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How to calculate uncertainties of neutron flux parameters and uncertainties of analysis results in k_0-NAA?

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Abstract A novel method is presented for the calculation of uncertainties of neutron flux parameters and element mass fractions and their uncertainties in k_0-neutron activation analysis (k_0-NAA) using the Kragten universally applicable spreadsheet technique. The results obtained are compared with other approaches for evaluation of uncertainties of the neutron flux parameters and element mass fractions, namely with the Kayzero for Windows, k0-IAEA and ERON programs. The differences observed are discussed in terms of how the above programs take into account various uncertainty sources and their correlations.

Keywords Neutron activation analysis · k_0 standardization · Uncertainty · Kragten approach

Introduction

Various attitudes to the uncertainty evaluation of results of k_0-based neutron activation analysis (k_0-NAA) have been employed so far. In the original approach proposed by De Corte [1] counting statistics is combined with an estimate of a systematic (intrinsic) uncertainty, so that the overall uncertainty of the analysis result is calculated as the square root of quadratic summation of the statistical counting error and the estimated systematic uncertainty. A grand mean of the systematic uncertainty has been estimated to amount of 3.5% relative [1], based on considerations with respect to uncertainties induced by the relevant steps and parameters, for not too extreme conditions of irradiation and counting, and for (n, γ) reactions with medium Q_0-values and with no special difficulties. This approach has been included in the first commercially available software Kayzero for Windows [2]. In another software for k_0 standardization, the k0-IAEA freeware, the combined uncertainty of results comprises standard uncertainties of the sample and flux monitor masses, k_0-values, counting statistics, χ^2_r propagation from the linear-least-squares solution to the linear system of equations in the holistic approach, as well as the uncertainties of neutron flux parameters, in which the negative correlation between f and α is taken into account [3]. Robouch et al. [4] proposed evaluation of the uncertainty budget for k_0-NAA using the "Universally applicable spreadsheet technique" developed by Kragten [5] followed by designing a web tool for calculating k_0-NAA uncertainties [6], which contains the relevant nuclear parameters for 11 elements and presumes that uncertainties of neutron flux parameters are known (have been determined) beforehand. Another attitude was used by Bučar and Smodiš, who emphasized the importance of the nuclide-specific and neutron fluence-specific approach in the uncertainty assessment of k_0-measurement results [7]. They calculated uncertainty contributions of nuclear and irradiation parameters for 71 isotopes [8], and developed the program ERON, which computes uncertainty propagation factors from the relevant formulae and calculates the combined uncertainty [9]. Furthermore, the program allows for uncertainty calculation of the measured parameters needed in k_0-NAA. The approach applied in this program has been experimentally tested [10].

During validation of k_0-NAA in our laboratory [11–13] with both Kayzero for Windows and k0-IAEA programs,

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and comparison of their performance, we have found surprisingly different uncertainties of the results reported by Kayzero for Windows and k0-IAEA. Therefore, we decided to study the uncertainty of the determination of the neutron flux parameters and k_0-NAA results using a novel Excel spreadsheet technique according to Kragten [5] and to compare the results obtained with some of the above approaches.

Theory and calculations

Neutron activation analysis using k_0 standardization is described with several equations consisting of nuclear constants and measured variables, all of them having a specific uncertainty. The mass fraction c_a of an analyte (a) in a sample irradiated with the whole spectrum of reactor neutrons is calculated according to well-known equation

$$c_a = \frac{\left(\frac{N_p}{S \cdot D \cdot C \cdot w \cdot t_m \cdot COI}\right)_a}{F_{c,Au}} \cdot \frac{1}{k_{0,Au}(a)} \cdot \frac{1}{G_{th,a} \cdot f + G_{e,a} \cdot Q_{0,a}(\alpha)} \cdot \frac{1}{\varepsilon_a} \cdot 10^6 \mu g \cdot g^{-1}, \quad (1)$$

where N_p is net peak area, S, D, and C are saturation, decay, and counting factors, respectively, w is sample mass, t_m is counting time, COI is coincidence correction factor, $F_{c,Au}$ is the comparator factor for Au (Eq. (9)), k_0 is a compound nuclear constant given by Eq. (6), G_{th} and G_e are correction factors for thermal and epithermal neutron self-shielding, respectively, f is the thermal-to-epithermal neutron flux ratio, α is the deviation from the $1/E$ epithermal flux distribution, Q_0 is the resonance integral-to-cross section ratio and ε is the detection efficiency.

