how we generated a specific gamma-ray detector efficiency calibration curve, over the energy range 250–1400 keV, based on data acquired during a neutron activation experiment conducted in March 1988. The detector in question is a coaxial Ge(Li) detector fabricated by ORTEC, Inc. [7]. The nominal full-energy-peak efficiency, as stated by the vendor, is $\approx 15\%$ relative to a 7.6 cm × 7.6 cm NaI(Tl) scintillation detector (for measurement of 1333 keV photons at a 25 cm source-to-detector distance). In the present experiment, a precise calibration of absolute point-source efficiency vs photon energy was developed for a counting position on the detector axis at a source-to-detector distance ≈ 20 cm.

The experimental data used in this exercise were obtained from measurements utilizing standard ^{60}Co (5.271 ± 0.001 y [8]), ^{137}Cs (30.174 ± 0.034 y [9]) and ^{152}Eu (13.33 ± 0.04 y [8]) sources. The values in parentheses are decay half-lives ($t_{1/2}$) for these activities. Each standard consists of a near-point source of active material deposited on a low-mass plastic backing. The sources originate from different laboratories, in fact from distinct countries [10–12]. Parameters for these sources are listed in tables 1 and 2. Thin layers of shim stock were used to insure that these sources were all counted in nearly identical geometries. Several counts were taken for each source to improve statistics and to test measurement reproducibility.

Full-energy-peak yields per unit livetime, C, for each of the 12 lines listed in table 2 were extracted from the recorded gamma-ray spectra. Only dominant, isolated lines were analyzed in the ^{152}Eu spectra. Detector efficiencies for all of these lines were then derived from the data. Let A be the source activity (in Bq) at the time of the count, B the number of photons emitted per disintegration (table 2), and ϵ the number of detected events in the full-energy-peak per photon emitted from the source (absolute full-energy-peak efficiency). These quantities are related through the equation

$$C = AB\epsilon. \tag{12}$$

Before applying eq. (12), the calibration activity A_0 (table 1) had to be converted to an effective activity A at the time of the measurement by application of the exponential decay law, i.e.,

$$A = A_0 \exp(-\lambda t), \tag{13}$$

where λ is the decay constant – related to half-life by

Table 1
Standard calibration sources

Source	Identity	Ref.	Calibration	
			Date	Activity [Bq]
^{60}Co	NBS-SRM-4203D-1	[10]	1 Feb. 1984	3.193×10^5 ($\pm 0.9\%$)
^{137}Cs	PTB-273-83	[11]	1 Jan. 1985	1.565×10^5 ($\pm 1.5\%$)
^{152}Eu	LMRI-EGMA-3-5243	[12]	20 Apr. 1979	4.208×10^5 ($\pm 1.5\%$)

Table 2
Gamma-ray lines from the standard calibration sources

Source	Ref.	Line number [a]	Energy [keV]	Branch [%]
^{60}Co	[9]	1	1173	100.0
		2	1333	100.0
^{137}Cs	[9]	3	662	85.0
^{152}Eu [b]	[10]	4	245	7.42
		5	344	26.4
		6	444	3.08
		7	779	13.0
		8	867	4.16
		9	964	14.5
		10	1086	11.8
		11	1112	13.6
		12	1408	20.7

[a] Label for the gamma-ray line.
[b] Only the gamma-ray lines used in the present calibration are listed.

the expression $\lambda = \ln 2/t_{1/2}$ – and t is the time elapsed since the standard was calibrated. Eq. (13) is strictly applicable only when the counting time interval is very short compared to the decay half-life. This condition was very well satisfied in the experiment.

Generation of the efficiency data covariance matrix, in accordance with eq. (2), involved examination of each factor in eqs. (12) and (13). The uncertainty in the measured peak yield per unit livetime, C, was obtained by propagating the statistical errors for those quantities employed in computing the full-energy-peak area, namely the spectrum total count and background count in the vicinity of the peak. A weighted average of the results of repeated experimental determinations of C, based on the explicit counting errors, was calculated for each gamma-ray line using the techniques described in refs. [19–21]. This is equivalent to generating a one-parameter fit, where that parameter is the expected or average value of corresponding experimental data for C. A χ^2 statistic is associated with this procedure. According to the discussion in appendix A, the expected value for this statistic is $(n-1)$, where n represents the number of values being averaged. Values of $\chi^2/(n-1) > 1$ were observed in several instances (all χ^2 values fell in the range 0.02–3.58), indicating that some of the counting results were afflicted by unidentified sources of error. Therefore, as discussed in ref. [21], the computed error in the weighted average of $C(l=1)$ was enhanced by the factor $[\chi^2/(n-1)]^{1/2}$ to account for this added "reproducibility effect" if $\chi^2/(n-1) > 1$; however, the error was not reduced if $\chi^2/(n-1) < 1$. The overall error in C was treated as random.

