Uncertainty evaluation of a modified elimination weighing for source preparation

F L Cacais¹,², J U Delgado¹ and V M Loayza²
¹ Laboratório Nacional de Metrologia das Radiações Ionizantes / Instituto de Radioproteção e Dosimetria – LNMRI/IRD – Brazil
² Instituto Nacional de Metrologia, Qualidade e Tecnologia – Inmetro – Brazil

E-mail: facacais@gmail.com

Abstract. Some modifications in elimination weighing method for radioactive source allowed correcting weighing results without non-linearity problems assign a uncertainty contribution for the correction of the same order of the mass of drop uncertainty and check weighing variability in series source preparation. This analysis has focused in knowing the achievable weighing accuracy and the uncertainty estimated by Monte Carlo method for a mass of a 20 mg drop was at maximum of 0.06%.

1. Introduction
In radionuclide metrology, radioactive sources preparation encompasses a weighing procedure able to achieve standard uncertainties below than 20 µg in the range from 10 mg to 100 mg [1]. The Elimination Weighing method meets this requirement for micro-drops deposition or dilution of a master solution using a plastic pycnometer [2]. In this weighing procedure three weighing steps are performed per source: the pycnometer is weighed before and after dispensing the drop of solution, and by knowing the mass of the drop (by the weighing difference), one or several standard weights [3] are added on the balance load receptor and the third weighing reading is recorded. The mass of the drop is obtained from the difference between first and third weighing thus avoiding non-linearity errors problems. To avoid correlations in series sources preparation this method suggests to weigh the pycnometer before each drop deposition. The absence of systematic errors between the weighing (evaporation, drying of a drop in capillary stem, zero drift of the balance) is checked by the criterion that the difference between third and second weighing readings should be in agreement with conventional mass [4] of standards within twice the uncertainty.

In despite of, by elimination weighing it is not possible to correct systematic errors without take into account non-linearity errors on the third and second weighing and its uncertainty contribution. Furthermore, this method does not provide any estimate to check variability in series sources preparation. Thus, in order to improve the reliability of the elimination method, this work proposes a modification that allows: correcting weighing results without non-linearity problems, assign a uncertainty contribution for correction of the same order of the mass of drop uncertainty and check weighing variability in series source preparation.

The modification consists in performer the second weighing in elimination method also with the same or different standard weights used in third weighing. In the original elimination method [5] the second weighing was performed by this way and it relies on the previously planned procedure. For an experienced staff the diameter of the stem tip of a laboratory-made pycnometer [6] is adjusted such the
mass per drop is previously known with 2 mg of difference from the true value. This approximation
could be improved by performing the weighing of some drops before to execute the weighing
procedure. Thus, the suitable amount of mass standards can be available close to the balance at
the moment of the weighing. By this way, the standard weights and the pycnometer are placed together on
the balance receptor at the second weighing and its mass is adjusted until the difference to first reading
is less than 3 mg (for 0.001 mg resolution balance) limiting non-linearity error [7].

By this proposal, one can obtain two weighing differences to form a restrained underdetermined
equation system which can be solved including a restrain, the mass of standard weights. This solution
provides a mass value of the standard weights in addition to the mass of the drop. The mass of the
standards could be used to estimate errors difference in weighing on some assumptions about linear
error structure (constant, increasing and different in one weighing from the two equal others). The
values for mass standards obtained from weighing of a series source preparing could be used to set a
long-run standard deviation [8] and to check weighing variability in source preparation serie, so
providing information to variability studies [9].

In this study the measurement models for the mass measurement are showed and an estimate of the
correction to linear errors in weighing is presented. A routinely assumed error structure on weighing is
defined to evaluate the applicability of correction and its uncertainty. The uncertainty to the correction
and mass values corrected are calculated by Monte Carlo method [10] to a simulated weighing
condition in order to evaluate the achievable accuracy for this modified method in order to implement
it.