When the bare triple-monitor method is employed to determine the neutron flux parameters α, f and $F_{c,Au}$, these parameters are calculated from a set of the following equations [1, 14]:

$$(a-b) \cdot Q_{0,1}(\alpha) \cdot \frac{G_{e,1}}{G_{th,1}} - a \cdot Q_{0,2}(\alpha) \cdot \frac{G_{e,2}}{G_{th,2}} + b \cdot Q_{0,3}(\alpha) \cdot \frac{G_{e,3}}{G_{th,3}} = 0, \quad (2)$$

where

$$a = \left[1 - \frac{A_{sp,2}}{A_{sp,1}} \cdot \frac{k_{0,Au}(1)}{k_{0,Au}(2)} \cdot \frac{\varepsilon_1}{\varepsilon_2}\right]^{-1}, \quad (3)$$

$$b = \left[1 - \frac{A_{sp,3}}{A_{sp,1}} \cdot \frac{k_{0,Au}(1)}{k_{0,Au}(3)} \cdot \frac{\varepsilon_1}{\varepsilon_3}\right]^{-1}, \quad (4)$$

$$Q_0(a) = \left\{\frac{Q_0 - 0.429}{\bar{E}_r^{\alpha}} + \frac{0.429}{0.55^{\alpha}(2\alpha+1)}\right\}, \quad (5)$$

$$k_{0,Au}(m) = \frac{M_{Au} \cdot \theta_m \cdot \sigma_{0,m} \cdot \gamma_m}{M_m \cdot \theta_{Au} \cdot \sigma_{0,Au} \cdot \gamma_{Au}}, \quad (6)$$

$$A_{sp} = \frac{N_p}{S \cdot D \cdot C \cdot w \cdot t_m \cdot COI}, \quad (7)$$

where $\bar{E}_r$ is the effective resonance energy, θ is the isotopic abundance, σ_0 is the microscopic cross section, M is the molar mass, and γ is the gamma-ray abundance (emission probability).

$$f = \frac{G_{e,1} \cdot \frac{k_{0,Au}(1) \cdot \varepsilon_1}{k_{0,Au}(2) \cdot \varepsilon_2} \cdot Q_{0,1}(\alpha) - G_{e,2} \cdot \frac{A_{sp,1}}{A_{sp,2}} \cdot Q_{0,2}(\alpha)}{G_{th,2} \cdot \frac{A_{sp,1}}{A_{sp,2}} - G_{th,1} \cdot \frac{k_{0,Au}(1) \cdot \varepsilon_1}{k_{0,Au}(2) \cdot \varepsilon_2}}, \quad (8)$$

$$F_{c,Au} = \frac{A_{sp,m} \cdot 10^{-6}}{k_{0,Au}(m) \cdot \varepsilon_m} \cdot \frac{1}{G_{th,m} \cdot f + G_{e,m} \cdot Q_{0,m}(\alpha)}. \quad (9)$$

.

For indexes 1–3 of A_{sp}, G_{th}, G_e, ε, and $k_{0,Au}$, see references [1, 14].

The equations (1)–(9) were inserted in three Excel files as follows. The first contains calculation of α, f, and $F_{c,Au}$ and their uncertainties for short-time irradiation using the Au+Mn+Rb monitor set [15] (Table 1).

The second file contains the calculation of α, f, and $F_{c,Au}$ and their uncertainties for long-time irradiation using the Au+Zr monitor set. In both cases the bare triple monitor method is used for the determination of α and f. The third file contains the calculation of element concentrations and their uncertainties (Table 2).

In case of the determination of neutron flux parameters, macros were used to avoid personal mistakes during the time-consuming determination of α in which 3×22 implicit equations are calculated in one step according to the Kragten method, exactly as described in [4, 5]. This computer application is further denoted as KRAGTEN-NPI. The following correlations were taken into account in KRAGTEN-NPI:

- between resonance-integral-to-cross-section ratios of monitor nuclides, $Q_{0,m}(\alpha)$—positive correlation, when calculating α and f uncertainties
- between resonance-integral-to-cross-section ratio of monitor nuclide, $Q_{0,m}(\alpha)$ and f—positive correlation, when calculating $F_{c,Au}$ and element mass fractions (this correlation is the same as between f and α mentioned by Rossbach et al. [3])
- between f and $F_{c,Au}$—negative correlation, when calculating element mass fractions.

