

Corrigendum

Corrigendum: The k_0 -INRIM software: a tool to compile uncertainty budgets in neutron activation analysis based on k_0 -standardisation (*Meas. Sci. Technol.* 31 017002)

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1. Introduction

This corrigendum addresses a mistake spotted in our original manuscript [1]. In particular, a typing error was identified in the reported model equation that k_0 -INRIM software implements to compute the analyte mass fraction, w_a , via the k_0 -standardisation method.

2. Mistakes

The correctly reported measurement model is displayed as follows and replaces equation (1) in the original paper:

$$w_a = \frac{\lambda \frac{(n_p/COI)(t_c/t_l)e^{-\mu(1-t_l/t_c)}}{(1-e^{-\lambda t_l})(1-e^{-\lambda t_c})} \Big|_a}{\lambda \frac{(n_p/COI)(t_c/t_l)e^{-\mu(1-t_l/t_c)}}{(1-e^{-\lambda t_l})(1-e^{-\lambda t_c})} \Big|_m} e^{(\lambda_a - \lambda_m)t_{dm} + \lambda_a \Delta t_d} \times \frac{k_{0\text{Au}}(m)}{k_{0\text{Au}}(a)} \frac{G_{th\ m} + \frac{G_{e\ m}}{f} \left(\frac{Q_{0\ m} - 0.429}{E_{r\ m}^\alpha} + \frac{0.429}{0.55^\alpha(1+2\alpha)} \right)}{G_{th\ a} + \frac{G_{e\ a}}{f} \left(\frac{Q_{0\ a} - 0.429}{E_{r\ a}^\alpha} + \frac{0.429}{0.55^\alpha(1+2\alpha)} \right)} \times e^{\sum_{i=1}^h a_i(E_{p\ m}^{2-i} - E_{p\ a}^{2-i})} \frac{(1 - \delta \varepsilon_{r\ m} \Delta d_m)}{(1 - \delta \varepsilon_{r\ a} \Delta d_a)} \frac{m_{std}}{m_{sm}} w_m. \quad (1)$$

In detail, the $2 - i$ exponents within the summation are here suitably placed above the monitor and analyte energies, $E_{p\ m}$

and $E_{p\ a}$, respectively, while in the original paper it was placed just outside the parenthesis $((E_{p\ m} - E_{p\ a})^{2-i})$. Accordingly, the same correction also applies in the bullet points list, after equation (1), where symbols are explained. Thus, the text of the sixteenth bullet point becomes ' a_i the h parameters of the model adopted to describe the full-energy γ -peak detection efficiency at the counting position, $e^{\sum_{i=1}^h a_i(E_{p\ m}^{2-i} - E_{p\ a}^{2-i})}$, with $h = 4, 5$ or 6 ' instead of ' a_i the h parameters of the model adopted to describe the full-energy γ -peak detection efficiency at the counting position, $e^{\sum_{i=1}^h a_i(E_{p\ m} - E_{p\ a})^{2-i}}$, with $h = 4, 5$ or 6 '.

3. Remarks

The original equation (1) was verbatim reported also in the k_0 -INRIM user's manual; consequently, the document will be soon updated to version 1.01 in order to be consistent with the corrected published paper. Users might easily check the number version of their downloaded manual, which is reported in the header of the first page.

It is worth stressing that the typing error was limited to the paper (and manual); the formula implemented in the original version of the software was not affected by it, as well as the validation performed on the software itself and the conclusions reported in the original paper.

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Reference

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Technical Note

The k_0 -INRIM software: a tool to compile uncertainty budgets in neutron activation analysis based on k_0 -standardisation

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Abstract

A software package was developed to evaluate the uncertainty of results provided by neutron activation laboratories adopting the k_0 -standardisation method in trace elements analysis. The outputs are stand-alone and editable spreadsheet budgets based on a measurement equation including more than 40 input quantities and written to consider the effect of correlations. The program, called k_0 -INRIM, is presented to potential users and freely distributed alongside the user's manual. The measurement equation is reported and the main features are described together with the results obtained in a validation test. An uncertainty budget compiled using the software output is given as an example.

Keywords: analytical chemistry, neutron activation analysis, uncertainty budget, software, k_0 -standardisation

 Supplementary material for this article is available [online](#)

1. Introduction

Analytical methods based on neutron activation analysis (NAA) are applied to determine trace amounts of elements in a wide range of materials. The multi-element capability of NAA is typically exploited with the k_0 -standardisation to realize the traceability to SI via the so-called k_0 factors [1] by using a standard of only one element selected as a monitor [2].

