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Title page

Names of the authors: Giancarlo D'Agostino⁽¹⁾, Luigi Bergamaschi⁽¹⁾, Marco Di
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

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

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

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

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

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

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

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

23 Abstract

The possibility of using neutron activation analysis to link up a secondary to a primary mono-elemental solution was investigated. A procedure was developed for the determination of the ratio between the mass fractions of two solutions. The use of a monitor element was essential to limit the effect of the non-uniformity of the neutron flux during irradiation. The proposed procedure was tested in the case of two molybdenum solutions having the same mass fraction. Although the experiment did not reach the goal, 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

Mono-elemental solutions with a mass fraction of 1 g kg⁻¹ are being used in almost every chemical laboratory in social, medical and industrial fields to calibrate analytical measurements. The accuracy of those solutions is essential for the reliability and 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 ($w_{pur} \ge 0.999 \text{ g s}^{-1}$) 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].

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

proposed procedure was experimentally tested in the case of two Mo solutions having thesame 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

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

70 with a relative expanded uncertainty of 0.1 %.

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

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

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

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

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

88 and

89
$$w_{mS1}(E_M) = \frac{w_{MS}(E_M)}{1 + \frac{m_{ES1} - m_{ev1}}{m_{1,MS}}}, \ w_{mS2}(E_M) = \frac{w_{MS}(E_M)}{1 + \frac{m_{ES2} - m_{ev2}}{m_{2,MS}}},$$
(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 ${}^{i}E$ of E and of an isotope ${}^{i}E_{M}$ of E_{M} in mS1,s and 93 mS2,s are

94
$$n_{\rm mS1,s}(^{i}{\rm E}) = \frac{x(^{i}{\rm E}) N_{\rm A} w_{\rm mS1}({\rm E}) m_{\rm mS1,s}}{M({\rm E})}, \ n_{\rm mS2,s}(^{i}{\rm E}) = \frac{x(^{i}{\rm E}) N_{\rm A} w_{\rm mS2}({\rm E}) m_{\rm mS2,s}}{M({\rm E})}, \quad (4)$$

96
$$n_{mS1,s}({}^{i}E_{M}) = \frac{x({}^{i}E_{M})N_{A}w_{mS1}(E_{M})m_{mS1,s}}{M(E_{M})}, n_{mS2,s}({}^{i}E_{M}) = \frac{x({}^{i}E_{M})N_{A}w_{mS2}(E_{M})m_{mS2,s}}{M(E_{M})}, (5)$$

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, $x({}^{i}E)$ and $x({}^{i}E_M)$ are the mole fractions of ${}^{i}E$ and ${}^{i}E_M$, 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
$$\tau = \frac{\left(1 + \frac{m_{1,MS} - m_{ev1}}{m_{ES1}}\right) \frac{n_{mS1,s}(^{i}E)}{m_{mS1,s}}}{\left(1 + \frac{m_{2,MS} - m_{ev2}}{m_{ES2}}\right) \frac{n_{mS2,s}(^{i}E)}{m_{mS2,s}}}.$$
 (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 ${}^{i}E$ and ${}^{i}E_{M}$.

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

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

108 where $C(t_d)$ 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 $C(t_d)$. The correction factors $\kappa_{td} = e^{-\lambda(t_d \,\mathrm{mS2,s^{-t_d}\,mS1,s})}$, $\kappa_{\mathrm{R}} = R_{\mathrm{mS2,s}}/R_{\mathrm{mS1,s}}$, 111 $\kappa_{\varepsilon} = \varepsilon_{\mathrm{mS2,s}}/\varepsilon_{\mathrm{mS1,s}}$, $\kappa_{\mathrm{ss}} = k_{\mathrm{ss}\,\mathrm{mS2,s}}/k_{\mathrm{ss}\,\mathrm{mS1,s}}$, $\kappa_{\mathrm{sa}} = k_{\mathrm{sa}\,\mathrm{mS2,s}}/k_{\mathrm{sa}\,\mathrm{mS1,s}}$ and 112 $\kappa_{\mathrm{g}} = k_{\mathrm{g}\,\mathrm{mS2,s}}/k_{\mathrm{g}\,\mathrm{mS1,s}}$ take the differences of decay time, reaction rate, detection 113 efficiency, self-shielding, self-absorption and geometry of the sub-samples into account.