2. Measurement model
On the assumption of the balance has been adjusted before weighing, the difference \( \Delta I_{1i} \) between the
first weighing, that includes the conventional mass of the drop \( m_{c,d} \), and the \( i \)th (2nd or 3rd) weighing
with standard weights of conventional mass \( m_{c,p} \) can be written as in equation (1).

\[
\Delta I_{1i} = m_{c,d} - m_{c,p_i} \tag{1}
\]

In equation (2), the difference \( \Delta I_{1i} \) includes the balance readings for 1st weighing \( R_1 \) and the \( i \)th
weighing \( R_i \), sensitivity error \( \Delta S \) and the buoyancy correction [11] which take in account the air
density \( \rho_a \), the conventional air density \( \rho_0 \) (1.2 kg m\(^{-3}\)), density of the master solution \( \rho_s \), density of
balance reference standards \( \rho_R \) and the density of standards weighed together with the solution \( \rho_c \).

\[
\Delta I_{1i} = \left( R_i - R_1 \right) \left( 1 - \frac{(\rho_a - \rho_0)}{\rho_R} \right) + \left( \rho_a - \rho_0 \right) \left( \frac{R_i - R_1}{\rho_s - \rho_c} \right) \left( 1 - \Delta S \right) \tag{2}
\]

From the two weighing differences a system of equations in matrix form can be mounted, as in equation (3).

\[
\begin{bmatrix}
\Delta I_{12} \\
\Delta I_{13}
\end{bmatrix} =
\begin{bmatrix}
1 & -1 & 0 \\
1 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
m_{c,d} \\
m_{c,p_1} \\
m_{c,p_2}
\end{bmatrix} \tag{3}
\]

This system could be solved regarding one (\( p_1 \)) or two (\( p_1 \) and \( p_2 \)) reference mass standards. The
solution of this system, on the assumption of one reference standard with conventional mass \( m_{c,p_1} \)
provides the measurement models in equations (4 – 5) for the conventional mass of the drop \( m_{c,d1R} \) (1R
means obtained by one reference), and for the estimated mass of the other standard \( m_{c,p_2} \).
mc_{d1R} = \left( R_1 - R_2 \right) \left( \frac{\rho_s - \rho_0}{\rho_R} \right) + \left( \rho_s - \rho_0 \right) \left( \frac{R_1}{\rho_s} - \frac{R_2}{\rho_2} \right) \left( 1 - \Delta S \right) + mc_{p1} - (e_1 - e_2) \quad (4)

mc_{p2} = \left( R_2 - R_3 \right) \left( \frac{\rho_s - \rho_0}{\rho_R} \right) + \left( \rho_s - \rho_0 \right) \left( \frac{R_3}{\rho_s} - \frac{R_2}{\rho_2} \right) \left( 1 - \Delta S \right) + mc_{p1} - (e_3 - e_2) \quad (5)

When the two standards are set as reference just one solution for the conventional mass of drop \( mc_{d2R} \) is possible. This solution is showed in equation (6).

\[
mc_{d2R} = \left[ \left( R_1 - R_2 + R_3 \right) - \frac{1}{2} \left( \frac{\rho_s - \rho_0}{\rho_R} \right) \right] + \left( \rho_s - \rho_0 \right) \left( \frac{R_1}{\rho_s} - \frac{R_2}{\rho_2} - \frac{R_3}{2\rho_2} \right) \cdot \left( 1 - \Delta S \right) + mc_{p1} + mc_{p2} - \frac{e_1 + e_2 + e_3}{2} \quad (6)
\]

In equations (4 – 6) , the terms \( e_1, e_2 \) and \( e_3 \) are the sum of readability and repeatability errors (zero mean with uncertainty) and it is not considered non-linearity error (avoided by method) and evaporation error (because it is corrected by this approach). If one performs weighing with two references the three equations can be used. However if the second weighing is carried out with the same standard of the first, only the two first equations should be used.