There are two error components for the source activity A, and their effects can be determined from eq. (13). The decay-constant ($t_{1/2}$ or λ) errors ($l=2$) were negligible, except for ^{152}Eu where the impact was $\approx 0.1\%$. The calibration (A_0) errors ($l=3$) were taken directly from information provided by the standards laboratories (table 1). Each of these error components is 100% correlated for gamma-ray lines from the same source and uncorrelated otherwise.

The final error component ($l=4$) considered here is attributed to the gamma-ray branching factor B. The branching errors were negligible for ^{60}Co [8] and amounted to 0.6% for ^{137}Cs [9]. Branching errors for specific gamma-ray lines of ^{152}Eu could be readily deduced from the documentation provided with this standard source [12]. These errors can be traced to determination of the relative peak yields for gamma rays, so they were treated as random in this experiment.

The measured efficiencies and associated error components deduced from this analysis are compiled in

Table 3
Gamma-ray detector efficiency calibration data

Line number [a]	Efficiency [b] [$\times 10^4$]	Component errors [c] [%]				Total error [c] [%]
		$l=1$	$l=2$	$l=3$	$l=4$	
1	3.089	0.4	0.0	0.9	0.0	1.0
2	2.783	0.4	0.0	0.9	0.0	1.0
3	5.016	0.3	0.0	1.5	0.6	1.6
4	12.69	0.2	0.1	1.5	2.1	2.6
5	9.278	0.1	0.1	1.5	1.5	2.1
6	7.337	0.4	0.1	1.5	1.6	2.2
7	4.315	0.3	0.1	1.5	1.7	2.3
8	4.031	0.4	0.1	1.5	1.3	2.0
9	3.681	0.2	0.1	1.5	1.6	2.2
10	3.320	0.3	0.1	1.5	2.2	2.7
11	3.284	0.2	0.1	1.5	1.5	2.1
12	2.683	0.2	0.1	1.5	1.3	2.0

[a] Label for the gamma-ray line (corresponds to table 2).
[b] Measured absolute detector full-energy-peak efficiency.
[c] Components are identified in the text (section 3); errors are given to the nearest 0.1%.

Table 4
Gamma-ray detector efficiency calibration-data macrocorrelation matrix [a]

	1	2	3	4	5	6	7	8	9	10	11	12
1	1											
2	0.84	1										
3	0	0	1									
4	0	0	0	1								
5	0	0	0	0.41	1							
6	0	0	0	0.39	0.48	1						
7	0	0	0	0.38	0.46	0.44	1					
8	0	0	0	0.43	0.52	0.50	0.49	1				
9	0	0	0	0.40	0.48	0.46	0.45	0.51	1			
10	0	0	0	0.33	0.40	0.38	0.37	0.42	0.38	1		
11	0	0	0	0.41	0.50	0.47	0.46	0.52	0.48	0.40	1	
12	0	0	0	0.44	0.53	0.51	0.49	0.56	0.51	0.42	0.53	1

[a] Correlations for the total errors presented in table 3, given to two-significant-figure accuracy; indices correspond to gamma-ray line labels from table 2.

table 3. These errors, and information on their assumed microcorrelations, were employed in computing matrix elements for the gamma-ray detector calibration-data covariance matrix, as prescribed by eq. (2). The resulting total errors are listed in table 3 and the corresponding macrocorrelation matrix appears in table 4. In this example the calibration results originating from different standard sources are completely independent (uncorrelated). This is very desirable because it reduces the chances that a serious systematic normalization error will perturb the calibration process. For this reason, it is always good experimental practice to use as diverse a collection of calibration standards as possible.

The process of fitting eq. (1) to the detector calibration data summarized in tables 2 to 4 was carried out using a code written in Fortran-77 for an IBM-compatible personal computer. Only two parameters ($m = 2$) were employed because no significant improvement in the fit was observed when additional parameters were introduced. The results of the two-parameter fit are as follows: $p_1 = 7.358$ ($\pm 0.9\%$), $p_2 = -0.8815$ ($\pm 1.0\%$), parameter error correlation $= -0.9932$ and $\chi^2 = 11.44$.