At present, the most comprehensive software packages available for processing k_0 -NAA data are Keyzero/SolcoiR and k_0 -IAEA [3]. The first is a commercial software implemented with the support of the initial developers of the k_0 -standardisation [4] whereas the latter is a free-of-charge

software designed for and distributed by the International Atomic Energy Agency (IAEA) [5].

Despite the fact that these software packages have been developed and tested, they do not include an evaluation of uncertainty following the Guide to the Expression of Uncertainty in Measurement (GUM) [6]. Specifically, the uncertainty evaluated by Keyzero/SolcoiR considers only the contribution due to counting statistics while the uncertainty evaluated by k_0 -IAEA is based on the outdated classification and propagation of random and systematic sources.

An additional software, named ERON, was designed and freely distributed in 2008 to properly evaluate the k_0 -NAA uncertainty [7]. However, since the output did not include the measurement result, its use requires a supplementary software to quantify the investigated element. Moreover, the effect of correlations was not entirely accounted for.

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To fill these gaps, we developed and tested a new data processing software, named k_0 -INRIM, based on a measurement equation modeling most of the presently recognized influencing factors. The outputs are uncertainty budgets in agreement with the GUM recommendations and compiled in stand-alone and user-adjustable spreadsheets described in [8]; the information required to quantify the investigated elements and to assess their uncertainties is included.

The k_0 -INRIM software overcomes the time-consuming compiling of the uncertainty budgets, one for each investigated element, which makes cumbersome the application of the spreadsheet approach [8]. In addition, the program implements original methodologies both for gamma-peak identification and for the calibration of the detector efficiency fully considering the effect of correlations. As a supplementary feature, detection limits according to the Currie's limit can be evaluated in the case of undetected elements.

k_0 -INRIM is free-of-charge and available for download together with the user's manual at the webpage of the Istituto Nazionale di Ricerca Metrologica.

Here we shortly present the software to potential users by (i) pointing out the adopted measurement model, (ii) describing the program features and (iii) showing the results obtained in a validation test, including the establishment of the uncertainty budget of a quantified element. Additional and more detailed information is given in the user's manual, also available in the supporting information (stacks.iop.org/MST/31/017002/mmedia) of this paper.

2. Measurement model

The k_0 -INRIM adopts the following equation to compute the mass fraction of the analyte in a measurement sample, w_a , traceable to the mass fraction of the monitor in a standard sample, w_m :

$$w_a = \frac{\lambda \frac{(n_p/COI) (t_c/t_l) e^{-\mu(1-t_l/t_c)}}{(1-e^{-\lambda t_l})(1-e^{-\lambda t_c})} \Big|_a e^{(\lambda_a - \lambda_m) t_{dm} + \lambda_a \Delta d}}{\lambda \frac{(n_p/COI) (t_c/t_l) e^{-\mu(1-t_l/t_c)}}{(1-e^{-\lambda t_l})(1-e^{-\lambda t_c})} \Big|_m} \times \frac{k_{0Au(m)}}{k_{0Au(a)}} \frac{G_{thm} + \frac{G_{em}}{f} \left(\frac{Q_{0m} - 0.429}{\bar{E}_{rm}^\alpha} + \frac{0.429}{0.55^\alpha(1+2\alpha)} \right)}{G_{tha} + \frac{G_{ea}}{f} \left(\frac{Q_{0a} - 0.429}{\bar{E}_{ra}^\alpha} + \frac{0.429}{0.55^\alpha(1+2\alpha)} \right)} e^{\sum_{i=1}^h a_i (E_{pm} - E_{pa})^{2-i}} \frac{(1 - \delta \varepsilon_{rm} \Delta d_m) m_{std}}{(1 - \delta \varepsilon_{ra} \Delta d_a) m_{sm}} w_m, \quad (1)$$

where subscripts a and m refer to the analyte and monitor, respectively, and

- $\lambda = \ln(2)/t_{1/2}$ is the decay constant of a radionuclide having a half-life time $t_{1/2}$;
- n_p is the number of counts in the full-energy γ -peak;
- COI is the true-coincidence correction factor;
- t_c and t_l are the counting and live times of the detection system, respectively;
- t_{dm} is the decay time of the monitor;

