



ISTITUTO NAZIONALE DI RICERCA METROLOGICA Repository Istituzionale

The linkup of mono-elemental solutions to the SI using INAA: a measurement procedure and the achievable uncertainty

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

Original

The linkup of mono-elemental solutions to the SI using INAA: a measurement procedure and the achievable uncertainty / D'Agostino, Giancarlo; Bergamaschi, Luigi; Di Luzio, Marco; Noordmann, Janine; Oddone, Massimo; Rienitz, Olaf. - In: JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY. - ISSN 0236-5731. - 309:2(2016), pp. 777-786. [10.1007/s10967-015-4676-2]

Availability:

This version is available at: 11696/51981 since: 2020-05-19T10:40:33Z

Publisher:

Springer

Published

DOI:10.1007/s10967-015-4676-2

Terms of use:

Visibile a tutti

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

Title page

2 Names of the authors: Giancarlo D'Agostino⁽¹⁾, Luigi Bergamaschi⁽¹⁾, Marco Di
3 Luzio^(1,2), Janine Noordmann⁽³⁾, Massimo Oddone⁽²⁾ and Olaf Rienitz⁽³⁾

4 Title: The linkup of mono-elemental solutions to the SI using INAA: a measurement
5 procedure and the achievable uncertainty

6 Affiliation(s) and address(es) of the author(s): (1) Istituto Nazionale di Ricerca
7 Metrologica (INRIM) - Unit of Radiochemistry and Spectroscopy, c/o Department of
8 Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia, Italy; (2) Department of
9 Chemistry – Radiochemistry Area, University of Pavia, via Taramelli 12, 27100 Pavia,
10 Italy; (3) Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116
11 Braunschweig, Germany

12 E-mail address of the corresponding author: g.dagostino@inrim.it

13

14 **The linkup of mono-elemental solutions to the SI using**
15 **INAA: a measurement procedure and the achievable**
16 **uncertainty**

17 D'Agostino G.¹, Bergamaschi L.¹, Di Luzio M.^{1,2}, Noordmann J.³, Oddone M.² and
18 Rienitz O.³

19 ¹*Istituto Nazionale di Ricerca Metrologica (INRIM), via Taramelli 12, 27100 Pavia, Italy*

20 ²*Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia, Italy*

21 ³*Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig,*
22 *Germany*

23 **Abstract**

24 The possibility of using neutron activation analysis to link up a secondary to a primary
25 mono-elemental solution was investigated. A procedure was developed for the
26 determination of the ratio between the mass fractions of two solutions. The use of a
27 monitor element was essential to limit the effect of the non-uniformity of the neutron flux
28 during irradiation. The proposed procedure was tested in the case of two molybdenum
29 solutions having the same mass fraction. Although the experiment did not reach the goal,
30 possible ways are suggested to reach the target expanded uncertainty of 0.1 %.

31 **Keywords**

32 Neutron activation analysis; metrological traceability; reference solution; molybdenum.

33 **Introduction**

34 Mono-elemental solutions with a mass fraction of 1 g kg^{-1} are being used in almost every
35 chemical laboratory in social, medical and industrial fields to calibrate analytical
36 measurements. The accuracy of those solutions is essential for the reliability and
37 comparability of the applied analyses.

38 Due to the importance of these calibration solutions, traceability to the SI is necessary.
39 Several national metrology institutes (NMIs) or designated institutes (DIs) provide
40 traceability by the use of high purity solid materials ($w_{\text{pur}} \geq 0.999 \text{ g g}^{-1}$) with completely
41 known impurities (metals and non-metals), yielding a purity with an associated expanded
42 uncertainty of less than 0.01 %. In some cases, the distribution of selected impurities
43 among subsamples of the solid materials have been also investigated [1]. Based on these
44 solid materials, primary reference solutions with an expanded uncertainty associated with
45 the mass fraction of less than 0.05 % are gravimetrically prepared and metrologically
46 monitored by NMIs [2].

47 As the pure and fully characterized materials and the primary solutions have a limited
48 availability and are very valuable concerning the characterization and preparation
49 process, secondary solutions are prepared using pure materials usually only characterized
50 regarding metallic impurities. Therefore, these secondary solutions must be linked up to
51 the primary solutions. The expanded measurement uncertainty of the linkup must be less
52 than 0.1 % to achieve a calibration measurement of commercial solutions with an
53 expanded uncertainty associated with the mass fraction of 0.3 %. Overall, this procedure
54 demonstrates an unbroken chain of calibrations to link up the measurement results in the
55 field to the SI [3].

56 In this framework, high precision measurements are needed to link up the solutions with
57 a relative expanded uncertainty of less than 0.1 %. In most cases, those measurements are
58 being performed using the inductively coupled plasma optical emission spectrometry
59 (ICP OES) technique.

60 Given that the application of instrumental neutron activation analysis (INAA) technique
61 is missing in this field, a measurement procedure is suggested and the related
62 measurement model is obtained from the neutron activation equation. In addition, the

63 proposed procedure was experimentally tested in the case of two Mo solutions having the
64 same mass fraction, i.e. when the ratio is expected to be the unit value.

65 **Measurement procedure and model**

66 The aim of the measurement is to link up an elemental solution ES1 to an elemental
67 solution ES2 having mass fractions $w_{ES1}(E)$ and $w_{ES2}(E)$ of an element E by determining
68 the ratio

$$69 \quad \tau = \frac{w_{ES1}(E)}{w_{ES2}(E)} \quad (1)$$

70 with a relative expanded uncertainty of 0.1 %.

71 To accomplish this aim, two measurement solutions, mS1 and mS2, are stocked in two
72 different containers by adding a sample (aliquot) of a monitor solution MS having a mass
73 fraction $w_{MS}(E_M)$ of a monitor element E_M to a sample of each elemental solution. Two
74 sub-samples of the measurement solutions, mS1,s and mS2,s, are used in the neutron
75 activation experiment.

76 To achieve the target uncertainty, attention has to be given to the evaporation of the
77 solution during handling. The elemental solution starts to evaporate with a mass rate α_{ES}
78 when it is transferred from its bottle to the container. After a time t_{MS} , the monitor
79 solution is pipetted into the container to obtain the final measurement solution. The
80 solution carries on evaporating during a time t_{ms} , with a mass rate α_{mS} , until a sub-sample
81 is taken and pipetted into an irradiation vial.

82 Hence, when the sub-samples are taken, the masses of the measurement solutions are
83 $m_{mS1} = m_{ES1} - \alpha_{E1} t_{MS1} + m_{1,MS} - \alpha_{mS1} t_{mS1}$ and $m_{mS2} = m_{ES2} - \alpha_{E2} t_{MS2} + m_{2,MS} - \alpha_{mS2} t_{mS2}$,
84 where m_{ES1} , m_{ES2} are the masses of the samples of ES1, ES2 and $m_{1,MS}$, $m_{2,MS}$ are the
85 additional masses of MS.

86 The mass fractions of E and E_M in the measurement solutions are

$$87 \quad w_{mS1}(E) = \frac{w_{ES1}(E)}{1 + \frac{m_{1,MS} - m_{ev1}}{m_{ES1}}}, \quad w_{mS2}(E) = \frac{w_{ES2}(E)}{1 + \frac{m_{2,MS} - m_{ev2}}{m_{ES2}}} \quad (2)$$

88 and

$$89 \quad w_{mS1}(E_M) = \frac{w_{MS}(E_M)}{1 + \frac{m_{ES1} - m_{ev1}}{m_{1,MS}}}, \quad w_{mS2}(E_M) = \frac{w_{MS}(E_M)}{1 + \frac{m_{ES2} - m_{ev2}}{m_{2,MS}}}, \quad (3)$$

90 respectively, where $m_{ev1} = \alpha_{E1} t_{MS1} + \alpha_{mS1} t_{mS1}$ and $m_{ev2} = \alpha_{E2} t_{MS2} + \alpha_{mS2} t_{mS2}$ are the
91 evaporated masses.