A conversion factor \( F \) should be multiplied to conventional mass of the drop to obtain its mass value. As in equation (7), this factor takes in account the conventional air density \( \rho_0 \), density of the master solution \( \rho_s \) and conventional standard weight density \( \rho_c \) (8000 kg m\(^{-3}\)).

\[
F = \left( \frac{1 - \rho_0}{\rho_c} \right) \quad (7)
\]

3. Errors structure

The errors in weighing (\( \delta_1, \delta_2, \delta_3 \)) were considered as additional linear terms in the equations of conventional mass values because for two weighing differences it is not possible to take conclusion about additional higher order systematic error as in mass comparisons [12]. The redefined values for the solution of matrix system \( mc_{d1R}, mc_{p2} \) and \( mc_{d2R} \) are showed in equations (8 – 10):

\[
mc_{d1R} = mc_{d1R} - \left( \delta_1 - \delta_2 \right) \quad (8)
\]

\[
mc_{p2} = mc_{p2} - \left( \delta_3 - \delta_2 \right) \quad (9)
\]

\[
mc_{d2R} = mc_{d2R} + \delta_1 - \left( \delta_2 + \delta_3 \right) \quad (10)
\]

For two references the errors difference (\( \delta_3 - \delta_2 \)) should be estimated from the difference between \( mc_{p2} \) and the calibration result \( mc_{p2C} \), however if only one reference was used (\( \delta_3 - \delta_2 \)) is \( (mc_{p2} - mc_{p1}) \) because \( mc_{p1} \) is determined from its calibration result. It is emphasized that the underlying hypothesis for this approach is no standard weights mass drift. This way, the estimate (\( \delta_3 - \delta_2 \)) can be written as in equations (11 – 12).
\[(\delta_1 - \delta_2)^* = mc_{p2} - mc_{p2C} \] (11)

\[(\delta_1 - \delta_2)^* = mc_{p2} - mc_{p1} \] (12)

Five assumptions about the difference of the systematic errors in weighing were studied:

a) Constant \((\delta_1 = \delta_3 = \delta_4)\), in this case the value \((\delta_3 - \delta_2) = 0\) and \((\delta_1 - \delta_2) = 0\), so no correction should be applied to \(mc_{d1R}\) or \(mc_{d2R}\). This case could occur in practice for zeroing balance before each weighing and evaporation and balance drift are constant but not necessarily negligible.

b) Linear increasing \((\delta_2 = \delta_3 + k\) and \(\delta_3 = \delta_2 + k)\), thus \((\delta_3 - \delta_2) = k\) and \((\delta_1 - \delta_2) = -k)\). Here \((\delta_3 - \delta_2)^*\) should be add with changed signal to \(mc_{d1R}\) and to \(mc_{d2R}\) added as \(1.5 \times (\delta_1 - \delta_2)^*\). The linear increasing shows commonly for linear evaporation and/or balance drift when balance is left to drift.

c) \((\delta_1 = \delta_3 \neq \delta_2)\) implies \((\delta_3 - \delta_2) = (\delta_1 - \delta_2)\), by this way the estimate \(-1 \times (\delta_1 - \delta_2)^*\) should be summed to \(mc_{d1R}\) and \(-0.5 \times (\delta_3 - \delta_2)^*\) to \(mc_{d2R}\). When the balance is zeroing before weighing, this case will most likely occur in drying of a drop in capillary stem or improper handling of standard weights or pycnometer in put them on the balance receptor.

d) \((\delta_1 = \delta_1 \neq \delta_3)\), in this case \((\delta_1 - \delta_2) = 0\) and the estimated value for \((\delta_1 - \delta_2)^*\) shows a value which should not correct \(mc_{d1R}\). This case should be true for improper handling of weights or pycnometer in the third weighing.

e) \((\delta_2 = \delta_3 \neq \delta_1)\), here \((\delta_3 - \delta_2) = 0\) implying that no correction should be applied when it should be. This case is the most likely to occur if the care previously to weighing as suggested in [2] was not taken.

From these assumptions, some conclusions can be taken about the applicability of the estimate \((\delta_1 - \delta_2)^*\) and its uncertainty \(u(\delta_1 - \delta_2)^*\):

1. \((\delta_3 - \delta_2)^* < u(\delta_1 - \delta_2)^*\): Cases a \((\delta_1 = \delta_2 = \delta_3 = 0)\), b \((\delta_1 = 0\) and \(k = 0)\) and c \((\delta_1 - \delta_2 = \delta_1 - \delta_2 = 0)\) are the fundamental hypothesis to a carefully weighing practice, for a trained staff, so \((\delta_3 - \delta_2)^* < u(\delta_1 - \delta_2)^*\) accomplishes it and no correction should be applied but the uncertainty should be applied. If there is some evidence that had occurred case e, uncertainty should be taken in the same way.