- $\Delta t_d = t_{da} - t_{dm}$ is the difference between the analyte and monitor decay times at their acquisition start times;
- t_i is the neutron irradiation time;
- μ is the excess counting loss constant of the detection system;
- $k_{0Au(m)}$ and $k_{0Au(a)}$ are the k_0 factors of monitor and analyte versus Au, respectively;
- G_{th} and G_e are the thermal and epithermal neutron self-shielding correction factors, respectively;
- f is the (conventional) sub- to epi-cadmium neutron flux ratio;
- α is the epi-cadmium neutron shape factor;
- Q_0 is the ratio of the resonance integral (for a $1/E$ neutron spectrum in the epi-cadmium region) to the thermal cross section;
- \bar{E}_r is the effective resonance energy;
- E_p is the energy of the γ -peak;
- a_i are the h parameters of the model adopted to describe the full-energy γ -peak detection efficiency at the counting position, $\sum_{i=1}^h a_i (E_{pm} - E_{pa})^{2-i}$, with $h = 4, 5$ or 6 ;
- $\delta \varepsilon_r$ is the relative variation of detection efficiency per unit of vertical position;
- Δd is the vertical position difference between the sample and the reference source used for efficiency calibration at the counting position; and
- m_{std} and m_{sm} are the standard and sample masses, respectively.

Definitions and details of the listed input quantities are given in [8].

3. Program features

The k_0 -INRIM code was implemented using the open-source Python programming language.

The current version is limited to γ -counting setups assuring the best accuracy, i.e. where the measurement and standard samples have a point-like geometry and are counted at the same position with respect to the detector end-cap. The detection efficiency calibration is performed using a multi-gamma reference source.

It is worth noting that model (1) applies to the activation and decay paths types I, IIB, IVB and VI defined in [9]. The user is informed in the case of complex activation and decay

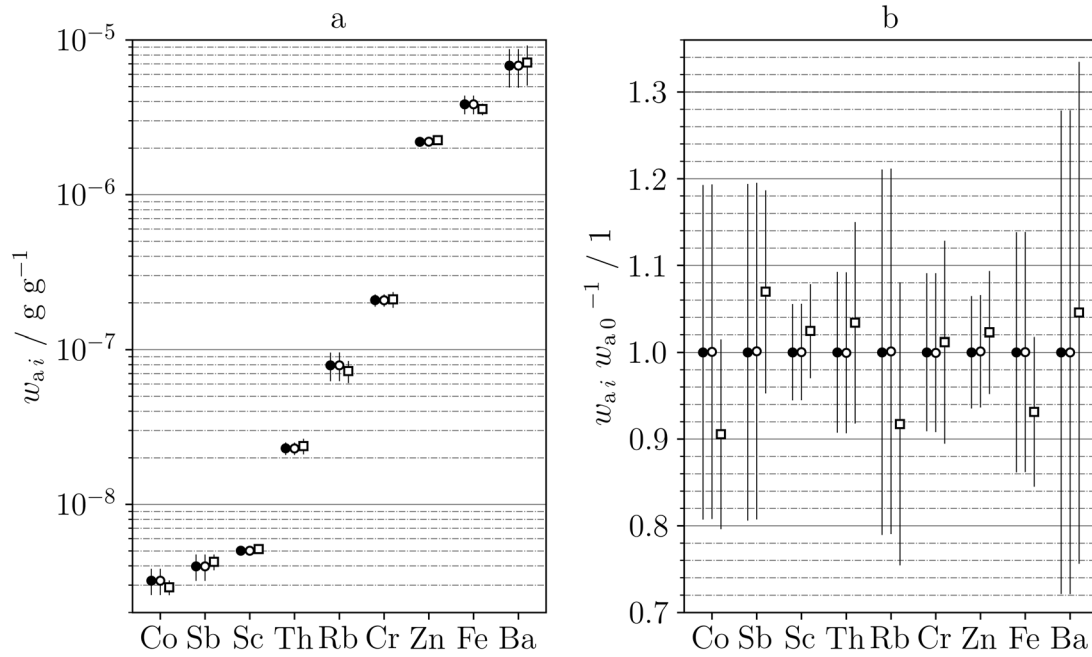


Figure 1. Absolute (a) and normalized (b) mass fractions obtained in the first and second test, w_{a1} (hollow circles) and w_{a2} (hollow squares), respectively, compared to the reference values, w_{a0} (solid circles). The error bars indicate a 95% confidence interval.

paths that are not yet implemented or when non-1/ ν nuclides requiring the application of Westcott formalism are selected.

Spectrum data can be imported by selecting an editable user template workbook or outputs from the commercial Ortec GammaVision or HyperLab gamma spectrum evaluation softwares. This significantly limits user errors during typing of the spectrum parameters, e.g. n_p , t_c and t_i , in the spreadsheet budgets proposed in [8].