92 The number of atoms of an isotope iE of E and of an isotope iE_M of E_M in $mS1,s$ and
93 $mS2,s$ are

$$94 \quad n_{mS1,s}({}^iE) = \frac{x({}^iE) N_A w_{mS1}(E) m_{mS1,s}}{M(E)}, \quad n_{mS2,s}({}^iE) = \frac{x({}^iE) N_A w_{mS2}(E) m_{mS2,s}}{M(E)}, \quad (4)$$

95 and

$$96 \quad n_{mS1,s}({}^iE_M) = \frac{x({}^iE_M) N_A w_{mS1}(E_M) m_{mS1,s}}{M(E_M)}, \quad n_{mS2,s}({}^iE_M) = \frac{x({}^iE_M) N_A w_{mS2}(E_M) m_{mS2,s}}{M(E_M)}, \quad (5)$$

97 respectively, where $m_{mS1,s}$ and $m_{mS2,s}$ are the masses of $mS1,s$ and $mS2,s$, N_A is the
98 Avogadro constant, $x({}^iE)$ and $x({}^iE_M)$ are the mole fractions of iE and iE_M , $M(E)$ and
99 $M(E_M)$ are the molar masses of E and E_M , respectively. Here and hereafter the subscript
100 M refers to the monitor element.

101 From (1), (2) and (4) it follows

$$102 \quad \tau = \frac{\left(1 + \frac{m_{1,MS} - m_{ev1}}{m_{ES1}}\right) \frac{n_{mS1,s}({}^iE)}{m_{mS1,s}}}{\left(1 + \frac{m_{2,MS} - m_{ev2}}{m_{ES2}}\right) \frac{n_{mS2,s}({}^iE)}{m_{mS2,s}}}. \quad (6)$$

103 The two sub-samples of the measurement solutions, mS1,s and mS2,s, are co-irradiated in
 104 a neutron flux to activate the target isotopes ${}^i\text{E}$ and ${}^i\text{E}_\text{M}$.

105 The counting of the γ -photons emitted during the radioactive decay of the radionuclide
 106 produced by activation of the target isotope ${}^i\text{E}$ allows to quantify the ratio

$$107 \quad \frac{n_{\text{mS1,s}}({}^i\text{E})}{n_{\text{mS2,s}}({}^i\text{E})} = \kappa_{\text{td}} \kappa_{\text{R}} \kappa_{\varepsilon} \kappa_{\text{ss}} \kappa_{\text{sa}} \kappa_{\text{g}} \frac{C_{\text{mS1,s}}(t_{\text{d mS1,s}})}{C_{\text{mS2,s}}(t_{\text{d mS2,s}})}, \quad (7)$$

108 where $C(t_{\text{d}})$ is the full-energy γ -peak detection count rate at a time t_{d} after the end of the
 109 irradiation; here and hereafter, the subscripts mS1,s and mS2,s are occasionally omitted
 110 in $C(t_{\text{d}})$. The correction factors $\kappa_{\text{td}} = e^{-\lambda(t_{\text{d mS2,s}} - t_{\text{d mS1,s}})}$, $\kappa_{\text{R}} = R_{\text{mS2,s}}/R_{\text{mS1,s}}$,
 111 $\kappa_{\varepsilon} = \varepsilon_{\text{mS2,s}}/\varepsilon_{\text{mS1,s}}$, $\kappa_{\text{ss}} = k_{\text{ss mS2,s}}/k_{\text{ss mS1,s}}$, $\kappa_{\text{sa}} = k_{\text{sa mS2,s}}/k_{\text{sa mS1,s}}$ and
 112 $\kappa_{\text{g}} = k_{\text{g mS2,s}}/k_{\text{g mS1,s}}$ take the differences of decay time, reaction rate, detection
 113 efficiency, self-shielding, self-absorption and geometry of the sub-samples into account.

114 In detail, λ is the decay constant of the produced radionuclide, R is the reaction rate per
 115 target isotope ${}^i\text{E}$, ε is the detection full-energy γ efficiency for a point-like source located
 116 at the center of mass of the sub-sample, k_{ss} , k_{sa} , and k_{g} are the neutron self-shielding, the
 117 gamma self-absorption and the geometry factors, respectively.

118 It is worth to note that in the case of a radionuclide which emits γ -photons with several
 119 energies E_{γ} , best results are achieved by using in (7) the mean value of the count rate

$$120 \quad \text{ratios, } \left. \frac{C_{\text{mS1,s}}(t_{\text{d mS1,s}})}{C_{\text{mS2,s}}(t_{\text{d mS2,s}})} \right|_{\text{m}}, \text{ obtained with different } E_{\gamma}.$$

121 The γ -counting is carried out using germanium detectors. The count rate $C(t_{\text{d}})$ is obtained
 122 by averaging n values, $C_i(t_{\text{d}})$, acquired in a γ -spectrometry sequence starting at a decay
 123 time $t_{\text{d}1}$ after the end of the irradiation and consisting of n consecutive counts performed
 124 during the decay of the produced radionuclide. More explicitly, each i^{th} count rate value,
 125 $C_i(t_{\text{d}})$, extrapolated to t_{d} from the i^{th} count of the sequence, starting at $t_{\text{d}i}$ and lasting $t_{\text{c}i}$, is

$$C_i(t_d) = \frac{\lambda n_{ci}}{e^{-\lambda(t_{di}-t_d)}(1-e^{-\lambda t_{ci}})} \frac{t_{ci}}{t_{ci}-t_{dead i}}, \quad (8)$$

127 where n_{ci} and $t_{dead i}$ are the net count of the full-energy γ -peak and the detection dead time
128 of the i^{th} count, respectively.

129 In the case of a $1/E^{1+\alpha}$ epithermal spectrum and if the target isotope ${}^i\text{E}$ is activated via a
130 (n,γ) reaction having a cross section with a $E^{-1/2}$ energy dependence, the reaction rate can
131 be described using the Høgdahl convention [4], $R = \Phi_{ep} \sigma_{0,E} (f + Q_{0,E}(\alpha))$, where Φ_{ep} is
132 the epithermal neutron flux, $f = \Phi_{th}/\Phi_{ep}$ is the thermal (sub-cadmium) to epithermal
133 neutron flux ratio, $\sigma_{0,E}$ is the (n,γ) cross section of ${}^i\text{E}$ at 0.0253 eV and

$$Q_{0,E}(\alpha) = (Q_{0,E} - 0.429) \bar{E}_r^{-\alpha} + \frac{0.429}{(2\alpha + 1) 0.55^\alpha}. \quad (9)$$

135 In (9) $Q_{0,E}$ is the ratio between the resonance integral of ${}^i\text{E}$ for a $1/E$ epithermal spectrum,
136 $I_{0,E}$, and $\sigma_{0,E}$, and \bar{E}_r is the effective resonance energy of ${}^i\text{E}$ [5].

137 Thus, the characteristics of the neutron energy spectrum affect the κ_R correction factor
138 according to

$$\kappa_R = \frac{\Phi_{ep2}(f_2 + Q_{0,E}(\alpha_2))}{\Phi_{ep1}(f_1 + Q_{0,E}(\alpha_1))}, \quad (10)$$

140 where Φ_{ep1} , f_1 , α_1 and Φ_{ep2} , f_2 , α_2 are referred to the irradiation positions of mS1,s and
141 mS2,s, respectively.

142 Several methods have been developed and used to measure the neutron flux parameters;
143 as examples, (i) the “Cd-covered multi-monitor”, the “Cd-ratio for multi-monitor” and
144 the “bare multi-monitor” methods for α , (ii) the “Cd-ratio” for Φ_{ep} and f , (iii) the “bare
145 bi-isotopic monitor” method for f [5]. These methods are usually applied offline, i.e.
146 before (or after) the experiment, by assuming that the neutron energy spectrum remains
147 constant and do not depend on the irradiation samples.

