



ISTITUTO NAZIONALE DI RICERCA METROLOGICA Repository Istituzionale

A preliminary test for the application of the k0 standardization method of neutron activation analysis at the Radiochemistry and Spectroscopy Laboratory of the Istituto

This is the author's accepted version of the contribution published as:

Original

A preliminary test for the application of the k0 standardization method of neutron activation analysis at the Radiochemistry and Spectroscopy Laboratory of the Istituto Nazionale di Ricerca Metrologica / Di Luzio, M.; Bergamaschi, L.; Oddone, M.; Prata, M.; Salvini, A.; D'Agostino, G.. - In: JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY. - ISSN 0236-5731. - 315:(2018), pp. 723-729. [10.1007/s10967-017-5694-z]

Availability:

This version is available at: 11696/56909 since: 2020-05-19T14:00:21Z

Publisher:

Springer

Published

DOI:10.1007/s10967-017-5694-z

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

SPRINGER

Copyright © Springer. The final publication is available at link.springer.com

(Article begins on next page)

1 **A preliminary test for the application of the k_0 -**
2 **standardization method of neutron activation analysis**
3 **at the Radiochemistry and Spectroscopy Laboratory of**
4 **the Istituto Nazionale di Ricerca Metrologica**

5 Names of the authors: M. Di Luzio^{1,2}, L. Bergamaschi¹, M. Oddone², M. Prata³, A. Salvini³
6 and G. D'Agostino¹

7 Title: A preliminary test for the application of the k_0 -standardization method of neutron
8 activation analysis at the Radiochemistry and Spectroscopy Laboratory of the Istituto
9 Nazionale di Ricerca Metrologica

10 Affiliation(s) and address(es) of the author(s):¹ Istituto Nazionale di Ricerca Metrologica
11 (INRIM), Unit of Radiochemistry and Spectroscopy, c/o Department of Chemistry –
12 ~~Radiochemistry Area~~, University of Pavia, via Taramelli 12, 27100 Pavia, Italy.

13 ² Department of Chemistry – ~~Radiochemistry Area~~, University of Pavia, via Taramelli 12,
14 27100 Pavia, Italy.

15 ³ Laboratorio di Energia Nucleare Applicata (LENA), University of Pavia, via Aselli 41,
16 27100 Pavia, Italy.

17 E-mail address of the corresponding author: m.diluzio@inrim.it

18

19 **A preliminary test for the application of the k_0 -**
20 **standardization method of neutron activation analysis**
21 **at the Radiochemistry and Spectroscopy Laboratory of**
22 **the Istituto Nazionale di Ricerca Metrologica**

23 M. Di Luzio^{1,2}, L. Bergamaschi¹, M. Oddone², M. Prata³, A. Salvini³ and G. D'Agostino¹

24 ¹ *Istituto Nazionale di Ricerca Metrologica (INRIM), Unit of Radiochemistry and*
25 *Spectroscopy, c/o Department of Chemistry – ~~Radiochemistry Area~~, University of Pavia,*
26 *via Taramelli 12, 27100 Pavia, Italy*

27 ² *Department of Chemistry – ~~Radiochemistry Area~~, University of Pavia, via Taramelli 12,*
28 *27100 Pavia, Italy*

29 ³ *Laboratorio di Energia Nucleare Applicata (LENA), University of Pavia, via Aselli 41,*
30 *27100 Pavia, Italy*

31 **Abstract**

32 The application of the k_0 -standardization method of neutron activation analysis offers the
33 great advantage to perform multi-elemental analyses using a single element as a
34 comparator. On the other hand, some knowledge of the neutron flux energy distribution is
35 mandatory. Recently, neutron flux parameters f and α in three irradiation channels of the
36 TRIGA Mark II nuclear reactor in Pavia were measured for the first time to allow the
37 application of the k_0 -standardization method at the Radiochemistry and Spectroscopy
38 Laboratory of the Istituto Nazionale di Ricerca Metrologica.

39 In this framework, a preliminary test was performed by analyzing a set of samples
40 irradiated in Central Channel, including a number of elements prepared with mono-
41 elemental solutions and a reference material. The results of all the selected elements were

42 in agreement with the expected value and confirmed the applicability of the k_0 -
43 standardization method in Central Channel.

44 **Keywords**

45 k_0 -method, TRIGA Mark II, Instrumental Neutron Activation Analysis, INRIM laboratory

46 **Introduction**

47 Since its definition [1], the k_0 -standardization method of neutron activation analysis
48 (NAA), hereafter called k_0 -NAA, introduced a much faster and routinely used version of
49 multi-elemental analysis compared to the relative standardization method. The possibility
50 to quantify sixty-seven elements present in the k_0 -database [2] using a unique comparator
51 replaced the cumbersome preparation of multi-standards mixtures.