The combined uncertainty of the result and the individual contributions to the variance are obtained via matrix computations to consider the correlations. Data and calculation formulae are included in the uncertainty budget spreadsheet created by the software.

The program was designed to simplify as much as possible the data processing. Specifically, the workflow of the analysis proceeds downwards in the main window of the software interface, from where secondary windows are opened by pressing action buttons to (i) set general settings, (ii) import the user template workbook, (iii) select the background spectrum, (iv) perform the efficiency calibration of the detector, (v) enter the neutron irradiation data, (vi) select the sample and standard spectra and the emissions of the investigated and monitor elements, respectively, (vii) select the elements for the detection limits and, finally, (viii) process the data.

4. Code validation and uncertainty budget example

The absence of errors in the software code was checked by processing experimental data previously collected to determine traces of Co, Sb, Sc, Th, Rb, Cr, Zn, Fe and Ba in a sample of cerebrospinal fluid. The spectrum data were elaborated with Ortec GammaVision and the uncertainty budgets, published in [8], were manually established with the spreadsheet

Table 1. Uncertainty budget of Cr in cerebrospinal fluid. The index column gives the relative contributions of the standard uncertainty $u(x_i)$ to the combined standard uncertainty, $u_c(y)$, of the output quantity Y , w_a . Only the input quantities X_i with an index greater than 1.0% are listed.

Quantity	Unit	Value	Standard uncertainty	Index
X_i	$[X_i]$	x_i	$u(x_i)$	%
n_{pa}	1	51998	1059	23.7
COI_m	1	0.857	0.017	22.5
$k_{0Au(a)}$	1	0.002620	0.000013	1.4
Q_{0a}	1	0.53	0.11	4.7
E_{pm}, E_{pa}, a_i	1	0.3567	0.0062	17.0
Δd_m	mm	0.00	0.29	10.4
Δd_a	mm	0.00	0.29	9.8
m_{std}	g	0.008470	0.000050	2.0
w_m	$g g^{-1}$	0.004597	0.000046	5.7
Y	$[Y]$	y	$u_c(x_i)$	
w_a	$g g^{-1}$	2.083×10^{-7}	8.7×10^{-9}	100

technique. Values and uncertainties, given in mass concentrations, were converted to mass fractions and used as a reference.

As a first test, the user template workbook was filled in with the published cerebrospinal fluid spectrum data and processed with k_0 -INRIM. As a second test, the collected cerebrospinal fluid spectra were elaborated with HyperLab and the outputs were straightforwardly imported and processed with k_0 -INRIM. In both cases, values and uncertainties of the remaining input quantities were kept fixed as in [8].

A comparison between the mass fraction values measured in the first and second test, w_{a1} and w_{a2} , respectively, and the reference values, w_{a0} , is shown in figure 1(a). In addition, data were normalized with respect to the reference and plotted in figure 1(b) to highlight minor discrepancies.

The outcome points out that the use of the software allows one to establish uncertainty budgets without introducing errors. In fact, there were no differences between values and uncertainties obtained in the first test with respect to the reference values. The departures observed in the second test were only due to differences of counts in the full-energy γ -peaks estimated with HyperLab and Ortec GammaVision; nevertheless, data are still compatible with the reference within their uncertainties.

As an example, table 1 reports the uncertainty budget of Cr compiled starting from the k_0 -INRIM output obtained in the second test.

5. Conclusions

k_0 -INRIM was developed and validated to establish uncertainty budgets of k_0 -NAA measurements. In agreement with the GUM recommendations, the effect of correlated input quantities was fully accounted for. This makes the program distinct among the existing software packages adopted for processing k_0 -NAA data.

Stand-alone spreadsheet budgets described in [8] and implementing the formulae used for calculation are given as output of the elaboration to allow later adjustments or assessments of the uncertainty evaluation. The computerization, including efficiency calibration of the detector and user assistance in peak identification, the possibility of importing outputs from the most-used gamma spectrometry software packages and the evaluation of the Currie's detection limits in the case of undetected elements, are the main improvements with respect to the manual compiling required by the spreadsheet approach.

In addition to the mass fraction of the investigated element, the percentage contribution of each input quantity to the combined uncertainty is computed to highlight the main influence factors. Users aiming at decreasing the uncertainty might take advantage of this information to plan next measurements.

The program is freely available and open to further developments, e.g. the extension to complex activation and decay paths or the possibility to count sample and standard at different distances from the detector end-cap.

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