On the other hand, correlations of the detection efficiencies of the analyte and of the monitor, and of the

Table 1 Example of calculation of α and its combined uncertainty with the KRAGTEN-NPI spreadsheet[a]

1s (%)	1s (abs)	Value	Variable	$A_{sp}(Au)$	$A_{sp}(Mn)$	$A_{sp}(Rb)$	$k_0(Au)$	$k_0(Mn)$	…	$G_{th}(Rb)$
1.2	5.07E + 8	4.09E + 10	***$A_{sp}(Au)$***	***4.14E + 10***	4.09E + 10	4.09E + 10	4.09E + 10	4.09E + 10	…	1
1.1	7.39E + 7	6.96E + 9	***$A_{sp}(Mn)$***	6.96E + 9	***7.03E + 9***	6.96E + 9	6.96E + 9	6.96E + 9	…	1
1.5	3.34E + 4	2.23E + 6	***$A_{sp}(Rb)$***	2.23E + 6	2.23E + 6	***2.26E + 6***	2.23E + 6	2.23E + 6	…	1
0	0	1	***$k_0(Au)$***	1	1	1	***1***	1	…	1
0.6	0.003	0.496	***$k_0(Mn)$***	0.496	0.496	0.496	0.496	***0.499***	…	1
1.5	1.52E-6	1.01E-4	***$k_0(Rb)$***	1.01E-04	1.01E-04	1.01E-04	1.01E-04	1.01E-04	…	1
1.5	4.51E-5	3.00E-3	***ε(Au)***	3.00E-03	3.00E-03	3.00E-03	3.00E-03	3.00E-03	…	1
1.5	2.32E-5	1.55E-3	***ε(Mn)***	1.55E-03	1.55E-03	1.55E-03	1.55E-03	1.55E-03	…	1
1.5	2.21E-5	1.47E-3	***ε(Rb)***	1.47E-03	1.47E-03	1.47E-03	1.47E-03	1.47E-03	…	1
1.8	0.3	15.7	***$Q_0(Au)$***	15.7	15.7	15.7	15.7	15.7	…	1
3	0.032	1.053	***$Q_0(Mn)$***	1.053	1.053	1.053	1.053	1.053	…	1
3	0.7	23.3	***$Q_0(Rb)$***	23.3	23.3	23.3	23.3	23.3	…	1
7	0.40	5.65	***$\bar{E}_r(Au)$***	5.65	5.65	5.65	5.65	5.65	…	1
11	51	468	***$\bar{E}_r(Mn)$***	468	468	468	468	468	…	1
3	11	364	***$\bar{E}_r(Rb)$***	364	364	364	364	364	…	1
1.0	0.01	1	***$G_e(Au)$***	1	1	1	1	1	…	1
1.0	0.01	1	***$G_e(Mn)$***	1	1	1	1	1	…	1
1.0	0.01	1	***$G_e(Rb)$***	1	1	1	1	1	…	1
1.0	0.01	1	***$G_{th}(Au)$***	1	1	1	1	1	…	1
1.0	0.01	1	***$G_{th}(Mn)$***	1	1	1	1	1	…	1
1.0	0.01	1	***$G_{th}(Rb)$***	1	1	1	1	1	…	***1.01***
		2.982	**a Eq. (3)**	2.911	3.046	2.982	2.982	2.947	…	2.982
		−9.736	**b Eq. (4)**	−11.209	−9.736	−8.387	−9.736	−9.736	…	−9.736
		−2.4E-6	**Equation (2)**	−1.9E-5	−1.7E-6	−3.6E-4	−2.4E-6	−2.8E-6	…	−1.2E-6
Uncertainty	**0.021**	**0.035**	**α**	**0.043**	**0.034**	**0.026**	**0.034**	**0.035**	…	**0.032**
Uncertainty	**60%**		**Contribution**	14%	0.3%	14%	0%	0.10%	…	1.2%

[a] Values of variables $x_i + dx_i$ (1s) are given in bold and italic letters

detection efficiencies and coincidence factors were neglected, similarly to the ERON program [9].

Experimental

One Au+Mn+Rb short-time monitor set [15] together with one SMELS 1 (synthetic multi-element standard) sample [16] were irradiated for 1 min in channel H1 of LVR-15 reactor in Řež at a thermal neutron fluence rate of 3.0×10^{13} cm^{-2} s^{-1}. They were measured after a 10-min decay time in the distance of 10 and 5 cm, respectively, from the cap of a coaxial HPGe detector (PGT, relative efficiency 20.3%, resolution FWHM 1.75 keV @1332.5 keV, peak-to-Compton (P/C) ratio 49.8:1).