52 The application of k_0 -NAA requires the knowledge of the ratio of the thermal to epithermal
53 neutron flux, f , and of the parameter α , describing the epithermal neutron flux $1/E^{1+\alpha}$, where
54 E is the neutron energy. Moreover, several additional parameters are included in the
55 measurement model, e.g. the irradiation time, the detection efficiency and the k_0 -factor.
56 Although the added parameters might reflect in a generally higher uncertainty compared
57 to the results obtained with the relative standardization method, the advantages of
58 application of k_0 -NAA are consistent.

59 Recently, aiming at the application of the k_0 -NAA at the Radiochemistry and Spectroscopy
60 Laboratory of the Istituto Nazionale di Ricerca Metrologica (INRIM), the f and α values
61 in three irradiation channels of the 250 kW TRIGA Mark II reactor operated by the
62 Laboratorio Energia Nucleare Applicata (LENA) of the University of Pavia were obtained
63 through neutron irradiations and γ -countings of a defined monitor set with and without a
64 Cd-cover [3]. In this framework, additional neutron activation and γ -counting experiments
65 were performed using known amounts of selected elements to check the agreement of the
66 results obtained with the k_0 -NAA with the expected values. A description of the adopted

67 measurement model, details of the experiment and the obtained results are reported in this
 68 study together with a preliminary evaluation of the measurement uncertainty.

69 Theory

70 A comprehensive description of the k_0 -standardization method can be found in [1],
 71 including several references to published papers. Here, for convenience of the reader, the
 72 basic equations used to build the measurement model are recalled.

73 The key parameter for the application of k_0 -NAA is the k_0 factor of an element of interest,
 74 i , with respect to Au:

$$75 \quad k_{0,Au}(i) = \frac{M_{Au}\theta_i\gamma_i\sigma_{0,i}}{M_i\theta_{Au}\gamma_{Au}\sigma_{0,Au}}, \quad (1)$$

76 where M is the molar mass, θ is the isotopic fraction, γ is the absolute gamma intensity and
 77 σ_0 is the $2200 \text{ m s}^{-1} (n,\gamma)$ reaction cross-section; subscripts i and Au refer to the element i
 78 and Au, respectively.

79 The co-irradiation of a sample ~~the analyte, a,~~ and a single comparator, c , yields the mass
 80 fraction of ~~an the~~ investigated analyte, ρ_a , in the sample, thanks to the introduction of $k_{0,Au}$
 81 factors. ~~Accordingly,~~ Specifically, the k_0 -NAA measurement model ~~adopted in this study,~~
 82 is:

$$83 \quad \rho_a = \frac{\left. \frac{\lambda n_p t_r/t_l}{(1-e^{-\lambda t_i}) e^{-\lambda t_d} (1-e^{-\lambda t_r})} \right|_a}{\left. \frac{\lambda n_p t_r/t_l}{(1-e^{-\lambda t_i}) e^{-\lambda t_d} (1-e^{-\lambda t_r})} \right|_c} \frac{w_c k_{0,Au}(c) G_{th,c} + G_{e,c} \frac{Q_{0,c}(\alpha)}{f} \varepsilon_{p,c}}{w k_{0,Au}(a) G_{th,a} + G_{e,a} \frac{Q_{0,a}(\alpha)}{f} \varepsilon_{p,a}}, \quad (2)$$

84 where $\lambda = \frac{\ln 2}{t_{1/2}}$ is the decay constant (with $t_{1/2}$ being the half-life of the activated
 85 radionuclide), n_p is the number of counts in the full-energy γ -peak corrected for true
 86 coincidences, t_l and t_r are the live and real times of the detection system, t_i and t_d are the
 87 irradiation and decay times, w_c is the mass of the comparator element and w is the mass of
 88 the sample containing the investigating analyte, $Q_0(\alpha) = \frac{Q_0 - 0.429}{\bar{E}_r^\alpha} + \frac{0.429}{(2\alpha+1)0.55^\alpha}$ is the

89 resonance integral to 2200 m s⁻¹ cross section ratio in a 1/E^{1+α} neutron spectrum, *f* is the
90 thermal to epithermal neutron flux ratio, ε_p is the full-energy γ-peak detection efficiency,
91 and *G*_{th} and *G*_e are the thermal and epithermal self-shielding factors; subscripts a and c
92 refer to the investigated analyte and the comparator, respectively.

93 In details, *Q*₀ is the resonance integral to 2200 m s⁻¹ cross section ratio in 1/*E* neutron
94 spectrum, \bar{E}_r is the effective resonance energy. Moreover, the ratio between efficiencies is
95 approximated, under the assumption that sample and comparator are acquired at the same
96 distance and far from the detector, with ~~composed by a reference efficiency and other three~~
97 ~~correction factors~~, $\frac{\varepsilon_{p,c}}{\varepsilon_{p,a}} = \frac{\varepsilon_{p,ref,c}}{\varepsilon_{p,ref,a}} \frac{d_{geo,a}^2}{d_{geo,c}^2} \frac{F_{att,c}^{self}}{F_{att,a}^{self}} \frac{F_{geo,c}}{F_{geo,a}}$, where $\frac{\varepsilon_{p,ref,c}}{\varepsilon_{p,ref,a}}$ is the ratio of detection
98 efficiencies of comparator and analytes at reference position, ~~*d*_{geo} is the counting distance~~
99 ~~from detector end cap~~, *F*_{att}^{self} is the self-attenuation correction factor [4] and *F*_{geo} is the
100 geometrical correction factor.