Table 5
Analysis of the quality of fit of a two-parameter curve to gamma-ray detector efficiency calibration data [a]

Line number [b]	Efficiency [$\times 10^4$]		Difference [c] [%]	Errors [%]		
	ϵ [c]	ϵ_c [d]		ϵ [c]	ϵ_c [d]	Combined [f]
1	3.089	3.090	N [g]	1.0	0.8	1.3
2	2.783	2.760	0.8	1.0	0.8	1.3
3	5.016	5.116	−2.0	1.6	0.8	1.8
4	12.69	12.29	3.2	2.6	1.5	3.0
5	9.278	9.110	1.8	2.1	1.2	2.4
6	7.337	7.275	0.8	2.2	1.0	2.4
7	4.315	4.432	−2.7	2.3	0.8	2.4
8	4.031	4.033	N	2.0	0.7	2.1
9	3.681	3.673	0.2	2.2	0.7	2.3
10	3.320	3.307	0.4	2.7	0.7	2.8
11	3.284	3.239	1.4	2.1	0.7	2.2
12	2.683	2.630	2.0	2.0	0.8	2.2

[a] Eq. (1) is fitted to data provided in tables 2–4.
[b] Label for the gamma-ray line (corresponds to table 2).
[c] Measured efficiency ϵ and its error from table 3.
[d] Calculated efficiency ϵ_c and its error, based on eq. (1), with $p_1 = 7.358$ and $p_2 = -0.8815$, and error propagation.
[e] $(\epsilon - \epsilon_c)/\epsilon$ in percent.
[f] Based on addition of errors in ϵ and ϵ_c in quadrature.
[g] N = negligible.

The parameters p_1 and p_2 are clearly very strongly anticorrelated. This is quite understandable since, in fitting a line (two parameters) to a set of nearly linear data, there is essentially no freedom to adjust one of the parameters (e.g., the slope p_2) without having to compensate in the opposite direction with the second parameter (e.g., the intercept p_1), in order to minimize the residuals χ^2 statistic). There are 10 degrees of freedom in this problem, so the value obtained for χ^2 per degree of freedom (equal to 1.144) is indeed fairly close to unity. The excellent quality of this fit is evident from the information appearing in table 5. Good consistency between the measured and calculated efficiencies is observed for all the calibration energies, i.e., the differences between the calculated and experimental efficiencies at the calibration energies are either of the order of or less than the combined experimental and computational errors (based on error propagation).

For demonstration purposes, calculated efficiencies, their errors and error correlations were determined at $E = 300$, 500, 700, 900, 1100 and 1300 keV, six equally spaced energies within the range of the fitted calibration curve. The results are summarized in table 6. Two features of this analysis are evident from this table:

(i) The errors in the calculated efficiencies are of the order of 1%, with larger uncertainties at the lower energies (where the density of calibration points, on a logarithmic scale, is lower than for higher energies).

(ii) These uncertainties in the calculated efficiencies are more strongly correlated for neighboring energy points than for more distant points, a result which is intuitively quite reasonable.

4. Summary

The example presented in section 3 demonstrates that the least-squares procedure described in section 2 (and in more detail in appendix A), coupled with use of the fitting formula given in eq. (1), is capable of yielding consistent (as quantified by a χ^2 statistic) fits of good quality (small uncertainties) to germanium detector gamma-ray efficiency calibration data. This method also provides rational estimates of the best-fit parameter uncertainties and their correlations. When such detailed information is available, it is possible to compute efficiencies at arbitrary energies within the range of applicability of the fitted curve and to predict their uncertainties and uncertainty correlations as well. Although we have discussed the fitting of germanium detector efficiency calibration data, it should be emphasized that this approach is quite general and can be applied to advantage in a variety of problems in experimental physics.