One Au+Zr long-time monitor set [14] (a 4 mm diameter disc of 99.8% Zr foil (Goodfellow UK, ZR000260 foil, 0.1 mm thickness) and a 0.1%Au–Al foil (Institute for Reference Materials and Measurements Belgium, Nuclear reference material IRMM-530a, 0.1 mm thickness) was irradiated together with one SMELS 2 and one SMELS 3 sample for 3 h in channel H8 of the above reactor at a thermal neutron fluence rate of 3.5×10^{13} cm^{-2} s^{-1}. The Au+Zr monitor and the SMELS 2 sample were measured after 2 days in the distance of 15 and 10 cm, respectively, the SMELS 3 sample was measured after 30 days of decay at a distance of 1 cm from the cap of another coaxial HPGe detector (Canberra, relative efficiency 77.8%, resolution FWHM 1.87 keV @1332.5 keV, P/C 82.5:1).

The detectors were connected to a Canberra Genie 2000 γ-spectrometer through a chain of linear electronics, which contained a loss-free counting module (LFC Canberra 599, dual mode) to correct for pile-up effect and dynamic changes of dead time. Canberra Genie 2000 software was used to control measurement and to evaluate the spectra obtained. Results were evaluated using Kayzero for Windows, k0-IAEA, ERON programs, and KRAGTEN-NPI spreadsheet computer application. The tolerance for peak identification was set to 1.2 keV (one sided).

Table 2 Example of calculation of the Au concentration and its combined uncertainty with the KRAGTEN-NPI spreadsheet[a]

1s (%)	1s (abs)	Value	Variable	A_{sp}	k_0	f	F_c	$Q_0(\alpha)$	G_{th}	G_e	ε
1.4	1.2E + 5	8.8E + 6	A_{sp}	***8.9E + 6***	8.8E + 6	8.8E + 6	8.8E + 6	8.8E + 6	8.8E + 6	8.8E + 6	8.8E + 6
0	0	1	k_0	1	***1***	1	1	1	1	1	1
17	4.5	26.6	f	26.6	26.6	***31.1***	26.6	26.6	26.6	26.6	26.6
14	45000	329000	F_c	329000	329000	329000	***374000***	329000	329000	329000	329000
3.7	0.5	14.8	$Q_0(\alpha)$	14.8	14.8	14.8	14.8	***15.3***	14.8	14.8	14.8
1.0	0.01	1	G_{th}	1	1	1	1	1	***1.01***	1	1
1.0	0.01	1	G_e	1	1	1	1	1	1	***1.01***	1
1.5	0.0001	7.8E-3	ε	7.8E-3	7.8E-3	7.8E-3	7.8E-3	7.8E-3	7.8E-3	7.8E-3	***7.9E-3***
Uncertainty	**5**	**82**	$c_{(Au)}$ **(mg/kg)**	**84**	**82**	**74**	**72**	**81**	**82**	**82**	**81**
Uncertainty	**6%**		**Contribution**	0.8%	0%	40%	58%	0.7%	0.2%	0.1%	0.9%

[a] Values of variables $x_i + dx_i$ (1s) are given in bold/italics letters

For the evaluation of element mass fractions only the gamma-lines recommended in [16] (see Table 3) were selected in the Kayzero for Windows, ERON and KRAGTEN-NPI.

In k0-IAEA program [3, 17], the overall uncertainty of element mass fractions is calculated by taking into account all peaks found (except for those that result from random summing), as manual deselection of several hundreds of "undesired" peaks would be too laborious. However, the "k_0-peaks" are given a weight 400 times larger than "non-k_0-peaks". Therefore, we assumed that the contribution of the "undesired" peaks to the overall uncertainty of element mass fractions should not be very significant. Uncertainties of constants in Eqs. (1)–(9) were taken from reference [18], and preferably from the International Union of Pure and Applied Chemistry (IUPAC) database [19]. Uncertainties of all other variables (e.g., t_{ir}, t_d,…) were obtained in the course of analysis. The uncertainties of G_{th}, G_e were set to 1% as in our case the sample and or monitor shapes are very close to ideal ones ($G_{th} = G_e = 1$ for most cases). The sample and/or monitor bag is a 25 mm diameter polyethylene (PE) disc (thickness 0.2 mm) and the sample and/or monitor height is ~1 mm. The *COI* factors and effective values of ε were determined from the absolute efficiency curve (in reference position) and the peak-to-total curve. These curves were fitted with an uncertainty lower than 1.5 and 1.0%, respectively, and therefore these values were also used as uncertainties of *COI* and ε. As decay constants of all nuclides used are very well known, their uncertainty used in calculations was set to 0.01%. The other sample and/or monitor input data together with their uncertainties are presented in Table 4.