101 In this study the mass of the sample, *w*, in eq. (2) is replaced with the mass of the
102 investigated analyte, *w*_a. Accordingly, ρ_a expresses the ratio, hereafter called *r*_a, of the
103 quantified to the expected mass of the analyte; in the case of an unbiased result, *r*_a = 1.

104 **Experimental**

105 Samples of the measured analytes were prepared starting from mono-elemental standard
106 solutions (VWR Chemicals, 1000 μg mL⁻¹) and IAEA-SOIL-7 reference material.

107 Known amounts of fifteen selected elements (Ag, Au, Ce, Cr, Cs, Hf, Ir, La, Re, Sb, Sc,
108 Se, Ta, Tb, Tm) from standard solutions were pipetted in seven 1 mL polyethylene (PE)
109 vials, 5 mm internal diameter, and cut to 4 mm internal height. Specifically, a small volume
110 of each elemental standard solution (in the range from 10 μL to 30 μL) was dropped on an
111 absorbent paper disc situated at the bottom of the corresponding vial.

112 Twelve elements (Au, Ce, Cs, Hf, Ir, Re, Sb, Sc, Se, Ta, Tb, Tm) were distributed among
113 four vials while three elements (Ag, Cr, La) were separately distributed in three vials

114 together with aliquots of a Co standard solution used as comparator. Co was used as
115 comparator because of its long half-life, comparable with that of the most part of the
116 investigated analytes. An additional vial was irradiated as a blank. The elements were
117 distributed among the vials with respect of the similar half-lives of the produced
118 radioisotopes and in order to avoid interferences among the analytical γ -peaks. ~~In details,~~
119 ~~a small volume for each selected solution (in the range from 10 μ L to 30 μ L) was dropped~~
120 ~~on an absorbent paper disc situated at the bottom of the corresponding vial.~~

121 Drop deposition was performed on an analytic balance calibrated with SI-traceable
122 weights. The vial was then placed under an IR lamp until the solution was completely dried.
123 The procedure was repeated for each standard in the same vial, for every vial with
124 exception of the blank. When all the liquid lying on the filter papers was dried, the vials
125 were sealed.

126 On the other hand, 153.84(1) mg of the IAEA-SOIL-7 reference material were weighed in
127 a 5 mL PE vial, in this case without the filter paper at the bottom, on the same analytical
128 balance and sealed. Here and hereafter, values in parenthesis indicate the standard
129 uncertainty and refer to the last digits if not stated otherwise. Relative moisture of the
130 reference material was evaluated and corrected accordingly.

131 The vials were placed in three vertical levels starting from the floor of the PE irradiation
132 container; the eight 1 mL vials occupied the lower levels grouped by four while the
133 reference material was placed on the higher level. The whole structure was then fixed by a
134 dummy plastic vial placed at the top. Figure 1 shows the composition scheme within the
135 irradiation container while Table 1 indicates the composition of each vial.

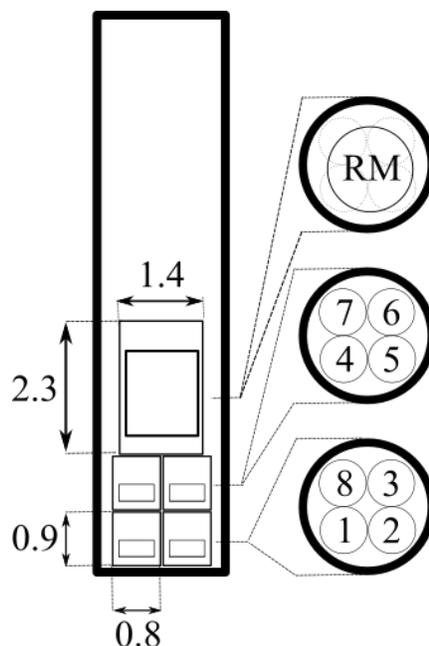
136 **Table 1** Identification code of each vial and the respective elemental content are listed. ~~The~~
137 ~~masses and the energy of the γ -photons [2] used for quantification is~~ also given.; ~~the soil~~
138 ~~mass is not corrected for the moisture. The value in parenthesis is the standard uncertainty~~
139 ~~and refers to the last digit.~~

Sample code	Content	Mass (mg)	Main γ (keV)
1	Co	0.02050(3)	1173.2
	Cr	0.02053(3)	320.1