This method is clearly quite demanding of detailed information concerning the calibration measurements, particularly with regard to the matter of errors. There are two objections which are sometimes raised in opposition to this approach. The first of these questions whether this method is any better than others in common use which do not require paying such detailed attention to errors. The answer to this objection is that careful attention to the experimental error sources and their magnitudes is indeed imperative if optimal use (i.e., proper weighting) is to be made of the calibration data in seeking best estimates for the fitting parameters. Any other approach will most likely lead to parameter estimates which are biased and not of minimum variance. If the detector is being calibrated for a sensitive experiment, e.g., for a precision spectroscopic measurement or for the determination of a reaction cross section which must be accurately established in order to meet the needs of a certain application, then the method is clearly justified. The second objection revolves around skepticism as to whether it is really possible in practice to produce reliable estimates for all the partial error components and their correlations, as required to construct the calibration-data covariance matrix $\mathbf{V}_\epsilon$ according to eq. (2). There is concern that faulty error estimates will lead to incorrect results. It is certainly true that flawed error estimates will thwart analytical meth-

Table 6
Calculated gamma-ray detector efficiencies, uncertainties and correlations based on a two-parameter fit to calibration data (based on eq. (1) and data provided in tables 2–4)

Energy [keV]	Calculated Efficiency [$\times 10^4$]	Total error [a] [%]	Correlations [b]					
300	10.28	1.3	1					
500	6.552	1.0	0.96	1				
700	4.870	0.8	0.84	0.96	1			
900	3.902	0.7	0.65	0.83	0.96	1		
1100	3.270	0.7	0.44	0.67	0.86	0.97	1	
1300	2.822	0.8	0.26	0.51	0.74	0.90	0.98	1

[a] Errors are given to nearest 0.1%.
[b] Correlations are given to two-significant-figure accuracy.

ods which rely on this information. However, it is our experience that reasonable error estimates can usually be made without excessive difficulty, provided that one develops the habit of carefully documenting the relevant details which are available during the course of an experiment. It is surprising how much critical information is lost or discarded in experiments, e.g., information which would insure reasonable estimation of the necessary error components, simply because most investigators are not trained to observe and record this information at the time when it is readily at hand to them during the course of the experiment. It is our opinion that routine exercise of appropriate experimental discipline, e.g., as required to produce and document the error information necessary for the conduct of data analysis exercises like the one described in this paper, will inevitably lead to improved experiments and therefore to higher-quality results.

Appendix A

The basic principles involved in generating the covariance matrix for a calibration data set, and then fitting these data with a specific parameterized formula (regression analysis) are discussed in ref. [5], in many textbooks (e.g., refs. [13–17]) and in earlier reports and articles from this laboratory (e.g., refs. [18–24]). However, a self-contained treatment of the mathematical formalism which is specifically applicable to the present problem is provided in this appendix for the convenience of the interested reader.

Regression analysis is a statistical procedure in which a collection of sampling results (experimental data) are represented by a chosen parameterized formula. The theory offers no a priori guidance as to what form this formula should take. This decision must be made by the investigator on the basis of other criteria, including experience. Once the choice of the formula is made, estimators are developed to derive the "best" possible values for the parameters. Since the fitted data are uncertain (have errors), it follows that the deduced parameters are also uncertain. There are two important advantages to employing regression formulas in which a linear relationship exists between the observables to be fitted and the parameters of the fitting function. The first and most obvious advantage is simplicity. The second advantage, which is the more important one, is that the well-known Gauss–Markov theorem can then be invoked. This theorem (as amended in 1957 by Aitken [25] to include correlated data) states that the least-squares method will provide estimators for these parameters which are both unbiased and of minimum variance. Consequently, this is the method of choice for solving this regression fitting problem.

Let ϵ represent an array of n experimentally determined detector efficiencies ϵ_i, corresponding to n gamma-ray energies E_i. The quality of the calibration depends strongly upon the number of the gamma-ray lines involved (the more the better) and the degree to which they provide a reasonably uniform coverage of the energy range ($E_{\min}$, $E_{\max}$). The uncertainties for these data are then represented by an $n \times n$ covariance matrix. The elements of this matrix, $V_{\epsilon ij}$, are constructed from a table of compiled partial error components, $e_{\epsilon il}$, by means of the formula

$$V_{\epsilon ij} = \sum_{l=1}^{L} S_{\epsilon ijl} e_{\epsilon il} e_{\epsilon jl} \quad (i, j = 1, \cdots, n), \tag{A.1}$$

where $S_{\epsilon ijl}$ is a typical element of $\mathbf{S}_{\epsilon l}$, the $n \times n$ microcorrelation matrix for the lth source of error. When a particular error source is random, the corresponding microcorrelation matrix is a diagonal unit matrix. However, if nonvanishing correlations exist (systematic error) this matrix cannot be diagonal. It is assumed that there are L distinct sources of experimental error and that no correlations exist between partial errors of different origin (i.e., with different l). The correlations of the covariance matrix $\mathbf{V}_\epsilon$ can be readily computed using the formula

$$C_{\epsilon ij} = V_{\epsilon ij} / \left(V_{\epsilon ii} V_{\epsilon jj} \right)^{1/2} \quad (i, j = 1, \cdots, n). \tag{A.2}$$

$\mathbf{C}_\epsilon$ is called the macrocorrelation matrix.