148 In our case, since the κ_R value is required with a relative expanded uncertainty of less
 149 than 0.1 %, online information is valuable. To reach this aim, the monitor solution is
 150 added to the elemental solution. If the Høgdahl convention applies to the target isotope
 151 ${}^i\text{E}_M$,

$$152 \quad \kappa_{M-R} = \frac{\Phi_{ep2}(f_2 + Q_{0,EM}(\alpha))}{\Phi_{ep1}(f_1 + Q_{0,EM}(\alpha))}. \quad (11)$$

153 From (10) and (11) it follows

$$154 \quad \kappa_R = \kappa_{M-R} \frac{1 + \frac{\alpha_Q Q_{0,E}(\alpha)}{f_1 + Q_{0,E}(\alpha)}}{1 + \frac{\alpha_Q Q_{0,E}(\alpha)}{f_1(1 + \alpha_f) + Q_{0,E}(\alpha)}}, \quad (12)$$

$$155 \quad \text{where } \alpha_Q = \frac{Q_{0,EM}(\alpha) - Q_{0,E}(\alpha)}{Q_{0,E}(\alpha)} \text{ and } \alpha_f = \frac{f_2 - f_1}{f_1}.$$

156 The counting of the γ -photons emitted during the radioactive decay of the radionuclide
 157 produced by activation of the target isotope ${}^i\text{E}_M$ allows to determine

$$158 \quad \kappa_{M-R} = (\kappa_{M-td} \kappa_{M-\varepsilon} \kappa_{M-ss} \kappa_{M-sa} \kappa_{M-g})^{-1} \frac{C_{M-mS2,s}(t_{dM-mS2,s}) n_{mS1,s}({}^i\text{E}_M)}{C_{M-mS1,s}(t_{dM-mS1,s}) n_{mS2,s}({}^i\text{E}_M)}. \quad (13)$$

159 According to (3) and (5), the ratio

$$160 \quad \frac{n_{mS1,s}({}^i\text{E}_M)}{n_{mS2,s}({}^i\text{E}_M)} = \frac{m_{mS1,s} \left(1 + \frac{m_{ES2} - m_{ev2}}{m_{2,MS}} \right)}{m_{mS2,s} \left(1 + \frac{m_{ES1} - m_{ev1}}{m_{1,MS}} \right)}. \quad (14)$$

161 In conclusion, the measurement model adopted to link up ES1 to ES2 is obtained from
 162 (6), (7), (12), (13) and (14):

$$\begin{aligned}
 163 \quad \tau = & \frac{m_{ES2}}{m_{ES1}} \frac{m_{1,MS}}{m_{2,MS}} \frac{C_{mS1,s}(t_{d\ mS1,s})}{C_{mS2,s}(t_{d\ mS2,s})} \frac{C_{M-mS2,s}(t_{d\ M-mS2,s})}{C_{M-mS1,s}(t_{d\ M-mS1,s})} , \\
 & \times \beta_R \kappa_{td} \kappa_{M-td}^{-1} \kappa_{ss} \kappa_{M-ss}^{-1} \kappa_{sa} \kappa_{M-sa}^{-1} \kappa_g \kappa_{M-g}^{-1} \kappa_\varepsilon \kappa_{M-\varepsilon}^{-1}
 \end{aligned} \quad (15)$$

$$164 \quad \text{where } \beta_R = \frac{1 + \frac{\alpha_Q Q_{0,E}(\alpha)}{f_1 + Q_{0,E}(\alpha)}}{1 + \frac{\alpha_Q Q_{0,E}(\alpha)}{f_1(1 + \alpha_f) + Q_{0,E}(\alpha)}} .$$

165 It is remarkable that the result is independent on the masses of the evaporated solutions
 166 m_{ev1} , m_{ev2} , on the masses of the irradiated sub-samples $m_{mS1,s}$, $m_{mS2,s}$ and on the
 167 epithermal flux at the irradiation positions Φ_{ep1} , Φ_{ep2} . Moreover, in case of (i) large f , (ii)
 168 $Q_{0,EM}(\alpha) \cong Q_{0,E}(\alpha)$ or (iii) $f_1 \cong f_2$, the result becomes less affected by the f , α , \bar{E}_r , $Q_{0,E}$,
 169 and $Q_{0,EM}$ values.

170 Experimental

171 The proposed procedure was tested using a Mo solution having a mass fraction
 172 $w(\text{Mo}) \approx 1 \text{ g kg}^{-1}$. In this preliminary experiment, a Co solution having a mass fraction
 173 $w(\text{Co}) \approx 1 \text{ g kg}^{-1}$ was adopted as the monitor solution. The Mo and Co solutions were
 174 obtained using ultrapure ammonium molybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{ H}_2\text{O}$, in
 175 water and ultrapure Co metal in 0.5 mol L^{-1} nitric acid, respectively.

176 A single measurement solution, mS, was prepared in a container by adding the Co
 177 solution to the Mo solution. Two sub-samples were taken and used for the neutron
 178 irradiation. This mimics the application of the procedure in the case of two Mo solutions
 179 having the same mass fraction, i.e. $w_{ES1}(E) = w_{ES2}(E)$, $m_{ES1} = m_{ES2}$, $m_{1,MS} = m_{2,MS}$. To
 180 attain the objective, (15) must be satisfied, i.e. $\tau = 1$, with a relative expanded
 181 uncertainty of 0.1 %.

182 The τ value was determined by counting (i) the 140.51 keV γ -photons emitted during the
 183 radioactive decay of ^{99}Mo and ^{99m}Tc in equilibrium conditions and produced by

184 activation of ^{98}Mo via the (n,γ) neutron capture reaction, and (ii) the 1173.23 keV and
185 1332.49 keV γ -photons emitted during the radioactive decay of ^{60}Co produced by
186 activation of ^{59}Co via the (n,γ) neutron capture reaction.

187 *Preparation of the measurement solution*

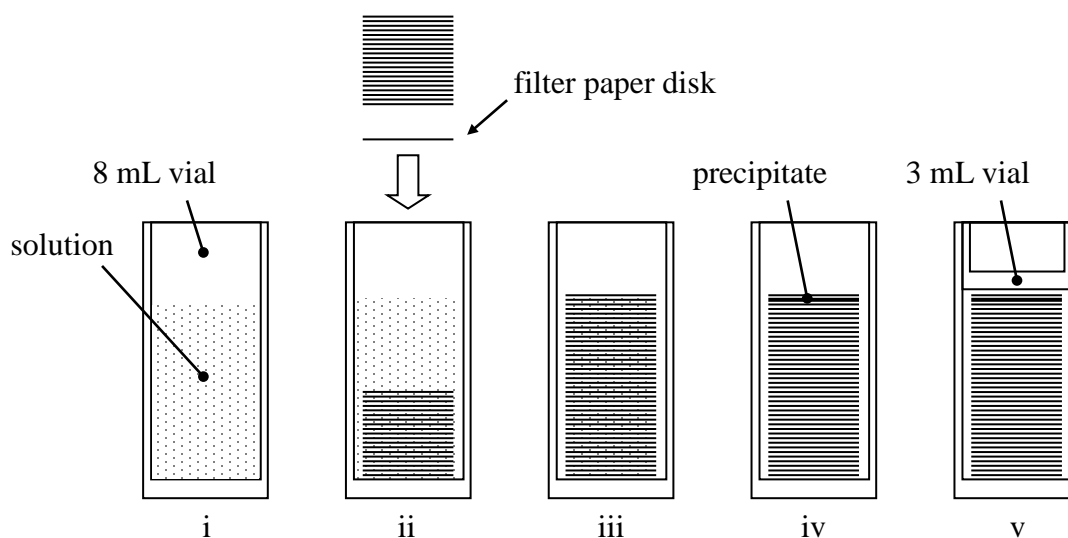
188 The measurement solution was prepared by pipetting the Co solution to a 25 mL
189 polytetrafluoroethylene (PTFE) flask filled with the Mo solution. To correct for the effect
190 of the evaporation, the mass of the measurement solution, m_{MS} , was recorded
191 continuously during its preparation with a sampling frequency of 1 Hz. The data were
192 collected using a digital analytical balance having a resolution of 0.01 mg and calibrated
193 with SI-traceable weights. It is noteworthy that, although the buoyancy affects the
194 weighing of the solution, the ratios of the masses in the model (15) eliminates the effect
195 on τ . Therefore, the weighed masses were not corrected for buoyancy.

196 The room temperature during the preparation was 26 °C. After setting to zero (tare) the
197 reading of the balance with the empty flask, (i) 21 mL of Mo solution, (ii) 125 μL of Co
198 solution and (iii) 6 mL of Mo solution were consecutively added at 179 s, 532 s and
199 993 s, respectively. The balance drift during the recording session was -0.02 mg.