2	Au	0.01044(2)	411.8	140
	Sb	0.02057(3)	564.2	
	Re	0.02063(4)	137.2	141
3	Sc	0.02056(3)	889.3	
	Ir	0.02047(3)	316.5	142
	Tb	0.02034(3)	879.4	
4	Co	0.02025(3)	1173.2	
	La	0.03011(5)	1596.2	143
5	Ce	0.02972(5)	145.4	
	Tm	0.02049(3)	84.3	144
	Hf	0.02055(4)	482.2	
6	Cs	0.02029(3)	604.7	145
	Se	0.03065(5)	136.0	
	Ta	0.02058(4)	1121.3	146
7	Co	0.02024(3)	1173.2	
	Ag	0.02027(3)	657.8	147
8	Blank	-	-	
RM	IAEA-SOIL-7	153.84(1)	Multiple	148

149

150 **Figure 1** The position of the samples within the irradiation container. An empty 8 mL PE
 151 vial was used to fix underneath vials in their position. Distances are in cm. Identifying
 152 codes visible in the figure are explained in Table 1



153

154 The neutron irradiation lasted 60 min and was performed at the Central Channel of the
155 TRIGA Mark II reactor. The Central Channel was chosen for the experiment because it is
156 the most widely used among the Pavia's TRIGA Mark II irradiation channels due to its
157 high conventional thermal flux, $6.11(12) \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ [3]. The container was placed
158 closest to the equator of the reactor core, at position 1. After 3 days from the end of the
159 irradiation, the PE vials were unpacked and externally rinsed with a diluted HNO_3 solution.

160 The detection system used for the counting of γ -emissions consisted of a 35% relative
161 efficiency coaxial Ge detector manufactured by CANBERRA, model GC3518, connected
162 to a digital signal processor ORTEC DSPEC 502 and a personal computer running
163 GammaVision [5] software. During counting, the end-cap of the detector was placed inside
164 a low-background graded lead shield located in an underground laboratory with controlled
165 temperature of 23 °C. The PE vials were put separately in different plastic counting
166 containers and centered with a rubber filler (i.e. a rubber disc placed in the counting
167 container; the disc had a hole in the center in which the vial was inserted). Each container
168 was placed on a sample holder at 10 cm from the detector end-cap. The number of counts
169 in the full energy γ -peaks were corrected for coincidences ; the correction was always
170 below 1% with the exception of $^{110\text{m}}\text{Ag}$ where it reached 2%.

171 A spectrum was acquired for each vial of standard solution by adjusting the counting time
172 to limit the contribution to the uncertainty due to counting statistics below the 0.5%. The
173 acquisitions lasted in a range between a few hours to two days and never overcame the
174 half-life of the evaluated radionuclides. For what concerns the IAEA-SOIL-7 sample, a
175 spectrum was acquired in a single acquisition lasting 6 days with the counting container
176 ~~vial~~ located at 10 cm from detector end-cap.

177 The values of the parameters included in the measurement model were obtained both from
178 the experimental and literature data, including a preliminary evaluation of the uncertainties.

179 The net areas of the γ -peaks and the relative uncertainties due to counting statistics were
180 obtained using the gaussian fit implemented in the algorithm WAN32 of GammaVision

181 software. Relative uncertainties ranged from 0.06% (Au and Ir) to 0.6% (Se) for the
182 acquisition of the analytes prepared with the mono-elemental standards solutions and from
183 0.9% (La) to 8.9% (Nd) for the acquisition of the analytes quantified in the IAEA-SOIL-7
184 reference material. Co comparators were acquired with statistical uncertainty within 0.3%
185 and 0.5%.

186 Live and real times were measured and recorded by the acquisition software with negligible
187 uncertainty. The relative dead time, $\frac{t_r - t_1}{t_r}$, was always lower than 1% except in the case of
188 acquisition of samples containing Au and Ir, vials 2 and 3, when it raised up to 9% and 8%,
189 respectively; in all cases, t_r was sufficiently smaller than $t_{1/2}$ of the acquired radioisotopes.
190 In addition, the pile up rejection circuit was active during acquisition.

191 The 3600 s irradiation time was measured from the attainment of criticality at 250 kW
192 power to the shut down. The reactor was powered on with the irradiation container already
193 inside the channel. Uncertainty on t_i was evaluated assuming a uniform probability
194 distribution within the interval ± 30 s of the measured irradiation time. [6]

195 In addition, a uniform probability distribution within the interval ± 60 s was conservatively
196 assumed for t_d , as clocks used to calculate the time difference from the irradiation end to
197 start counting, were not automatically synchronized to each other. The standard uncertainty
198 of t_d resulted to be 34 s. Since the decay times ranged from 93.5 h to 281.0 h, the
199 contribution to the combined uncertainty was negligible.