Our objective is to fit the n-fold efficiency calibration data set with a linear expression having the general form

$$z = g(\epsilon) = \sum_{k=1}^{m} p_k f_k(E) \quad (m < n). \tag{A.3}$$

We are particularly interested in the case where $g(\epsilon) = \ln \epsilon$ and $f_k(E) = (\ln E)^{k-1}$, since this corresponds to eq. (1). The first step in this process is to determine the covariance matrix for z which is obtained from ϵ by the transformations $z_i = g(\epsilon_i)$, for $(i = 1, \cdots, n)$. This analysis involves the well-known law of error propagation,

$$\mathbf{V}_z = \mathbf{T}^+ \mathbf{V}_\epsilon \mathbf{T}, \tag{A.4}$$

where $\mathbf{T}$ is the matrix consisting of the elements $T_{ij} = \delta_{ij} (\partial g_i / \partial \epsilon_i)$ and δ_{ij} is the Kronecker delta function. The symbol "+", as a superscript, denotes matrix transposition. From eq. (A.4) and this definition of $\mathbf{T}$ it follows that the elements of $\mathbf{V}_z$ are given by the formula

$$V_{zij} = (\partial g_i / \partial \epsilon_i) V_{\epsilon ij} (\partial g_j / \partial \epsilon_j) \quad (i, j = 1, \cdots, n). \tag{A.5}$$

The uncertainty correlations for z and ϵ are identical, i.e., $\mathbf{C}_z = \mathbf{C}_\epsilon$.

The fitting of eq. (A.3) to efficiency calibration data involves estimating the parameter vector $\boldsymbol{p}$ (consisting of elements p_k) so that to a good approximation

$$z_i \approx \sum_{k=1}^{m} p_k f_k(E_i) \quad (i = 1, \cdots, n). \tag{A.6}$$

In equivalent matrix notation,

$$z \approx \mathbf{A}p, \tag{A.7}$$

where the $n \times m$ matrix $\mathbf{A}$, composed of the elements $f_k(E_i)$, is known as the calibration design matrix. The symbol " $\approx$ " appearing in eqs. (A.6) and (A.7) signifies approximate equality. Exact equality is not possible, even for the best choice of parameters p_k, since real experimental data can never be perfectly fitted by a regression formula involving fewer parameters than data ($m < n$). Since eq. (A.3) is linear in the p_k, $\mathbf{A}$ does not depend upon p! As indicated above, an unbiased estimator with minimum variance for p can be obtained by the least-squares method. The quantity to be minimized is the quadratic expression

$$\chi^2 = (z - \mathbf{A}p)^+ \mathbf{V}_z^{-1}(z - \mathbf{A}p). \tag{A.8}$$

The symbol "-1", as a superscript, denotes matrix inversion. We remark in this context that $\mathbf{V}_\epsilon$, and thus $\mathbf{V}_z$, must be positive definite in order to represent real physical errors and to insure the existence of the inverse $\mathbf{V}_z^{-1}$ [24]. It is clear that the experimental detector efficiencies are actually calculated from several more elementary physical quantities which are directly measured in the laboratory. Therefore, as a consequence of the central-limit theorem, it is reasonable to assume that these indirectly derived efficiencies are nearly normally distributed. Thus χ^2, as defined by eq. (A.8), is a statistic which should approximately follow a chi-square probability distribution with $(n - m)$ degrees of freedom. The expected value of the χ^2 statistic is $\langle \chi^2 \rangle = (n - m)$. The quantity χ^2 (when calculated from eq. (A.8) using the least-squares solution parameter vector p) therefore plays a valuable role in testing the goodness of fit. As long as the solution vector p leads to a value of $\chi^2 \leq (n - m)$, the results of the fit are considered to be acceptable. However, significantly larger values of χ^2 generally signal the presence of one or more of the following conditions:

(i) The scatter in the efficiency calibration data is inconsistent with $\mathbf{V}_\epsilon$, indicating that the errors have been underestimated.