In detail, λ is the decay constant of the produced radionuclide, *R* is the reaction rate per target isotope ^{*i*}E, ε is the detection full-energy γ efficiency for a point-like source located at the center of mass of the sub-sample, k_{ss} , k_{sa} , and k_g are the neutron self-shielding, the 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 ratios,
$$\frac{C_{\text{mS1,s}}(t_{\text{d mS1,s}})}{C_{\text{mS2,s}}(t_{\text{d mS2,s}})}\Big|_{\text{m}}$$
, obtained with different E₇.

121 The γ -counting is carried out using germanium detectors. The count rate $C(t_d)$ is obtained 122 by averaging *n* values, $C_i(t_d)$, acquired in a γ -spectrometry sequence starting at a decay 123 time $t_{d\,1}$ 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 $C_i(t_d)$, extrapolated to t_d from the *i*th count of the sequence, starting at $t_{d\,i}$ and lasting $t_{c\,i}$, is

126
$$C_{i}(t_{d}) = \frac{\lambda n_{ci}}{e^{-\lambda (t_{d}i^{-t_{d}})} (1 - e^{-\lambda t_{ci}})} \frac{t_{ci}}{t_{ci} - t_{deadi}},$$
(8)

127 where $n_{c i}$ 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*}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*}E at 0.0253 eV and

134
$$Q_{0,E}(\alpha) = (Q_{0,E} - 0.429)\overline{E}_{r}^{-\alpha} + \frac{0.429}{(2\alpha + 1)0.55^{\alpha}}.$$
 (9)

135 In (9) $Q_{0,E}$ is the ratio between the resonance integral of ^{*i*}E for a 1/*E* epithermal spectrum,

136 $I_{0,E}$, and $\sigma_{0,E}$, and \overline{E}_r is the effective resonance energy of ^{*i*}E [5].

137 Thus, the characteristics of the neutron energy spectrum affect the $\kappa_{\rm R}$ correction factor 138 according to

139
$$\kappa_{\rm R} = \frac{\Phi_{\rm ep2}(f_2 + Q_{0,\rm E}(\alpha_2))}{\Phi_{\rm ep1}(f_1 + Q_{0,\rm E}(\alpha_1))}, \tag{10}$$

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.

Several methods have been developed and used to measure the neutron flux parameters; as examples, (i) the "Cd-covered multi-monitor", the "Cd-ratio for multi-monitor" and the "bare multi-monitor" methods for α , (ii) the "Cd-ratio" for Φ_{ep} and f, (iii) the "bare bi-isotopic monitor" method for f [5]. These methods are usually applied offline, i.e. before (or after) the experiment, by assuming that the neutron energy spectrum remains constant and do not depend on the irradiation samples. In our case, since the $\kappa_{\rm R}$ value is required with a relative expanded uncertainty of less than 0.1 %, online information is valuable. To reach this aim, the monitor solution is added to the elemental solution. If the Høgdahl convention applies to the target isotope $^{i}E_{\rm M}$,

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

153 From (10) and (11) it follows

154
$$\kappa_{\rm R} = \kappa_{\rm M-R} \frac{1 + \frac{\alpha_{\rm Q} \, Q_{0,\rm E}(\alpha)}{f_1 + Q_{0,\rm E}(\alpha)}}{1 + \frac{\alpha_{\rm Q} \, Q_{0,\rm E}(\alpha)}{f_1(1 + \alpha_f) + Q_{0,\rm E}(\alpha)}}, \tag{12}$$

155 where
$$\alpha_{\rm Q} = \frac{Q_{0,\rm EM}(\alpha) - Q_{0,\rm E}(\alpha)}{Q_{0,\rm E}(\alpha)}$$
 and $\alpha_{\rm f} = \frac{f_2 - f_1}{f_1}$.