200 Masses of elements contained in the samples prepared with the standard solutions
201 (comparators and analytes) were obtained from the weighed pipetted solutions using the
202 certified density and elemental concentration values. The certificate of analytical balance
203 reported 0.008 mg ($k = 2$) calibration uncertainty in the range between 10 mg and 100 mg.
204 Water evaporation played an important role during mass measurement of the solutions. An
205 approximated time of 15 s was waited after the liquid deposition until the reading. During
206 this period, a previously estimated $6 \mu\text{g s}^{-1}$ evaporation rate was considered to correct for
207 the evaporated mass. The resulting 90 μg mass was conservatively considered as the half-
208 width of a uniform probability distribution assigned to the weighted mass. The

209 corresponding relative standard uncertainty on mass ranged from 0.17% to 0.49%,
210 depending on the pipetted volume. Density and mass concentration were retrieved from the
211 certificates with uncertainties 0.001 g cm^{-3} and $0.001 \text{ } \mu\text{g mL}^{-1}$, respectively [7].
212 Accordingly, in the case of standard solutions, the uncertainty of the w_a in eq. (2) is not
213 significant.

214 For what concerns the reference material, the weighed mass of sample was corrected for
215 moisture content. The moisture was measured by weighing about 500 mg of a
216 representative subsample on a Mettler Toledo HC103 thermal balance. The resulting
217 moisture content was 1.51% of the weighed mass and a value of 0.1515(13) g dry mass
218 was assigned to the reference material. The expected mass values for each investigated
219 analyte in IAEA-SOIL-7 were calculated from the respective recommended mass fraction
220 values stated in the certificate of the reference sheet material [8]. It is worth to note that the
221 95% confidence interval reported in the reference sheet are significant, i.e. between a few
222 and tens of percent.

223 Neutron flux parameters f and α for Central Channel were previously measured with
224 irradiations of a monitor set with and without Cd cover [3]. Relative uncertainties were
225 assigned from the average of the values obtained from each monitor for f , and according to
226 the formula described by De Corte, for α [9]. The resulting values are $f = 15.6(3)$ and $\alpha =$
227 $-0.036(6)$. Although the Co comparators were located at a different height (see Figure 1),
228 the measured specific count rates were in agreement to each other, confirming that no
229 visible differences in neutron flux intensity were appreciable in such positions. Therefore,
230 the neutron flux was considered constant in the zone occupied by irradiation vials and the
231 Co comparator in vial 1 was used to quantify all the analytes.

232 The values of k_0 , Q_0 , \bar{E}_r and $t_{1/2}$ were retrieved, together with their respective standard
233 uncertainties, for each nuclide of interest from the k_0 -database [2]. Relative standard
234 uncertainties of k_0 , Q_0 and \bar{E}_r , when not explicitly reported, were assigned to 5%, 20% and
235 50%, respectively, as indicated in k_0 -database guidelines.

236 The detection efficiency curve was obtained from a spectrum collected with a multi- γ
237 calibration point source, 3 mm diameter, (12ML01EGMA15) placed at 10 cm from the

238 end-cap. A polynomial curve was fitted to the data. The main contribution to the
239 uncertainty of the detection efficiency was due to sample positioning. In fact, albeit vials
240 containing the samples were accurately fixed at the center of their respective counting
241 container, the vertical position represented an issue due to a non-perfect alignment of filter
242 paper at the bottom of sample vials. A uniform probability distribution within the interval
243 ± 0.2 cm was assigned to the counting distance. At the 10 cm reference distance, the
244 corresponding standard uncertainty was 0.1 cm. Consequently, 1% relative standard
245 uncertainty due to positioning contributed to the detection efficiency.

246 Geometric and self-absorption factors were only considered in the evaluation of reference
247 material as its shape strongly differed from that of the point-like multi- γ source used for
248 calibration. Value of F_{geo} was analytically evaluated from geometrical features of the
249 IAEA-SOIL-7 within its irradiation vial and corresponded to a correction factor of 0.985
250 (a decrease in efficiency in the order of 1.5% with respect to the reference point source)
251 with negligible uncertainty, while values of $F_{\text{att}}^{\text{self}}$ were calculated using energy dependent
252 mass attenuation coefficients retrieved from literature [10].