Results and discussion

The neutron flux parameters together with their combined uncertainties (k = 1) were determined using Kayzero for Windows, k0-IAEA and KRAGTEN-NPI spreadsheet. As the k0-IAEA program uses the adapted Høgdal convention of activation rate [3], it is valid [20] that

$$f_{k0-IAEA} = f + 0.429, \tag{10}$$

and the comparator factor $F_{c,Au}$ is related to the conventional thermal neutron flux according to Eq. (11)

$$F_{c,Au} = \frac{\varphi_{th}}{3.47 \cdot f \cdot 10^{10}} . \tag{11}$$

Concerning k0-IAEA, which does not compute the comparator factor, this parameter was calculated manually for the purpose of this comparison only. Table 5 shows a comparison of the α, f, and $F_{c,Au}$ values calculated by the three programs with the use of both monitor sets for short- and long-

Table 3 Nuclear data used for the calculation of element mass fractions and their uncertainties with the KRAGTEN-NPI spreadsheet

Element	Nuclide measured	$\bar{E}_r^a$ (eV)	Q_0^a	λ (s^{-1})	E_γ (keV)	k_0^a
Cl	^{38}Cl	13700 (4.7)	0.69 (4.1)	3.10E-4	1642.7	1.97E-3 (1.4)
Cr	^{51}Cr	7530 (11.0)	0.53 (2.4)	2.90E-7	320.1	2.62E-3 (0.5)
Mn	^{56}Mn	468 (11.0)	1.053 (2.6)	7.47E-5	846.8	4.96E-1 (0.6)
					1810.7	1.35E-1 (0.4)
Fe	^{59}Fe	637 (24.0)	0.975 (1.0)	1.80E-7	1099.3	7.77E-5 (0.5)
					1291.6	5.93E-5 (0.4)
Zn	^{65}Zn	2560 (10.0)	1.908 (4.9)	3.28E-8	1115.5	5.72E-3 (0.4)
Cu	^{66}Cu	766 (17.0)	1.06 (4.9)	2.26E-3	1039.2	1.86E-3 (0.5)
Se	^{75}Se	29.4 (4.1)	10.8 (6.5)	6.70E-8	264.7	7.11E-3 (0.7)
Br	^{82}Br	152 (9.2)	19.3 (3.1)	5.45E-6	554.3	2.38E-2 (1.1)
					619.1	1.45E-2 (0.8)
					776.5	2.76E-2 (0.8)
Rb	^{88}Rb	364 (3.0)	23.3 (3.0)	6.50E-4	898.0	1.01E-4 (1.5)
Zr	^{95}Zr	6260 (4.0)	5.31 (3.3)	1.25E-7	756.7	1.10E-4 (1.3)
	^{97m}Nb	338 (2.1)	251 (1.0)	1.32E-2	743.4	1.24E-5(0.3)
Mo	^{99}Mo	241 (20.0)	53.1 (6.3)	2.92E-6	181.1	4.15E-5 (0.6)
In	^{114m}In	6.4 (15.0)	24.2 (1.7)	1.62E-7	190.3	1.06E-3 (0.8)
					739.5	8.46E-5 (0.7)
I	^{128}I	57.6 (4.0)	24.8 (2.7)	4.62E-4	442.9	1.12E-2 (1.7)
Cs	^{134m}Cs	9.3 (11.0)	11.8 (3.0)	6.63E-5	127.5	5.48E-3 (1.7)
Tm	^{170}Tm	4.8 (2.1)	13.7 (1.6)	6.24E-8	84.3	3.26E-2 (1.7)
Au	^{198}Au	5.65 (7.0)	15.7 (1.8)	2.98E-6	411.8	1 (0.0)
Th	^{233}Pa	54.4 (0.9)	11.5 (3.6)	2.97E-7	300.1	4.37E-3 (0.3)
					311.9	2.52E-2 (0.5)
					340.5	2.95E-3 (0.7)

[a] Uncertainties in parenthesis given in per cent [18, 19]