200 A straight line was fitted to the data collected between (i) 223 s and 524 s, (ii) 623 s and
201 919 s, (iii) 1025 s and 1285 s. The evaporation rates were found to be $2.1 \times 10^{-6} \text{ g s}^{-1}$,
202 $2.0 \times 10^{-6} \text{ g s}^{-1}$ and $3.3 \times 10^{-6} \text{ g s}^{-1}$. According to the fitted data, the masses of the added
203 solutions at steps (i), (ii) and (iii) were $m_{\text{ES}} = 20.96218(4)$ g, $m_{\text{MS}} = 0.12572(4)$ g and
204 $m_{\text{ES}} = 6.07041(4)$ g, respectively. Here and hereafter, unless otherwise specified, the
205 brackets refer to the standard uncertainty. The residuals of the fitted data were on average
206 within ± 0.02 mg. However, since there are also spikes up to 0.04 mg, an uncertainty of
207 0.04 mg was assigned to the measured masses.

208 *Preparation of the irradiation samples*

209 Two sub-samples, 2 mL volumes, of the measurement solution, hereafter called samples,
210 were taken and pipetted in two different 8 mL polyethylene (PE) vials. Afterwards,
211 80 filter paper disks (12 mm diameter) obtained from a single sheet using a cutting punch
212 were inserted in both the PE vials. The paper disks were subsequently dried using an IR
213 lamp and pressed using a slice of a 3 mL vial sealed to the 8 mL vial. It was assumed that
214 the Mo and Co content of the pipetted solutions precipitates completely in the paper
215 disks; this was confirmed by subsequent measurements with the emptied PE vials. The
216 preparation of a sample for irradiation is summarized in Fig. 1.



217

218 **Fig. 1** Preparation of an irradiation sample; (i) the pipetted sub-sample of the
219 measurement solution, (ii) and (iii) insertion of the filter paper disks, (iv) paper disks
220 after drying, (v) sealed PE vial

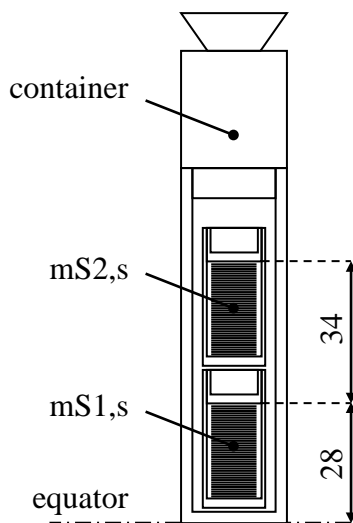
221 The visual inspection of the PE vials after drying was evidence for a precipitation largely
222 occurring in the upper part of the piled disks (see the picture in Fig. S1). This was proof
223 that the Mo and Co solutes were not homogeneously distributed in the paper disks. Since
224 the mass fraction of the Co solution in the measurement solution was at 10^{-3} level, the
225 pipetted 2 mL solution consisted of 2 mg of Mo and the observed precipitate could have
226 been ammonium molybdate tetrahydrate.

227 To limit the effect of external contaminations, the PE vials, the tweezers used to handle
228 the filter paper disks were cleaned in an ultrasonic bath with diluted HNO_3 and the
229 cutting punch was washed with isopropyl alcohol. The water was purified using a

230 Millipore system ($\rho \geq 18 \text{ M}\Omega$). Concerning the filter paper, a previous neutron activation
231 experiment carried out with the disks did not show any contamination of Co and Mo.

232 *Neutron irradiation and gamma spectrometry*

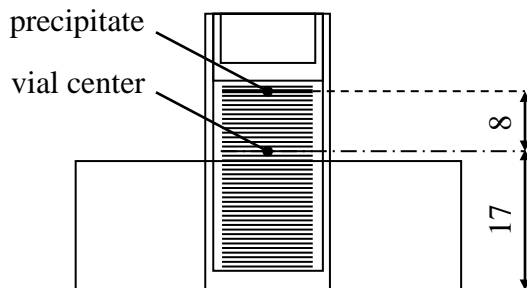
233 The neutron irradiation lasted 3 h and was performed in the central channel of the
234 250 kW TRIGA Mark II reactor at the Laboratory of Applied Nuclear Energy (LENA) of
235 the University of Pavia. The nominal thermal and epithermal neutron fluxes were about
236 $6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and $5.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, resulting in a nominal f value of 10.9. The
237 samples were put in a PE container used for irradiation. Fig. 2 shows the position of the
238 container and the samples with respect to the equator of the reactor core.



239

240 **Fig. 2** Position of the irradiation container and the samples with respect to the equator of
241 the reactor core; dimensions are in mm

242 After the neutron irradiation, the samples were extracted from the container, rinsed with
243 diluted HNO_3 and fixed to a γ -counting container (Fig. 3).

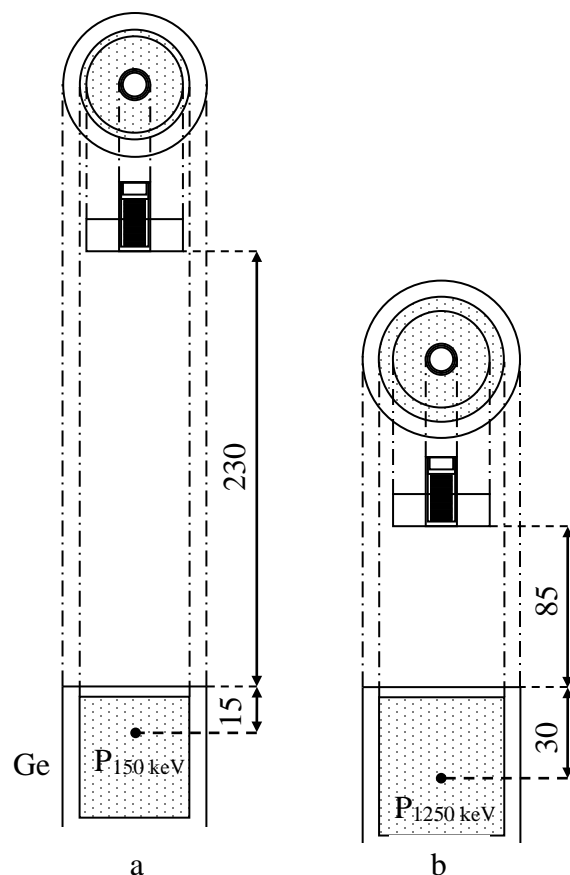


244

245 **Fig. 3** Position of the sample with respect to the γ -counting containers; dimensions are in
246 mm

247 The γ -detection was carried out using a detector Canberra GC3518 (relative efficiency
248 35 %, 1.80 keV FWHM resolution at 1332 keV), and a detector ORTEC[®] GEM50P4-83
249 (66 mm crystal diameter, 50 % relative efficiency, 1.90 keV FWHM resolution at
250 1332 keV).

251 Six γ -spectrometry sequences were recorded with a digital signal processor
252 ORTEC[®] DSPEC 502 and a personal computer running the software for data acquisition
253 ORTEC[®] Gamma Vision [6]. The first four sequences were performed with the GC3518
254 and concerned the 140.51 keV γ -emission of ⁹⁹Mo and ^{99m}Tc in equilibrium conditions.
255 The latter two γ -spectrometry sequences were performed with the GEM50P4-83 and
256 concerned the 1173.23 keV and 1332.49 keV γ -emission of ⁶⁰Co. Each sequence
257 consisted of n counts performed by adjusting on-line the counting window to reach a
258 0.23 % counting uncertainty. The dead to counting time ratio, t_{dead}/t_c , of the detection
259 systems during the data collection was always below 2.5 %. The position of the γ -
260 counting containers with respect to the detector during the first four and the latter two
261 sequences are displayed in Fig. 4a and Fig. 4b, respectively. In particular, the distances
262 between the bottom of the γ -counting container and the end-cap of the detector were
263 $d_{\text{GC3518}} = 230$ mm and $d_{\text{GEM50P4-83}} = 85$ mm.