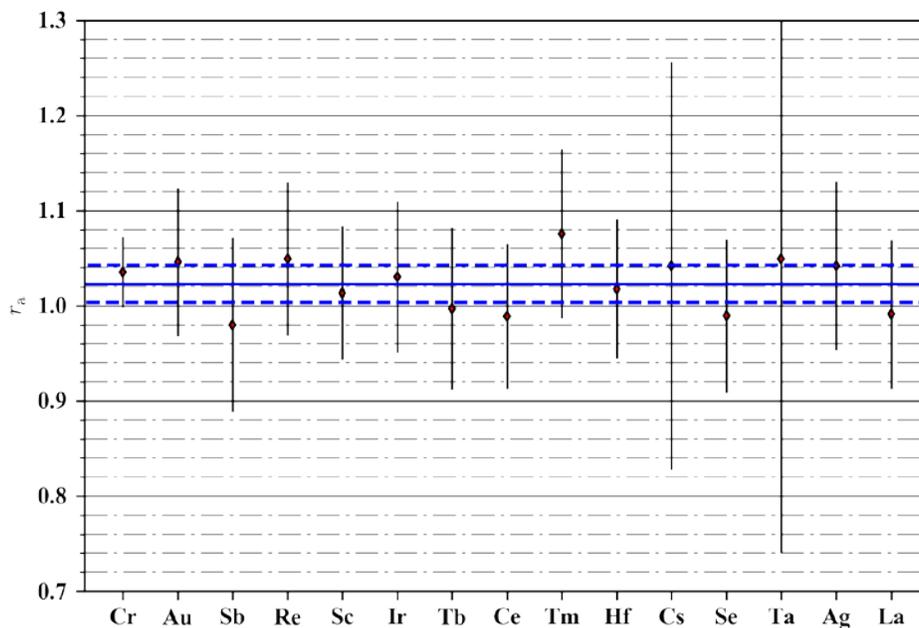
253 Values of r_a were obtained according to eq. (2) while combined uncertainties were
254 evaluated with quadratic propagation of standard uncertainty for each input quantity using
255 its respective sensitivity coefficient. The sensitivity coefficient was calculated by
256 averaging the coefficients obtained after perturbation of the input quantity by +1 and -1
257 standard uncertainty. The calculations were performed using a Microsoft Excel
258 spreadsheet.

259 **Results and discussion**

260 The results obtained with samples prepared from mono-elemental solutions and from the
261 reference material are reported in Figure 2 and 3, respectively.

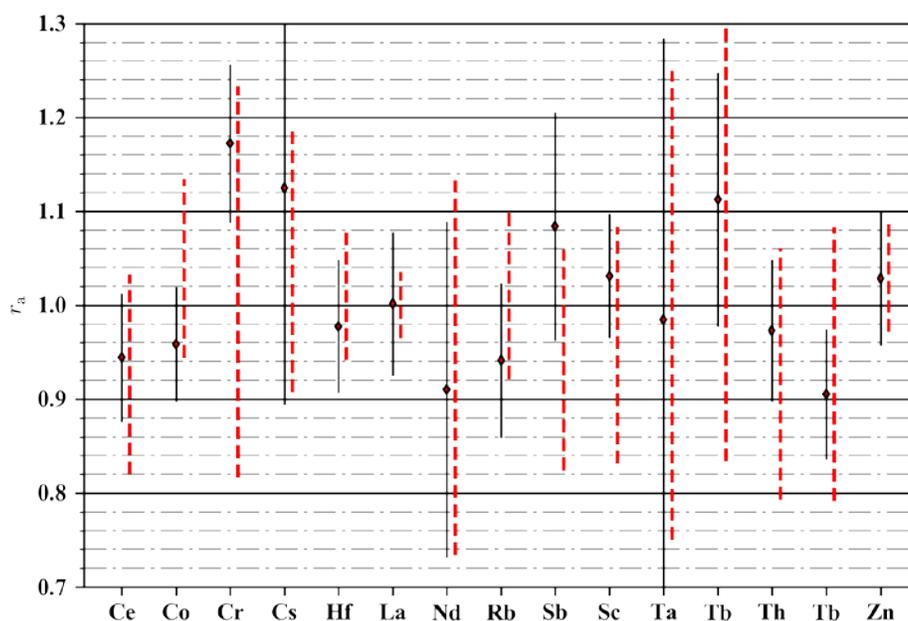
262 **Figure 2** Values for r_a Mass fractions of fifteen elements obtained measured with samples
263 prepared from mono-elemental standard solutions. The error bars indicate a 95%

264 confidence interval. The horizontal solid line indicates the weighted average of results and
 265 the dashed lines the associated 95% confidence interval.



266

267 **Figure 3** Values for r_a of fifteen elements obtained measured with the sample of the IAEA-
 268 SOIL-7 reference material. The solid error bars indicate the 95% confidence interval of the
 269 measured values while the dashed error bars indicate the 95% confidence interval of the
 270 expected recommended values.



271

272 The u -score statistical test [11] was performed using the quantified and expected values by
 273 considering the respective expanded uncertainties at 95% confidence level; the obtained u -
 274 scores were always lower than 0.9 confirming the good agreement with the expected
 275 values.

276 In the case of the standard solutions, a weighted average of the obtained results was
 277 calculated using the standard uncertainty of each result as a weight and plotted in Figure 2
 278 (horizontal solid line) to compare the overall results with the expected unity value. It is
 279 worth to note that, since the uncertainties of the expected values are not significant, the
 280 uncertainty of the expected unity values can be neglected.