Table 4 Sample and monitor input data[a]

	w	t_{ir} (s)	t_d (s)	t_m (s)
Au+Mn+Rb monitor set	Au: 10.18 ± 0.03 μg	60 ± 0.5	600 ± 0.5	600 ± 0.001
	Mn: 15.81 ± 0.05 μg			
	Rb: 493.9 ± 1.5 μg			
Au+Zr monitor set	Au–Al foil: 2.87 ± 0.01 mg	10800 ± 60	208306 ± 60	900 ± 0.001
	Zr foil: 10.87 ± 0.01 mg			
SMELS 1	52.80 ± 0.01 mg	60 ± 0.5	600 ± 0.5	600 ± 0.001
SMELS 2	24.20 ± 0.01 mg	10800 ± 60	296253 ± 60	1200 ± 0.001
SMELS 3	45.11 ± 0.01 mg	10800 ± 60	2666192 ± 60	5400 ± 0.001

[a] Standard uncertainties are given for all parameters except for the Au+Mn+Rb monitor masses, where the combined uncertainties are listed

time activations (in channels H1 and H8, respectively) and their uncertainties (Kayzero for Windows does not calculate them). It can be seen from Table 5 that the values of α and f calculated with k0-IAEA and KRAGTEN-NPI for both channels H1 and H8 agree with each other within the uncertainty interval and that the values of α and f calculated by Kayzero for Windows are within the uncertainty interval evaluated by the two other programs. The $F_{c,Au}$ values evaluated with k0-IAEA and KRAGTEN-NPI agree within uncertainty interval. However, the $F_{c,Au}$ values evaluated by Kayzero for Windows for channels H1 and H8 (without uncertainties) do not fall within the uncertainty interval of values computed by the k0-IAEA. This is obviously due to the small uncertainties of $F_{c,Au}$ values obtained by the latter program by a simple conversion according to Eq. (11). The uncertainties of all neutron flux parameters calculated by

Table 5 Comparison of values of neutron flux parameters and their combined uncertainties calculated with different programs

Program	Channel H1			Channel H8		
	α	f	$F_{c,Au}$	α	f	$F_{c,Au}$
Kayzero for Windows	0.034	25.6	337737	0.043	44.6	221165
k0-IAEA[a]	0.042 ± 0.015 (35%)[b]	24.7 ± 1.3 (5.3%)[b]	365200 ± 4700 (1.3%)[b]	0.041 ± 0.008 (21%)[b]	45 ± 3 (6.6%)[b]	233100 ± 2600 (1.1%)[b]
KRAGTEN-NPI	0.035 ± 0.019 (54%)[b]	26.6 ± 4.5 (17%)[b]	329000 ± 45000 (14%)[b]	0.045 ± 0.020 (44%)[b]	44 ± 8 (18%)[b]	219000 ± 33000 (15%)[b]

[a] Different convention of activation rate, $F_{c,Au}$ calculated manually

[b] Relative uncertainty in percent

KRAGTEN-NPI are much higher, twice or more, than those evaluated by the k0-IAEA program. Nevertheless, the uncertainties of α values calculated by the former approach are not in contradiction with the De Corte's statement that "the overall uncertainties are of" the order of 5–10% for high α's ($\alpha \sim 0.1$) to 50% or more for α's approaching zero ($\alpha \sim 0.01$) [1]. The Kragten method allows for inspection how the uncertainties of individual parameters contribute to the overall uncertainty. It has been found, by such an analysis, that uncertainties of k_0 factors, values of Q_0, ε and *COI* factors are most responsible for the combined uncertainties of the neutron flux parameters. Obviously, these input uncertainties correspond to the present knowledge, and cannot be improved by the performance of laboratory work in individual k_0-NAA laboratories, but only by an improvement of the uncertainties given in databases [18, 19] by concerted actions of the whole k_0-NAA community.

The element mass fractions and their uncertainties evaluated by the programs and/or computer codes Kayzero for Windows, k0-IAEA and KRAGTEN-NPI are compared in Table 6.

The program ERON calculates uncertainties only, thus relative uncertainties in percent with regard to the mass fractions obtained with Kayzero for Windows are given in Table 6. No uncertainties were evaluated using the Excel spreadsheet developed by Younes and Robouch [6], because their web tool has been found to be not fully functional, e.g., when other than demonstration data were input, the calculated combined uncertainty did not change when different uncertainties of α and f were entered. In Table 6, only results for those elements are presented, for which uncertainties of input parameters, such as values of k_0, Q_0 and $\bar{E}_r$, of the relevant nuclides are given in databases [18, 19]. Minor differences of the element mass fractions calculated by the individual programs are due to variations of neutron flux parameters evaluated by the programs and computational details, such as weighing factors of the peaks taken into account. For instance, in Kayzero for Windows and KRAGTEN-NPI, the N_p values of "k_0-peaks" are weighed by the reciprocal statistical counting error raised to the second power, in k0-IAEA the "k_0-peaks" are given a weight 400 timer larger than "non-k_0-peaks", etc.