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

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

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

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

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

163
$$\tau = \frac{m_{\rm ES2}}{m_{\rm ES1}} \frac{m_{\rm 1,MS}}{m_{\rm 2,MS}} \frac{C_{\rm mS1,s}(t_{\rm d\,mS1,s})}{C_{\rm mS2,s}(t_{\rm d\,mS2,s})} \frac{C_{\rm M-mS2,s}(t_{\rm d\,M-mS2,s})}{C_{\rm M-mS1,s}(t_{\rm d\,M-mS1,s})}, \qquad (15)$$
$$\times \beta_{\rm R} \kappa_{\rm td} \kappa_{\rm M-td}^{-1} \kappa_{\rm ss} \kappa_{\rm M-ss}^{-1} \kappa_{\rm sa} \kappa_{\rm M-sa}^{-1} \kappa_{\rm g} \kappa_{\rm M-g}^{-1} \kappa_{\rm \epsilon} \kappa_{\rm M-\epsilon}^{-1}$$

164 where
$$\beta_{\rm R} = \frac{1 + \frac{\alpha_{\rm Q} Q_{0,\rm E}(\alpha)}{f_1 + Q_{0,\rm E}(\alpha)}}{1 + \frac{\alpha_{\rm Q} Q_{0,\rm E}(\alpha)}{f_1(1 + \alpha_{\rm f}) + Q_{0,\rm E}(\alpha)}}$$

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

170 **Experimental**

171 The proposed procedure was tested using a Mo solution having a mass fraction 172 $w(Mo) \approx 1 \text{ g kg}^{-1}$. In this preliminary experiment, a Co solution having a mass fraction 173 $w(Co) \approx 1 \text{ g kg}^{-1}$ was adopted as the monitor solution. The Mo and Co solutions were 174 obtained using ultrapure ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$, 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 ⁹⁹Mo and ^{99m}Tc in equilibrium conditions and produced by

activation of ⁹⁸Mo 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 ⁶⁰Co produced by 186 activation of ⁵⁹Co 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, $m_{\rm mS}$, 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 μ L 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 919 s, (iii) 1025 s and 1285 s. The evaporation rates were found to be 2.1×10^{-6} g s⁻¹, 201 2.0×10^{-6} g s⁻¹ and 3.3×10^{-6} g s⁻¹. According to the fitted data, the masses of the added 202 203 solutions at steps (i), (ii) and (iii) were $m_{\text{ES}} = 20.96218(4)$ g, $m_{\text{MS}} = 0.12572(4)$ g and 204 $m_{\rm ES} = 6.07041(4)$ 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*

217

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.



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

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

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

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

232 *Neutron irradiation and gamma spectrometry*

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 6×10^{12} cm⁻² s⁻¹ and 5.5×10^{11} cm⁻² 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.



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

- After the neutron irradiation, the samples were extracted from the container, rinsed with
- 243 diluted HNO₃ and fixed to a γ -counting container (Fig. 3).



244

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

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

251 Six *y*-spectrometry sequences were recorded with a digital signal processor ORTEC® DSPEC 502 and a personal computer running the software for data acquisition 252 ORTEC® Gamma Vision [6]. The first four sequences were performed with the GC3518 253 and concerned the 140.51 keV *y*-emission of ⁹⁹Mo and ^{99m}Tc in equilibrium conditions. 254 255 The latter two y-spectrometry sequences were performed with the GEM50P4-83 and concerned the 1173.23 keV and 1332.49 keV γ -emission of ⁶⁰Co. Each sequence 256 257 consisted of *n* counts performed by adjusting on-line the counting window to reach a 0.23 % counting uncertainty. The dead to counting time ratio, t_{dead}/t_c , of the detection 258 259 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 $d_{\text{GC3518}} = 230 \text{ mm}$ and $d_{\text{GEM50P4-83}} = 85 \text{ mm}$.