281 Instead, in the case of the IAEA-SOIL-7, the 95% confidence intervals associated to the
 282 recommended values and reported in the reference sheet, are significant. The
 283 corresponding intervals were calculated and plotted in Figure 3 (vertical dashed lines) to
 284 compare each result with the expected values.

285 The quantified and expected masses of for the elements from standard solutions and from
 286 IAEA-SOIL-7 material are reported in Table 2 and Table 3, respectively.

287 **Table 2** Comparison between quantified mass for elements from standard solutions and
 288 respective expected values. The standard uncertainty of the quantified masses is indicated
 289 within parenthesis and refers to the last digits; the (negligible) standard uncertainty of the
 290 expected masses is omitted.

Element	Quantified mass (g)	Expected mass (g)
Cr	$2.125(38) \times 10^{-5}$	2.053×10^{-5}
Au	$1.092(40) \times 10^{-5}$	1.044×10^{-5}
Sb	$2.016(94) \times 10^{-5}$	2.057×10^{-5}
Re	$2.165(83) \times 10^{-5}$	2.063×10^{-5}
Sc	$2.084(72) \times 10^{-5}$	2.056×10^{-5}
Ir	$2.109(81) \times 10^{-5}$	2.047×10^{-5}
Tb	$2.027(86) \times 10^{-5}$	2.034×10^{-5}
Ce	$2.94(11) \times 10^{-5}$	2.972×10^{-5}
Tm	$2.204(91) \times 10^{-5}$	2.049×10^{-5}
Hf	$2.092(75) \times 10^{-5}$	2.055×10^{-5}
Cs	$2.11(22) \times 10^{-5}$	2.029×10^{-5}
Se	$3.03(12) \times 10^{-5}$	3.065×10^{-5}
Ta	$2.16(32) \times 10^{-5}$	2.058×10^{-5}
Ag	$2.112(90) \times 10^{-5}$	2.027×10^{-5}
La	$2.98(12) \times 10^{-5}$	3.011×10^{-5}

291

292 **Table 3** Comparison between quantified mass for elements from IAEA-SOIL-7 and
 293 respective expected values. For the quantified masses the standard uncertainty, referring to
 294 the last digits, is indicated within parenthesis while for expected masses, the intervals at
 295 95% confidence level are given.

Element	Quantified mass (g)	Expected mass (g)	Expected mass 95% confidence interval (g)
Ce	$8.73(31) \times 10^{-6}$	9.24×10^{-6}	$7.58 \times 10^{-6} - 9.55 \times 10^{-6}$
Co	$1.293(40) \times 10^{-6}$	1.35×10^{-6}	$1.27 \times 10^{-6} - 1.53 \times 10^{-6}$
Cr	$1.066(37) \times 10^{-5}$	9.09×10^{-6}	$7.42 \times 10^{-6} - 1.12 \times 10^{-5}$
Cs	$9.20(94) \times 10^{-7}$	8.18×10^{-7}	$7.42 \times 10^{-7} - 9.70 \times 10^{-7}$
Hf	$7.55(27) \times 10^{-7}$	7.73×10^{-7}	$7.27 \times 10^{-7} - 8.33 \times 10^{-7}$
La	$4.25(16) \times 10^{-6}$	4.24×10^{-6}	$4.09 \times 10^{-6} - 4.39 \times 10^{-6}$
Nd	$4.14(40) \times 10^{-6}$	4.55×10^{-6}	$3.33 \times 10^{-6} - 5.15 \times 10^{-6}$
Rb	$7.27(31) \times 10^{-6}$	7.73×10^{-6}	$7.12 \times 10^{-6} - 8.48 \times 10^{-6}$
Sb	$2.79(15) \times 10^{-7}$	2.58×10^{-7}	$2.12 \times 10^{-7} - 2.73 \times 10^{-7}$

Sc	$1.297(40) \times 10^{-6}$	1.26×10^{-6}	$1.05 \times 10^{-6} - 1.36 \times 10^{-6}$
Ta	$1.19(18) \times 10^{-7}$	1.21×10^{-7}	$9.09 \times 10^{-8} - 1.52 \times 10^{-7}$
Tb	$1.011(61) \times 10^{-7}$	9.09×10^{-8}	$7.58 \times 10^{-8} - 1.36 \times 10^{-7}$
Th	$1.209(46) \times 10^{-6}$	1.24×10^{-6}	$9.85 \times 10^{-7} - 1.32 \times 10^{-6}$
Tb	$3.29(12) \times 10^{-7}$	3.64×10^{-7}	$2.88 \times 10^{-7} - 3.94 \times 10^{-7}$
Zn	$1.621(54) \times 10^{-5}$	1.58×10^{-5}	$1.53 \times 10^{-5} - 1.71 \times 10^{-5}$

296

297 The relative standard uncertainty reached in the analysis of the mono-elemental standard
298 solutions was about 4%, with the exception of Cs and Ta, when it reached about 15% due
299 to the non-recommended Q_0 values. In general, the main contributor to the combined
300 uncertainty, evaluated via eq. (2), was the detection efficiency. In the case of Cs and Ta,
301 the major contribution came from the uncertainty assigned to non-recommended Q_0 values,
302 i.e. $Q_{0,Cs} = 12.7(25)$ and $Q_{0,Ta} = 33.3(66)$.