As can be seen from Table 6, the expanded uncertainties ($k = 2$) of mass fractions determined with Kayzero for Windows are in most cases significantly lower compared to those calculated with KRAGTEN-NPI [5]. This suggests that adding a 3.5% systematic uncertainty (for all elements/nuclides) to the statistical counting error, which is used in the former program, leads to an uncertainty underestimate. In case of k0-IAEA program the expanded uncertainties of mass fractions vary from very low, about 3.5%, to very high, about 50%. For instance, the expanded uncertainties of Cs, I, In, Tm, and Zn mass fractions are much higher compared to other programs, without being clear from which uncertainty component these high values originate. Gold was not found by the k0-IAEA program and a 100% detection limit was reported only, although the peak was present in the spectrum [13].

Since the ERON v.4 program calculates the neutron flux parameter α with either the Cd-ratio or the Cd-covered multi-monitor method [9], neither of which could be used in this work, the α and f values and their uncertainties determined with the KRAGTEN-NPI spreadsheet method were used to calculate the relative expanded uncertainties of the mass fractions given in Table 6. These uncertainties are for some elements somewhat lower, for some elements somewhat higher than those evaluated by the KRAGTEN-NPI spreadsheet method. These differences seem to be caused by two reasons. The first reason is that the authors of ERON converted the "error" of the k_0, Q_0 and $\bar{E}_r$ values taken from the IUPAC database [19] to the standard uncertainty by considering the rectangular uncertainty distribution [8], i.e., they calculated the standard uncertainty as an "error" from the database divided by $\sqrt{3}$. However, the same data ("error" from the IUPAC database [19]) are declared in other sources as an uncertainty (without any specification) [1] or an uncertainty specified as the relative standard error [18]. Therefore, we used the "error" data from the IUPAC database [19] as a standard

Table 6 Comparison of element mass fractions and their expanded uncertainties (k = 2) evaluated by various programs[a]

Sample/Element	Assigned values (mg/kg)	Kayzero for Windows (mg/kg)	k0-IAEA (mg/kg)	KRAGTEN-NPI (mg/kg)	ERON[b]
SMELS 1					
Au	82.7 ± 1.7 (2.1%)	82 ± 6 (7.3%)	82 ± 3 (3.7%)	82 ± 10 (12.2%)	(6.4%)
Cl	4330 ± 170 (3.9%)	4700 ± 400 (8.5%)	4920 ± 170 (3.5%)	4700 ± 400 (8.5%)	–
Cs	897 ± 37 (4.1%)	940 ± 70 (7.4%)	970 ± 300 (30.9%)	940 ± 120 (12.7%)	(7.6%)
Cu	3930 ± 120 (3.1%)	4300 ± 300 (7.0%)	4300 ± 500 (11.6%)	4200 ± 400 (9.5%)	(13.0%)
I	152 ± 5 (3.3%)	158 ± 11 (7.0%)	150 ± 40 (26.7%)	160 ± 30 (18.8%)	(9.4%)
Mn	113.9 ± 3.3 (2.9%)	123 ± 9 (7.3%)	123 ± 11 (8.9%)	120 ± 10 (8.3%)	(13.1%)
SMELS 2					
Au	3.93 ± 0.07 (1.8%)	4.0 ± 0.3 (7.5%)	4.0 ± 0.4 (10.0%)	4.1 ± 0.4 (9.8%)	(6.0%)
Br	157 ± 5 (3.2%)	163 ± 12 (7.4%)	157 ± 12 (7.6%)	170 ± 30 (17.6%)	(7.4%)
Mo	5170 ± 250 (4.8%)	5100 ± 400 (7.8%)	5000 ± 700 (14.0%)	5300 ± 1300 (24.5%)	(15.6%)
Th	3670 ± 180 (4.9%)	3700 ± 300 (8.1%)	3500 ± 300 (8.6%)	3700 ± 500 (13.5%)	–
Zn	6570 ± 200 (3.0%)	6300 ± 500 (7.9%)	6300 ± 1100 (17.5%)	6500 ± 600 (9.2%)	(10.0%)
SMELS 3					
Au	0.901 ± 0.016 (1.8%)	1.01 ± 0.18 (17.8%)	Not found	1.0 ± 0.2 (20.0%)	(17.6%)
Cr	86.7 ± 2.6 (3.0%)	89 ± 7 (7.9%)	98 ± 3 (3.1%)	91 ± 6 (6.6%)	(10.8%)
Fe	8200 ± 190 (2.3%)	8300 ± 600 (7.2%)	9200 ± 1500 (16.3%)	8400 ± 700 (8.3%)	(10.6%)
In	462 ± 19 (4.1%)	500 ± 40 (8.0%)	520 ± 140 (26.9%)	510 ± 70 (13.7%)	(7.1%)
Se	131 ± 6 (4.6%)	134 ± 10 (7.5%)	136 ± 18 (13.2%)	137 ± 19 (13.9%)	(7.2%)
Th	26.2 ± 0.9 (3.4%)	27 ± 2 (7.4%)	29 ± 4 (13.8%)	28 ± 4 (14.3%)	–
Tm	23.3 ± 0.7 (3.0%)	23.4 ± 1.7 (7.3%)	27 ± 14 (51.9%)	24 ± 3 (12.5%)	(7.0%)
Zn	618 ± 11 (1.8%)	620 ± 50 (8.1%)	700 ± 140 (20.0%)	640 ± 60 (9.4%)	(10.0%)
Zr	4580 ± 100 (2.2%)	4800 ± 400 (8.3%)	5400 ± 1600 (29.6%)	5000 ± 2000 (40.0%)	(9.1%)

