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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 forty 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.

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 the Keyzero/SolcoiR and the k_0-IAEA [3]. The first is a commercial software [4] implemented with the support of the initial developers of the k_0-standardisation [5] whereas the latter is a free of charge software designed for and distributed by the International Atomic Energy Agency (IAEA) [6].

Despite the fact that these software packages have been developed and tested, they do not include the evaluation of the uncertainty following the Guide to the expression of Uncertainty in Measurement (GUM) [7]. Specifically, the uncertainty evaluated by the Keyzero/SolcoiR considers only the contribution due to counting statistics [8] while the uncertainty evaluated by the k_0-IAEA is based on the outdated classification and propagation of random and systematic sources [9].

An additional software, named ERON, was designed and freely distributed in 2008 to properly evaluate the k_0-NAA uncertainty [10]. 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 considered for.

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 [11]; 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 elements, which makes cumbersome the application of the spreadsheet approach [11]. 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.

The 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 [12].

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 available also in the supporting information 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,

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

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 an 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,
- $t_{d\,m}$ is the decay time of the monitor,
- $\Delta t_d = t_{d\,a} - t_{d\,m}$ 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,
- $k_{0\,Au}(m)$ and $k_{0\,Au}(a)$ 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,
- $\overline{E}_r$ is the effective resonance energy,
- E_p is the energy of the γ-peak,
- a_i are the h parameters of the model adoped to describe the full-energy γ-peak detection efficiency at the counting position, $e^{\sum_{i=1}^{h} a_i \left(E_{pm}-E_{pa}\right)^{2-i}}$, 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 [11].

3. Program features

The k_0-INRIM code was implemented using the open-source Python programming language [13].

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 to note that model (1) applies to the activation and decay paths types I, IIB, IVB and VI defined in [14]. The user is informed in the case of complex activation and decay paths that are not yet implemented or when non $1/v$ 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 [15] or HyperLab [16] gamma spectrum evaluation software. This significantly limits user errors during typing of the spectrum parameters, e.g. n_p, t_c and t_l, in the spreadsheet budgets proposed in [11].

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 [11], were manually established with the spreadsheet 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 the 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 the k_0-INRIM. In both cases, values and uncertainties of the remaining input quantities were kept fixed as in [11].

The comparison between the mass fraction values measured in the first and second test, $w_{a\,1}$ and $w_{a\,2}$, respectively, and the reference values, $w_{a\,0}$, is shown in figure 1a. In addition, data were normalized with respect to the reference and plotted in figure 1b to highlight minor discrepancies.