303 The uncertainty of the quantified elements in the IAEA-SOIL-7 reference material showed
304 an analogue situation. In general, 5% relative uncertainty was achieved for the best results.
305 The main contributors to the combined uncertainty were the detection efficiency and the
306 Q_0 values. In the case of Nd, also the poor counting statistics had a significant effect.

307 **Conclusions**

308 The application of the k_0 -NAA at the INRIM Radiochemistry and Spectroscopy Laboratory
309 of the Istituto Nazionale di Ricerca Metrologica using the LENA 250 kW TRIGA Mark II
310 reactor was preliminary tested. Results obtained from the analysis of fifteen elements in
311 seven samples prepared from mono-elemental standard solutions and fifteen elements in
312 one sample of a reference material were in good agreement with the expected values. This
313 outcome is an incentive to adopt, in a near future, the routinely use of the k_0 -NAA
314 standardisation method in addition to the presently adopted relative standardisation
315 method.

316 However, the weighted average of the results obtained from standard solutions yielded a
317 value that was 2% higher than expected with an expanded uncertainty that didn't cover the

318 bias. This highlights the possible presence of some uncorrected systematic effect or an
319 underestimation of the evaluated uncertainty that deserves further investigations.

320 Moreover, albeit the uncertainty evaluation anticipated that results were mainly affected
321 by the detection efficiency, the Q_0 values, especially when marked as non-recommended
322 in the k_0 -database, can have a dramatic impact on the overall uncertainty when evaluated
323 in poorly-thermalized facilities like the TRIGA Mark II reactor. Consequently, efforts
324 dedicated to additional measurements of the non-recommended Q_0 values are required.

325 **Acknowledgements**

326 This work was funded by the Italian ministry of education, university, and research
327 (awarded project P6-2013, implementation of the new SI).

328 **References**

- 329 1. De Corte F (1987) The k_0 -standardization method: a move to the optimization of Neutron
330 Activation Analysis. University of Gent, Belgium.
- 331 2. k_0 -database.
332 [http://www.kayzero.com/k0naa/k0naaorg/Nuclear_Data_SC/Entries/2016/1/11_New_](http://www.kayzero.com/k0naa/k0naaorg/Nuclear_Data_SC/Entries/2016/1/11_New_k0-data_Library_2015.html)
333 [k0-data_Library_2015.html](http://www.kayzero.com/k0naa/k0naaorg/Nuclear_Data_SC/Entries/2016/1/11_New_k0-data_Library_2015.html)
- 334 3. Di Luzio M, Oddone M, Prata M, Alloni D, D'Agostino, G (2017) Measurement of the
335 neutron flux parameters f and α at the Pavia TRIGA Mark II reactor. *J Radioanal Nucl*
336 *Chem.* 312:75-80.
- 337 4. Boshkova T, Minev L (2001) Corrections for self-attenuation in gamma-ray
338 spectrometry of bulk samples. *Appl Radiat Isot.* 54: 777-783.
- 339 5. Gamma Vision version 7 – User manual. [http://www.ortec-online.com/-](http://www.ortec-online.com/-/media/ametektortec/manuals/a66-mnl.pdf)
340 [/media/ametektortec/manuals/a66-mnl.pdf](http://www.ortec-online.com/-/media/ametektortec/manuals/a66-mnl.pdf)
- 341 6. JCGM/WG1 (2008) Evaluation of measurement data – Guide to the expression of
342 uncertainty in measurement. BIPM, Sevrès.
- 343 7. VWR International. <https://us.vwr.com/store/>

- 344 8. IAEA-SOIL-7 reference sheet. https://nucleus.iaea.org/rpst/Documents/rs_iaea-soil-
345 7.pdf
- 346 9. De Corte F, Sordo-El Hammami K, Moens L, Simonits A, De Wispelaere A, Hoste J
347 (1981) The accuracy and precision of the experimental α -determination in the $1/E^{1+\alpha}$
348 epithermal reactor-neutron spectrum. *J Radioanal Nucl Chem.* 62:209-255.
- 349 10. Al-Masri M S, Hasan M, Al-Hamwi A, Amin Y, Doubal A W (2013) Mass
350 attenuation coefficients of soil and sediment samples using gamma energies from 46.5
351 to 1332 keV. *J Environ Radioact.* 116:28-33.
- 352 11. Shakhashiro A, Sansone U, Trinkl A, Benesch T (2006) Report on the IAEA-CU-
353 2006-01 proficiency test on the determination of radionuclides and trace elements in
354 soil and compost. IAEA, Seibersdorf