[a] Relative expanded (k = 2) uncertainties in per cent are given in parenthesis

[b] Relative expanded (k = 2) uncertainties with respect to the mass fractions determined with Kayzero for Windows

uncertainty for the calculation with the KRAGTEN-NPI spreadsheet method without any conversion. The second reason for the differences between uncertainties calculated by the ERON program and the KRAGTEN-NPI spreadsheet is that the authors of the former program neglected the correlations between resonance-integral-to-cross-section ratios of monitor nuclides, $Q_{0,m}(\alpha)$, between resonance-integral-to-cross-section ratio of monitor nuclide, $Q_{0,m}(\alpha)$ and f, and between f and $F_{c,Au}$.

It seems that the above correlations were also not taken into account in the first attempt to use the Kragten approach for calculating the uncertainties of k_0-NAA results [4]. Moreover, the statement of the authors of this paper that the k_0-NAA systematic uncertainty is generally of the order of 2.8% appears to be an oversimplification, which is in contradiction with the recommendation to calculate "the intrinsic uncertainty" for each nuclide separately [8].

Conclusions

In this work four methods of uncertainty determination in k_0-NAA were compared. The statement of Smodiš and Bučar [7] that most of the attempts dealing with the measurement uncertainty in k_0-NAA, which were carried out so far, addressed only certain steps of the k_0-NAA process, or most of the steps only partially, and almost none of them systematically estimated all of the contributions to the overall uncertainty, based on recent international recommendations, seems to be correct. It also explains the differences of uncertainties of neutron flux parameters and element mass fractions observed in this work. We believe that the proposed KRAGTEN-NPI computation tool, which calculates the uncertainty of both neutron flux parameters and element mass fractions in a simple and transparent way, overcomes the shortcomings of the previous approaches, because all most significant uncertainty sources (including correlations of the relevant parameters) are taken into account.

The present version of the KRAGTEN-NPI computation tool has been designed for uncertainty calculation of neutron flux parameters with the bare triple-monitor method, because this is the only method, which can be used at our multi-purpose research reactor at Řež. This version is available on demand for use in other laboratories. It can be easily adjusted for other methods for determination of the

neutron flux parameters. Most of them, especially the Cd-covered multi-monitor method are inherently able to provide more precise results of the neutron flux parameters. Thus, in other laboratories, which can use alternative methods of determination of the neutron flux parameters, lower uncertainties of element mass fractions can be achieved than those obtained in this work.

Nevertheless, further improvements of uncertainties of k_0-NAA results can only be achieved by improvements of uncertainties of the individual nuclear parameters, especially of k_0, Q_0 and $\bar{E}_r$ values. For many important nuclides the uncertainties of Q_0 and $\bar{E}_r$ values are even missing in the IUPAC database [8]. Thus, there is an urgent need to upgrade the database with the missing data by including the data from other compilations and/or by their measurement. The latter approach should be preferred, because it should also yield an improvement of the existing uncertainties of the k_0 and Q_0 values (for $\bar{E}_r$ the calculation is the method to be preferred).

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