264

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

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

273	Table 1 The sample, the decay time, $t_{d,1}$, and the number of collected counts, <i>n</i> , in each
274	sequence

sequence	sample	<i>t</i> _{d 1} / 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**

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

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





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

The mean values of the 140.51 keV ⁹⁹Mo, ^{99m}Tc count rates recorded with the mS1.s and 290 the mS2,s samples, extrapolated to $t_{d mS1,s} = 94.1 \text{ h}$ and $t_{d mS2,s} = 118.3 \text{ h}$, were 291 $C_{\rm mS1,s}(t_{\rm d\ mS1,s}) = 187.589(61)\ {\rm s}^{-1}$ 292 and $C_{\rm mS2,s}(t_{\rm d\,mS2,s}) = 125.486(36) \, {\rm s}^{-1},$ 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, († \sim ١

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

The 1173.23 keV and 1332.49 keV 60 Co count rates are reported in Fig. 6.





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

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

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

311 *Correction Factors*

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, respectively, i.e. about 0.4 times $t_{1/2}(^{99}Mo, ^{99m}Tc)$ and 8×10^{-3} times $t_{1/2}(^{60}Co)$. 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 $k_{\rm ss mS1,s} = k_{\rm ss mS2,s}, \quad k_{\rm M-ss mS1,s} = k_{\rm M-ss mS2,s}.$ Similarly, the γ -self-absorption factors $k_{\text{sa mS1,s}} = k_{\text{sa mS2,s}}$, $k_{\text{M-sa mS1,s}} = k_{\text{M-sa mS2,s}}$ and the geometry factors $k_{\text{g mS1,s}} = k_{\text{g mS2,s}}$, 321 $k_{\text{M-g mS1,s}} = k_{\text{M-g mS2,s}}$. 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 322 323 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 energy, E_{γ} , and is defined by a point, $P_{E\gamma}$ (see Fig. 4). A previous characterization of the 326 detectors showed that the distance between the end-cap and $P_{E\gamma}$ is $d_{150 \text{ keV}} = 15 \text{ mm}$ for 327 the GC3518 and $d_{1250 \text{ keV}} = 30 \text{ mm}$ for the GEM50P4-83. The distance betwen the center 328 of the PE vial and the bottom of the γ -counting container, d_c , and the distance between 329 330 the center of the PE vial and the precipitate, $d_{\rm p}$, were 17 mm and 8 mm, respectively (see 331 Fig. 3). The detection efficiency correction factors are

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

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

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

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

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

354 Uncertainty budget

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

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

Quantity	Unit	Value	Standard uncertainty	Index
X_i	$[X_i]$	Xi	$u(x_i)$	%
<i>m</i> _{1,MS}	g	0.12572	0.00004	0.0
m _{2,MS}	g	0.12572	0.00004	0.0
$m_{\rm ES1}$	g	27.03259	0.00006	0.0

$m_{\rm ES2}$	g	27.03259	0.00006	0.0
$C_{\mathrm{mS1,s}}/C_{\mathrm{mS2,s}}$	1	1.49490	0.00065	0.0
$C_{\text{M-mS2,s}}/C_{\text{M-mS1,s}}$	1	0.85708	0.00055	0.1
$\beta_{ m R}$	1	1.000	0.010	22.8
Ktd	1	0.77554	0.00000	0.0
K _{M-td}	1	0.99452	0.00000	0.0
$\kappa_{ss} (\kappa_{M-ss})^{-1}$	1	1.00000	0.00000	0.0
$\kappa_{\rm sa} (\kappa_{\rm M-sa})^{-1}$	1	1.00000	0.00000	0.0
$\kappa_{g} (\kappa_{M-g})^{-1}$	1	1.00000	0.00000	0.0
Κε	1	1.000	0.009	18.5
<i>К</i> М-ғ	1	1.000	0.016	58.5
Y	[<i>Y</i>]	У	$u_{\rm c}(y)$	
τ	1	0.999	0.019	100.0

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

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

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

377 **Conclusions**

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

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

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437 Supplementary information

438 Irradiation samples



439



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
$$\frac{C_{\rm rsu}(t_{\rm d})}{C_{\rm usd}(t_{\rm d})} = \frac{1 - \frac{\Delta d}{d}}{1 + \frac{\Delta d}{d}},$$
 (S1)

445 where $C_{rsu}(t_d)$, $C_{rsd}(t_d)$ 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.