264

265 **Fig. 4** Position of the γ -counting containers (a) with respect to the detector GC3518
 266 during ^{99}Mo and $^{99\text{m}}\text{Tc}$ detection and (b) with respect to the detector GEM50P4-83 during
 267 the ^{60}Co detection. The point $P_{E\gamma}$ defines the (virtual) vertical position within the Ge
 268 crystal where the detection efficiency ε tends to infinite; dimensions are in mm

269

The sequence number, the sample, the decay time at the beginning of the sequence, t_{d1} ,
 270 and the number of collected counts, n , are summarized in table 1. The first sequence
 271 started about 4 days after the end of the irradiation to assure a negligible effect due to the
 272 ^{99}Mo and $^{99\text{m}}\text{Tc}$ equilibrium conditions [5].

273

Table 1 The sample, the decay time, t_{d1} , and the number of collected counts, n , in each
 274 sequence

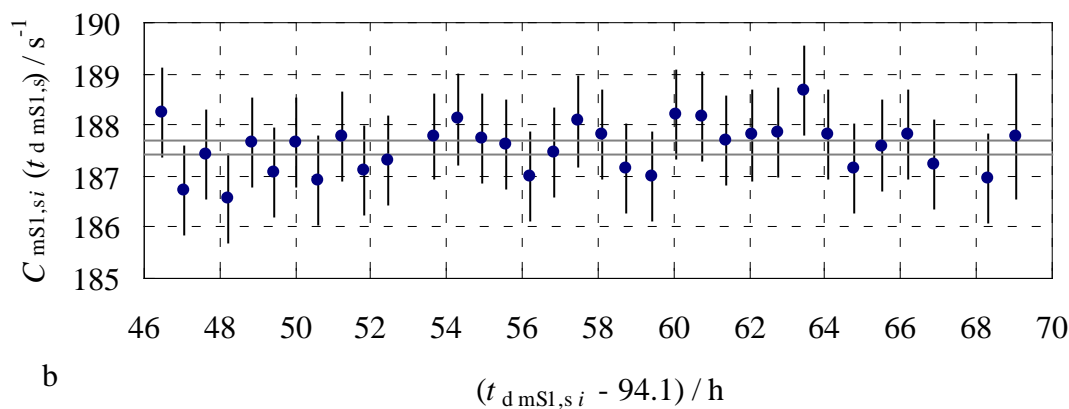
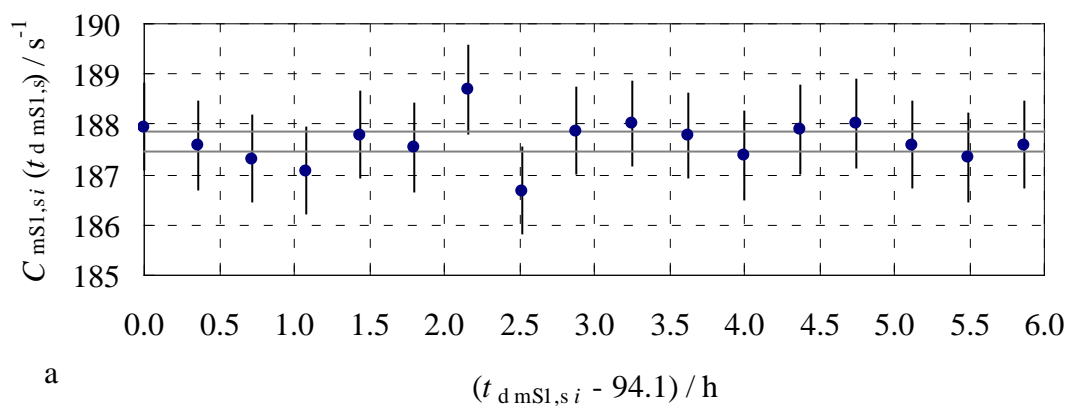
sequence	sample	t_{d1} / h	counts / n
1	mS1,s	94.1	17
2	mS2,s	118.3	38
3	mS1,s	152.9	36
4	mS2,s	163.6	27

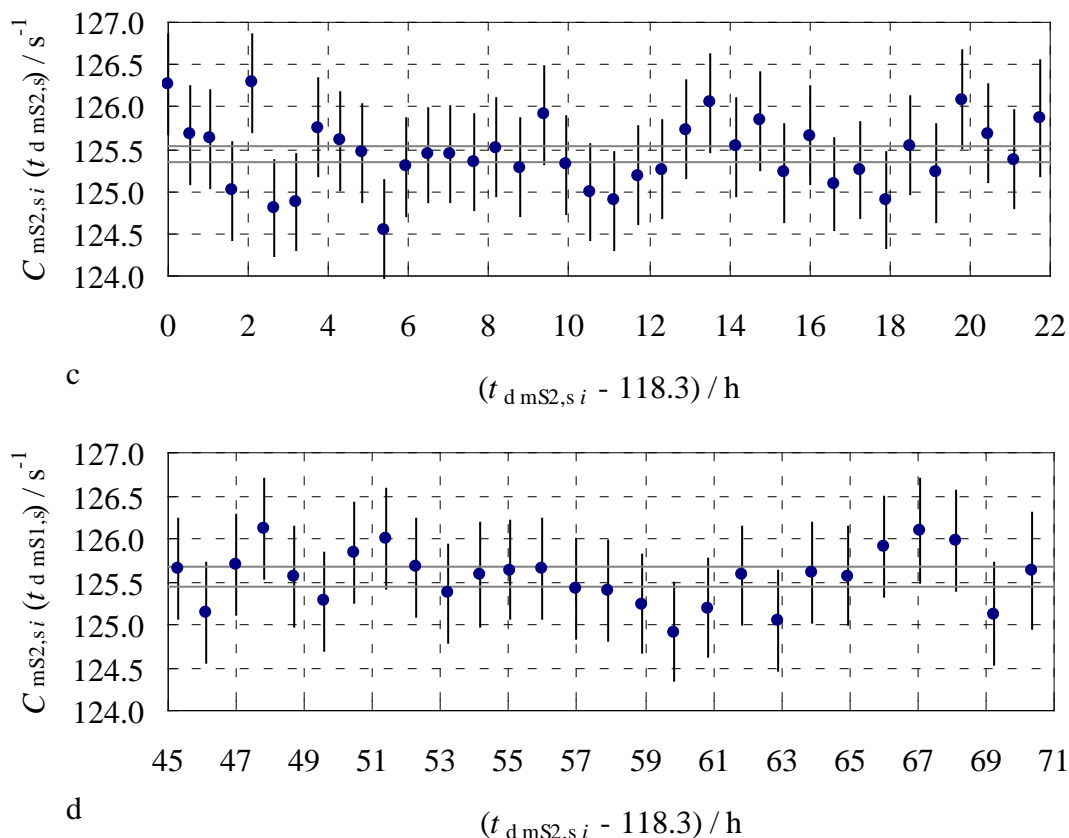
5	mS1,s	692	14
6	mS2,s	1058	22

275 Results and discussion

276 The count rate of the i^{th} count of the sequence, $C_i(t_d)$, was computed according to (8). The
 277 decay constants, $\lambda = \ln(2) / t_{1/2}$, were calculated using the half-life literature values, i.e.
 278 $t_{1/2}({}^{99}\text{Mo}, {}^{99\text{m}}\text{Tc}) = 65.976(24) \text{ h}$ (in equilibrium conditions) and
 279 $t_{1/2}({}^{60}\text{Co}) = 1925.28(14) \text{ d}$ [7, 8]. The net count, $n_{c,i}$, was obtained by fitting the full-
 280 energy γ -peak with the algorithm implemented on the Gamma Vision software (analysis
 281 engine wan32 G53W2.06).

282 The 140.51 keV ${}^{99}\text{Mo}, {}^{99\text{m}}\text{Tc}$ count rates, extrapolated to $t_{d \text{ mS1,s}} = 94.1 \text{ h}$ and
 283 $t_{d \text{ mS2,s}} = 118.3 \text{ h}$, are reported in Fig. 5. Here and hereafter, the error bars indicate the
 284 95 % confidence interval due to counting statistics.