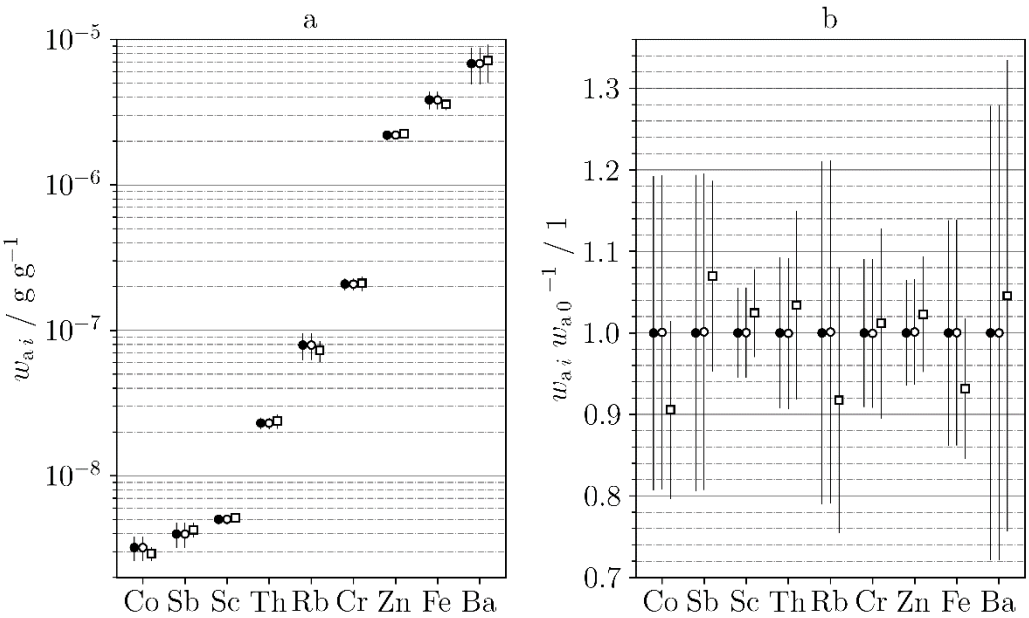

Figure 1. Absolute (a) and normalized (b) mass fractions obtained in the first and second test, $w_{a\,1}$ (hollow circles) and $w_{a\,2}$ (hollow squares), respectively, compared to the reference values, $w_{a\,0}$ (solid circles). The error bars indicate a 95% confidence interval.

The outcome points out that the use of the software allows establishing 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.

Quantity	Unit	Value	Standard uncertainty	Index

X_i	$[X_i]$	x_i	$u(x_i)$	%
$n_{p\,a}$	1	51998	1059	23.7
COI_m	1	0.857	0.017	22.5
$k_{0\,Au}(a)$	1	0.002620	0.000013	1.4
$Q_{0\,a}$	1	0.53	0.11	4.7
$E_{p\,m}$, $E_{p\,a}$, 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

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.

5. Conclusions

The 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 considered for. This makes the program distinct among the existing software packages adopted for processing k_0-NAA data.

Stand-alone spreadsheet budgets described in [11] 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.

References

[1] Kolotov V P and De Corte F 2004 Compilation of k_0 and related data for neutron-activation analysis (NAA) *Pure Appl. Chem.* **76** 1921-1925

[2] Tian W, Ni B, Cao L, Zhang Y and Wang P 2002 Metrological role of neutron activation analysis. II Parametric INAA – an ideal back-up for INAA as a primary ratio method of measurement *Accred. Qual. Assur.* **7** 50-54

[3] Kubesova M and Kucera J 2011 Comparison of Kayzero for Windows and k0-IAEA software packages for k_0 standardisation in neutron activation analysis *Nucl. Instrum. Methods Phys. Res. A* **654** 206-212

[4] Kayzero for Windows, k_0-ware, The Netherlands www.kayzero.com

[5] Simonits A, De Corte F and Hoste J 1975 Single-comparator methods in reactor neutron activation analysis *J. Radioanal. Nucl. Chem.* **24** 31-46

[6] Rossbach M. Blaauw M, Bacchi M A and Lin X 2007 The k_0-IAEA program *J. Radioanal. Nucl. Chem.* **274** 657-662

[7] Guide to the Expression of Uncertainty in Measurement, International Organization for Standardisation (ISO), Geneva, 1993

[8] Kayzero for Windows for reactor neutron activation analysis (NAA) using the k_0 standardisation method *User's Manual* version 1.0

[9] Software for single-comparator instrumental neutron activation analysis *The k0-IAEA program manual* version 5.0

[10] Bucar T and Smodis B 2008 Computer-assisted uncertainty assessment of k_0-NAA measurement results *Nucl. Instrum. Methods Phys. Res. A* **595** 647-652

[11] D'Agostino G, Di Luzio M and Oddone M 2018 An uncertainty spreadsheet for the k_0-standardisation method in Neutron Activation Analysis *J. Radioanal. Nucl. Chem.* **318** 1261-1269

[12] Website of the Istituto Nazionale di Ricerca Metrologica www.inrim.eu

[13] Python programing language, Python Software Foundation, version 3.6 www.python.org

[14] de Corte F 1987 The k_0-standardisation, a move to the optimization of neutron activation analysis. Habilitation Thesis, University of Gent, Belgium

[15] GammaVision for Windows, Ortec, version 7.02.01

[16] Hyperlab gamma spectroscopy software, Hyperlabs Software, version 2014.1