(ii) There exist one or more "wild" data points which need to be re-examined, and possibly eliminated, followed by reanalysis of the data.

(iii) The numerical procedure suffers from limitations in computer precision (round-off errors).

(iv) The selected regression formula provides a poor model for fitting the calibration data.

We have found that condition (iv) is a distinct possibility for the formula in eq. (1) if the lower energy of the calibration range, $E_{\min}$, lies considerably below 200 keV. This is a region where the full-energy-peak efficiency for many germanium detectors is observed to vary strongly with photon energy. A reasonably broad calibration energy range can be accommodated by eq. (1) for a suitable choice of m, but there may be pragmatic limitations (usually associated with condition (iii) above).

Minimization of χ^2 [eq. (A.8)] is equivalent to satisfying the set of conditions $\partial(\chi^2)/\partial p_k = 0$ ($k = 1, \cdots, m$), commonly called the normal equations. Their solution, p, is given by the formula

$$p = (\mathbf{A}^+ \mathbf{V}_z^{-1} \mathbf{A})^{-1} \mathbf{A}^+ \mathbf{V}_z^{-1} z. \tag{A.9}$$

It follows from an application of error propagation that the $m \times m$ covariance matrix $\mathbf{V}_p$ for p is given by

$$\mathbf{V}_p = (\mathbf{A}^+ \mathbf{V}_z^{-1} \mathbf{A})^{-1}. \tag{A.10}$$

If the solution provided by eqs. (A.9) and (A.10) yields an acceptable value of χ^2, we are then able to calculate the detector efficiencies $\epsilon_{c\nu}$ for an arbitrarily selected set of energies E_ν ($\nu = 1, \cdots, N$) falling in the range ($E_{\min}$, $E_{\max}$), with some measure of confidence. Furthermore, the theory provides a rational estimate of the corresponding $N \times N$ covariance matrix $\mathbf{V}_{\epsilon c}$ for these results. The efficiencies $\epsilon_{c\nu}$ are readily derived from eq. (1). Determination of $\mathbf{V}_{\epsilon c}$ is somewhat more difficult, but it essentially involves an exercise in error propagation. First, we compute the elements of the $N \times N$ covariance matrix $\mathbf{V}_{zc}$ for the collection of values $z_{c\nu}$ ($\nu = 1, \cdots, N$) which result from an application of eq. (A.3). It is evident that the appropriate error propagation formula is

$$\mathbf{V}_{zc} = \mathbf{A}_c^+ \mathbf{V}_p \mathbf{A}_c, \tag{A.11}$$

where the $m \times N$ matrix $\mathbf{A}_c$ is composed of the elements $f_k(E_\nu)$. We shall keep in mind the fact that $f_k(E_\nu) = (\ln E_\nu)^{k-1}$ in the present application. According to a discussion appearing earlier in this appendix, the uncertainty correlations for the calculated efficiencies $\epsilon_{c\nu}$ are the same as those for the corresponding values $z_{c\nu}$. The standard deviation (error) in $z_{c\nu}$ is related to its variance by the formula $\sigma_{zc\nu} = (V_{zc\nu\nu})^{1/2}$. Since $z_{c\nu} = g(\epsilon_{c\nu})$, it follows that the standard deviation in $\epsilon_{c\nu}$ can be obtained from the expression

$$\sigma_{\epsilon c\nu} = \sigma_{zc\nu} / \mathrm{abs}\left[(\partial g/\partial \epsilon)_{\epsilon = \epsilon_{c\nu}}\right],$$

where abs[#] denotes absolute value. Finally, since in the present work $g(\epsilon) = \ln \epsilon$, we conclude that $\sigma_{\epsilon c\nu} = \epsilon_{c\nu}\sigma_{zc\nu}$. The elements of the covariance matrix for the calculated efficiencies, $\mathbf{V}_{\epsilon c}$, can then be generated by combining these results. The appropriate expression is

$$V_{\epsilon c\nu\lambda} = \sigma_{\epsilon c\nu} C_{\epsilon c\nu\lambda} \sigma_{\epsilon c\lambda}, \quad (\nu, \lambda = 1, \cdots, N), \tag{A.12}$$

where $C_{\epsilon c\nu\lambda}$ is an element of the correlation matrix $\mathbf{C}_{\epsilon c}$, which is identical to the correlation matrix $\mathbf{C}_{zc}$ associated with the covariance matrix $\mathbf{V}_{zc}$ given by eq. (A.11).

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