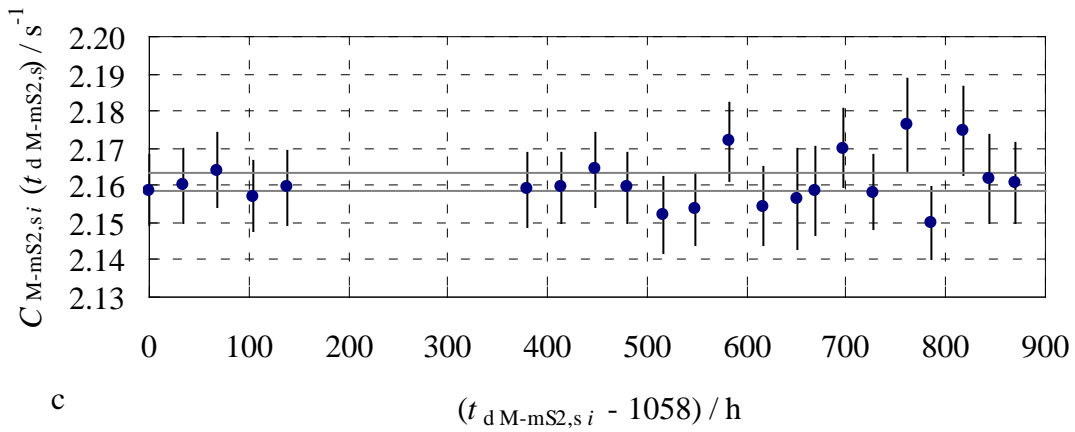
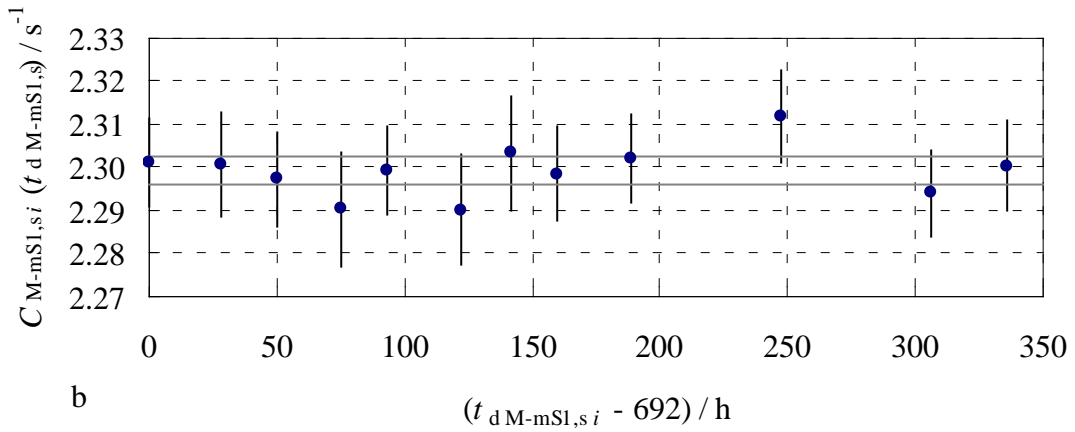
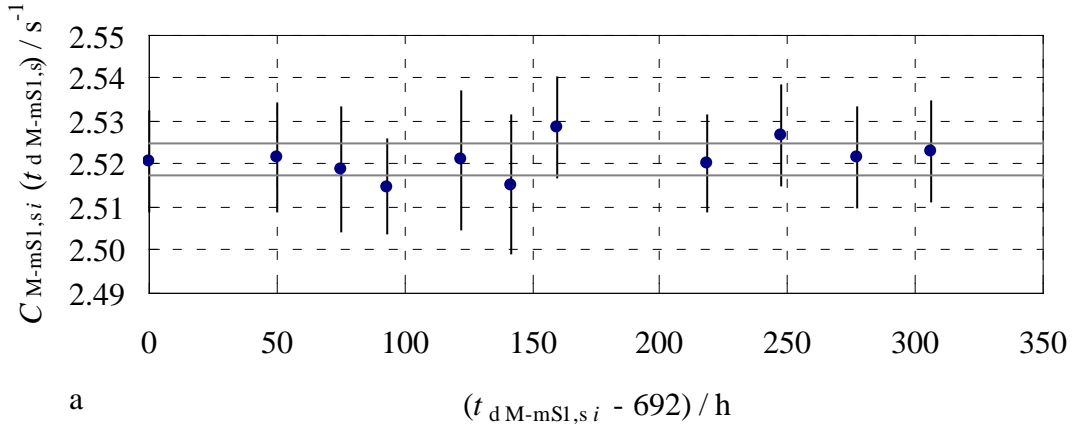


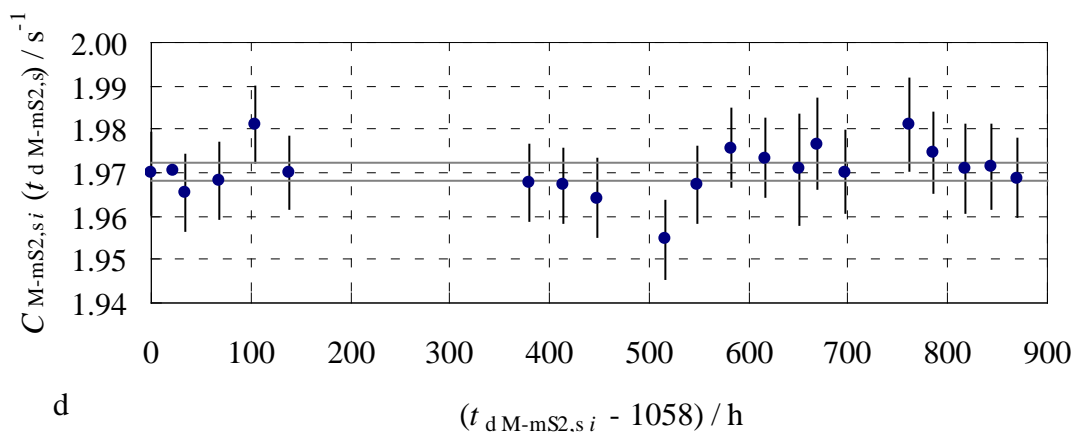
285 **Fig. 5** The 140.51 keV ^{99}Mo , $^{99\text{m}}\text{Tc}$ count rates of the mS1,s sample extrapolated to
 286 $t_{d\text{ mS1,s}} = 94.1$ h and recorded during (a) the sequence 1 and (b) the sequence 3. The
 287 140.51 keV ^{99}Mo , $^{99\text{m}}\text{Tc}$ count rates of the mS2,s sample extrapolated to $t_{d\text{ mS2,s}} = 118.3$ h
 288 and recorded during (c) the sequence 2 and (d) the sequence 4. The horizontal lines show
 289 the 95 % confidence interval associated to the mean of the count rate values

290 The mean values of the 140.51 keV ^{99}Mo , $^{99\text{m}}\text{Tc}$ count rates recorded with the mS1,s and
 291 the mS2,s samples, extrapolated to $t_{d\text{ mS1,s}} = 94.1$ h and $t_{d\text{ mS2,s}} = 118.3$ h, were
 292 $C_{\text{mS1,s}}(t_{d\text{ mS1,s}}) = 187.589(61) \text{ s}^{-1}$ and $C_{\text{mS2,s}}(t_{d\text{ mS2,s}}) = 125.486(36) \text{ s}^{-1}$, respectively
 293 (uncertainties are due to counting statistics). The horizontal lines in Fig. 5 show the 95 %
 294 confidence interval associated to the mean of the count rates values. The count rate ratio,

295
$$\frac{C_{\text{mS1,s}}(t_{d\text{ mS1,s}})}{C_{\text{mS2,s}}(t_{d\text{ mS2,s}})},$$
 was $1.49490(65) \text{ s}^{-1}$.

296 The 1173.23 keV and 1332.49 keV ^{60}Co count rates are reported in Fig. 6.





297 **Fig. 6** (a) The 1173.23 keV and (b) the 1332.49 keV ^{60}Co count rates of the mS1,s
 298 sample recorded during the sequence 5 and extrapolated to $t_{d M-mS1,s} = 692$ h. (c) The
 299 1173.23 keV and (d) the 1332.49 keV ^{60}Co count rates of the mS2,s sample recorded
 300 during the sequence 6 and extrapolated to $t_{d M-mS2,s} = 1058$ h. The horizontal lines show
 301 the 95 % confidence interval associated to the mean of the count rate values

302 The mean values of the 1173.23 keV ^{60}Co count rates recorded with the mS1,s and the
 303 mS2,s samples, extrapolated to $t_{d M-mS1,s} = 692$ h and $t_{d M-mS2,s} = 1058$ h, were
 304 $C_{M-mS1,s}(t_{d M-mS1,s}) = 2.5212(19) s^{-1}$ and $C_{M-mS2,s}(t_{d M-mS2,s}) = 2.1609(11) s^{-1}$, respectively;
 305 the mean values of the 1332.49 keV ^{60}Co count rates recorded with the mS1,s and the
 306 mS2,s samples, extrapolated to $t_{d M-mS1,s} = 692$ h and $t_{d M-mS2,s} = 1058$ h, were
 307 $C_{M-mS1,s}(t_{d M-mS1,s}) = 2.2991(16) s^{-1}$ and $C_{M-mS2,s}(t_{d M-mS2,s}) = 1.9704(10) s^{-1}$, respectively
 308 (uncertainties are due to counting statistics). The horizontal lines in Fig. 6 show the 95 %
 309 confidence interval associated to the mean of the ^{60}Co count rates values. The weighted

310 mean value of the count rate ratios, $\left. \frac{C_{M-mS2,s}(t_{d M-mS2,s})}{C_{M-mS1,s}(t_{d M-mS1,s})} \right|_m$, was $0.85708(55) s^{-1}$.

311 Correction Factors

312 The differences $t_{d mS2,s} - t_{d mS1,s}$ and $t_{d M-mS2,s} - t_{d M-mS1,s}$ were 24.2 h and 366 h,
 313 respectively, i.e. about 0.4 times $t_{1/2}(^{99}\text{Mo}, ^{99m}\text{Tc})$ and 8×10^{-3} times $t_{1/2}(^{60}\text{Co})$.
 314 Accordingly, $\kappa_{td} = 0.77554$ and $\kappa_{M-td} = 0.99452$ with negligible uncertainties.

315 The measurement solutions had a similar Mo and Co mass fraction and the pipetted
 316 subsamples had the same volume. In the case of a 1 mm thick, 12 mm diameter sample
 317 with 2 mg Mo and 10 μg Co, the neutron self-shielding factor is 0.998 for Mo and 1.000
 318 for Co, i.e. 0.2 % epithermal neutron self-shielding for Mo. Even if the solutes were not
 319 uniformly distributed in the paper disks, the neutron self-shielding factors
 320 $k_{\text{ss mS1,s}} = k_{\text{ss mS2,s}}$, $k_{\text{M-ss mS1,s}} = k_{\text{M-ss mS2,s}}$. Similarly, the γ -self-absorption factors
 321 $k_{\text{sa mS1,s}} = k_{\text{sa mS2,s}}$, $k_{\text{M-sa mS1,s}} = k_{\text{M-sa mS2,s}}$ and the geometry factors $k_{\text{g mS1,s}} = k_{\text{g mS2,s}}$,
 322 $k_{\text{M-g mS1,s}} = k_{\text{M-g mS2,s}}$. Thus, $\kappa_{\text{ss}} = \kappa_{\text{M-ss}}^{-1} = \kappa_{\text{sa}} = \kappa_{\text{M-sa}}^{-1} = \kappa_{\text{g}} = \kappa_{\text{M-g}}^{-1} = 1$ with negligible
 323 uncertainty.

324 The full-energy γ -peak detection efficiency ε tends to infinite in a (virtual) vertical
 325 position within the Ge crystal of the detector [9]. This position depends on the γ -photon
 326 energy, E_γ , and is defined by a point, P_{E_γ} (see Fig. 4). A previous characterization of the
 327 detectors showed that the distance between the end-cap and P_{E_γ} is $d_{150\text{ keV}} = 15$ mm for
 328 the GC3518 and $d_{1250\text{ keV}} = 30$ mm for the GEM50P4-83. The distance between the center
 329 of the PE vial and the bottom of the γ -counting container, d_c , and the distance between
 330 the center of the PE vial and the precipitate, d_p , were 17 mm and 8 mm, respectively (see
 331 Fig. 3). The detection efficiency correction factors are

$$332 \quad \kappa_\varepsilon = \frac{(d_{\text{Mo}} + \Delta d_{\text{Mo2}})^2}{(d_{\text{Mo}} + \Delta d_{\text{Mo1}})^2} \quad \text{and} \quad \kappa_{\text{M-}\varepsilon} = \frac{(d_{\text{Co}} + \Delta d_{\text{Co2}})^2}{(d_{\text{Co}} + \Delta d_{\text{Co1}})^2}, \quad (16)$$

333 where Δd_{Mo1} and Δd_{Mo2} are the distances between the Mo center of mass and the center
 334 of the PE vial in sample 1 and 2, Δd_{Co1} and Δd_{Co2} are the distances between the
 335 Co center of mass and the center of the PE vial in sample 1 and 2,
 336 $d_{\text{Mo}} = d_{150\text{ keV}} + d_{\text{GC3518}} + d_c = 262$ mm and $d_{\text{Co}} = d_{1250\text{ keV}} + d_{\text{GEM50P4-83}} + d_c = 132$ mm.
 337 As examples, if in both the samples all the Mo and Co were in the precipitate, i.e.
 338 $\Delta d_{\text{Mo1}} = \Delta d_{\text{Mo2}} = \Delta d_{\text{Co1}} = \Delta d_{\text{Co2}} = d_p$, $\kappa_\varepsilon = \kappa_{\text{M-}\varepsilon}^{-1} = 1$. Instead, if in sample 2 only a
 339 fraction of Mo and Co was in the precipitate, i.e. $\Delta d_{\text{Mo1}} = \Delta d_{\text{Co1}} = d_p$ and
 340 $\Delta d_{\text{Mo2}} = \Delta d_{\text{Co2}} = d_p - \Delta d_p$, in the case of $\Delta d_p = 4$ mm, $\kappa_\varepsilon = 0.985$ and $\kappa_{\text{M-}\varepsilon} = 0.971$.

341 Since the actual positions of Mo and Co centers of mass were not measured,
 342 $\Delta d_p = \pm 4$ mm (uniform distribution) was preliminary assigned. Accordingly,
 343 $\kappa_\varepsilon = 1.000(9)$ and $\kappa_{M-\varepsilon} = 1.000(16)$.

344 The literature Q_0 values for ^{98}Mo and ^{59}Co are 53.1(33) and 1.993(60) [10]. Experimental
 345 data for the α value at the LENA irradiation channel are missing. However, based on the
 346 $\alpha = -0.051(8)$ value at the central channel of the TRIGA Mark II reactor operating in
 347 Ljubljana [11], from (9) it follows that $Q_{0,\text{Mo}}(\alpha) = 70(9)$, $Q_{0,\text{Co}}(-0.051) = 2.5(6)$ and
 348 $\alpha_Q = -0.965(10)$.

349 Due to the 10.9 nominal f value, about 85% of the ^{60}Co activity was produced by thermal
 350 neutrons. As the ^{60}Co count rate of sample 2 to the count rate of sample 1 ratio was about
 351 0.86, the Φ_{th1} was approximately 16 % higher than Φ_{th2} and a possible variation of f could
 352 be expected. In the case of $\alpha_f = \pm 0.025$ (uniform distribution) and 10 % relative
 353 uncertainty for the f value, $\beta_R = 1.000(10)$.

354 *Uncertainty budget*

355 The application of (15) to the experimental data collected in this study gave a ratio
 356 $\tau = 0.999(19)$. The provisional uncertainty budget calculated according to the Guide to
 357 the Expression of Uncertainty in Measurement [12] is reported in table 2.

358 **Table 2** Uncertainty budget of the measured ratio τ . The input quantities x_i are given in
 359 the text. The index column gives the relative contributions of $u(x_i)$ to the combined
 360 standard uncertainty, $u_c(y)$, of τ

Quantity	Unit	Value	Standard uncertainty	Index
X_i	$[X_i]$	x_i	$u(x_i)$	%
$m_{1,\text{MS}}$	g	0.12572	0.00004	0.0
$m_{2,\text{MS}}$	g	0.12572	0.00004	0.0
m_{ES1}	g	27.03259	0.00006	0.0

m_{ES2}	g	27.03259	0.00006	0.0
$C_{mS1,s}/C_{mS2,s}$	1	1.49490	0.00065	0.0
$C_{M-mS2,s}/C_{M-mS1,s}$	1	0.85708	0.00055	0.1
β_R	1	1.000	0.010	22.8
κ_{td}	1	0.77554	0.00000	0.0
κ_{M-td}	1	0.99452	0.00000	0.0
$\kappa_{ss} (\kappa_{M-ss})^{-1}$	1	1.00000	0.00000	0.0
$\kappa_{sa} (\kappa_{M-sa})^{-1}$	1	1.00000	0.00000	0.0
$\kappa_g (\kappa_{M-g})^{-1}$	1	1.00000	0.00000	0.0
κ_ε	1	1.000	0.009	18.5
$\kappa_{M-\varepsilon}$	1	1.000	0.016	58.5
Y	[Y]	y	$u_c(y)$	
τ	1	0.999	0.019	100.0

361 Given that the variation of the shape of the neutron energy spectrum and the detection
 362 efficiency were the main influence factors, the following ways are suggested to reduce
 363 their effects.

364 In particular, the measurement model shows that the adoption of a monitor element
 365 having a Q_0 value similar to the Q_0 value of ^{99}Mo makes the result almost independent on
 366 f , α , $Q_{0,E}$, and $Q_{0,EM}$ values. The best choice among the potential target elements is the
 367 ^{116}Sn , which is neutron activated to ^{117}Sn via (n, γ) capture reaction and detected via the
 368 158.56 keV γ -photons emitted during the radioactive decay of ^{117}Sn ($t_{1/2} = 13.76(4)$ d
 369 [13]). The outcome of the $Q_0 = 56.3(11)$ value [10] of ^{116}Sn might be a $\beta_R = 1$ with a
 370 relative uncertainty below 0.01 %.

371 Moreover, the actual position of the radionuclide center of mass with respect to the center
 372 of the 8 mL PE vial can be experimentally determined by counting the sample right-side-
 373 up and up-side-down. See equation (S1) in the supplementary information for detail.
 374 Hence, the knowledge of the Δd_p value and the increase of the distance of the samples

375 from the detector during the γ -counting might limit the κ_{ε} and $\kappa_{M-\varepsilon}$ relative uncertainty
376 below 0.1 %.

377 **Conclusions**

378 The possibility of using the INAA technique to determine the ratio of the mass fractions
379 of two mono-elemental solutions with a relative expanded uncertainty of less than 0.1 %
380 was investigated. To reach the target uncertainty, the addition of a monitor solution to the
381 elemental solution was essential to correct for possible variation of the neutron energy
382 spectrum at the irradiation positions. A procedure was developed and the related
383 measurement model was obtained from the neutron activation equation.

384 The proposed measurement procedure was applied in a feasibility test in the case of two
385 Mo solutions having the same mass fraction, i.e. obtained from the same solution, and
386 using Co as the monitor element. The departure of the measured ratio from the unit value
387 (-0.1 %) was in agreement with the evaluated 1.9 % relative uncertainty. The uncertainty
388 budget pointed out that the main contributors were the variation of the shape of the
389 neutron energy spectrum and the detection efficiency.

390 The target 0.1 % relative expanded uncertainty was not achieved. Nevertheless, the use of
391 INAA to link up Mo solutions to the SI is promising; a considerable decrease of the
392 measurement uncertainty might be reached by improved sample preparation and an
393 improved γ -counting technique.

394 **Acknowledgements**

395 Financial support by the European Metrology Research Programme (EMRP) is gratefully
396 acknowledged (EMRP-SIB09 “Purity standards for challenging elements”) [14]. The
397 EMRP is jointly funded by the EMRP participating countries within the European
398 Association of National Metrology Institutes (EURAMET). The authors are grateful to
399 the referee for providing constructive comments and help in improving the contents of
400 this paper.

401 **References**

- 402 1. D'Agostino G, Bergamaschi L, Giordani L, Oddone M, Kipphardt H, Richter S (2014)
403 Use of Instrumental Neutron Activation Analysis to investigate the distribution of
404 trace elements among subsamples of solid materials. *Metrologia* 51:48-53
- 405 2. Kaltenbach A, Noordmann J, Görlitz V, Pape C, Richter S, Kipphardt H, Kopp G,
406 Jährling R, Rienitz O, Güttler B (2015) Gravimetric preparation and characterization
407 of primary reference solutions of molybdenum and rhodium. *Anal Bioanal Chem*
408 407:3093-3102
- 409 3. Rienitz O, Schiel D, Görlitz V, Jährling R, Vogl J, Lara-Manzano J V, Zoń A, Fung W
410 H, Buzoianu M, Cacicano de Sena R, Augusto dos Reis L, Valiente L, Yim Y H, Hill S,
411 Champion R, Fiscaro P, Bing W, Turk G C, Winchester M R, Saxby D, Merrick J,
412 Hioki A, Miura T, Suzuki T, Linsky M, Barzev A, Máriássy M, Cankur O, Ari B,
413 Tunç M, Konopelko L A, Kustikov Y A, Bezruchko M (2012) Final report on CCQM-
414 K87: Mono-elemental calibration solutions. *Metrologia* DOI 10.1088/0026-
415 1394/49/1A/08010
- 416 4. Høgdahl OT (1965) Proceedings of the Symposium on Radiochemical Methods of
417 Analysis 1:23-40
- 418 5. De Corte F (1987) The k_0 -Standardisation Method. A move to the optimization of
419 Neutron Activation Analysis. Ed. Ryksuniversiteit Gent Faculteit Van de
420 Wettenschappen
- 421 6. GammaVision (2006) Version 6.08; Advanced Measurement Technology, Inc.:
422 Berwyn, PA
- 423 7. Browne E, Tuli J K (2011) *Nucl Data Sheets* 112:275-446
- 424 8. Browne E, Tuli J K (2013) *Nucl Data Sheets* 114:1849-2022
- 425 9. Gilmore G, Hemingway J D (1995) *Practical Gamma-ray Spectrometry*, New York,
426 Wiley
- 427 10. Kolotov VP, De Corte F (2004) Compilation of k_0 and related data for NAA in the
428 form of electronic database (IUPAC Technical Report). *Pure Appl. Chem.* 76:1921-
429 1925

- 430 11. Jovanovic S, Vukotic P, Smodis B, Jacimovic R, Mihaljevic N, Stegnar P (1989)
431 Epithermal neutron flux characterization of the TRIGA Mark II reactor, Ljubljana,
432 Yugoslavia, for use in NAA. J. Radioanal. Nucl. Chem. 129:343-349
433 12. JGCM 100:2008 (2008) Evaluation of measurement data - Guide to the expression of
434 uncertainty in measurement
435 13. Blachot J (2002) Nucl Data Sheets 95:679-836
436 14. Online available at <http://www.ptb.de/emrp/sib09.html>

437 **Supplementary information**

438 *Irradiation samples*



439

440 **Fig. S1** The precipitates in the upper part of the piled disks of the PE vials after drying

441 *Position of the radionuclide center of mass*

442 The distance between the radionuclide center of mass with respect to the center of the
443 8 mL PE vial, Δd , can be determined by using the following formula:

444

$$\frac{C_{\text{rsu}}(t_d)}{C_{\text{usd}}(t_d)} = \frac{1 - \frac{\Delta d}{d}}{1 + \frac{\Delta d}{d}}, \quad (\text{S1})$$

445 where $C_{\text{rsu}}(t_d)$, $C_{\text{rsd}}(t_d)$ are the count rates recorded with the right-side-up and up-side-
446 down sample, respectively, and d is the distance between the center of the 8 mL PE vial
447 and the (virtual) vertical position where the detector efficiency tends to infinite.