2. \((\delta_3 - \delta_2)^* > u(\delta_1 - \delta_2)^*\): Case b can occur even for a carefully weighing so \((\delta_1 - \delta_2)^*\) and the uncertainty should be applied to the mass of the drop. Case e and d relies on the technician judgment. For case e applies the correction and uncertainty, however for case d no correction is applied but the uncertainty will be.

Due to errors structure, \((\delta_3 - \delta_2)^*\) is correlated with \(mc_{d1R}\) and \(mc_{d2R}\) thus, in according to the multiplicative term for \((\delta_1 - \delta_2)^*\) to correct mass, the correlation effect could be higher or lower.

4. Uncertainty evaluation

In order to evaluate if the uncertainty of mass achievable by this method complies with weighing requirements, the uncertainty for estimate \((\delta_1 - \delta_2)^*\), mass corrected \(md_{d1R}\), mass corrected \(md_{d2R}\) and conventional mass \(mc_{p2}\) were calculated to a 20 mg weight for a simulated weighing condition close to the real. The uncertainty was calculated by Monte Carlo method to \(1 \times 10^6\) trials.

The environmental conditions taken in these calculations are: temperature variation within 21.5 °C \(\leq T \leq 22.5 °C\), pressure variation is 995 hPa \(\leq p \leq 1005 hPa\), relative humidity variation within 40% \(\leq h \leq 60%\). By these values, the air density value is 1.181(12) kg m\(^{-3}\) [13]. The assumed density of master solution is 1000(3) kg m\(^{-3}\), the density of balance reference weights is 8000(200) kg m\(^{-3}\) and the density of standard weights 8000(15) kg m\(^{-3}\). The balance was adjusted before the weighing and loads are centred carefully.

The Table 1 shows the uncertainty components, probability distribution and parameters to be used in Monte Carlo simulation for the uncertainty of \((\delta_1 - \delta_2)^*\) and mass corrected \(md_{d1R}\), \(mc_{p2}\) and \(md_{d2R}\).
Table 1: Parameters for uncertainty simulation by Monte Carlo method.

| Uncertainty component          | Distribution | Parameters | Unit   |
|-------------------------------|--------------|------------|--------|
| Readability (zero)            | R(-a,a)      | a = 1      | µg     |
| Readability (load)            | R(-a,a)      | a = 1      | µg     |
| Repeatability                 | N(µ,σ²)      | µ = 0 ; σ  = 4 | µg |
| Sensitivity tolerance         | R(-a,a)      | a = 1.5 x 10⁻⁶ |       |
| Temperature sensitivity       | R(-a,a)      | a = 5.8 x 10⁻⁷ |       |
| Air density                   | N(µ,σ²)      | µ = 1.181 ; σ = 0.012 | kg m⁻³ |
| Solution density              | N(µ,σ²)      | µ = 1000 ; σ = 3 | kg m⁻³ |
| Balance standard density      | R(-a,a)      | a = 200    | kg m⁻³ |
| Standard weights 1 density    | N(µ,σ²)      | µ = 8000 ; σ = 15 | kg m⁻³ |
| Mass instability of weight 1  | R(-a,a)      | a = 6      | µg     |
| Mass weights 1 20 mg E₂       | N(µ,σ²)      | µ = 20 x 10³ ; σ = 1.5 | µg |
| Standard weights 2 density    | N(µ,σ²)      | µ = 8000 ; σ = 15 | kg m⁻³ |
| Mass instability of weight 2  | R(-a,a)      | a = 6      | µg     |
| Mass weights 2 20 mg E₂       | N(µ,σ²)      | µ = 20 x 10³ ; σ = 1.5 | µg |

| Additional parameters | Value | Unit |
|-----------------------|-------|------|
| R₁= R₂= R₃            | 2000  | mg   |
| ρ₂=ρ₃                 | 1.095 | kg m⁻³ |
| ρ₀                    | 1.2   | kg m⁻³ |
| ρ₉                    | 8000  | kg m⁻³ |

Table 2 shows the uncertainty for (δ₁ – δ₂)* and mass corrected md₁R, mc₂ and md₂R. Additionally, the non-corrected mass uncertainty, relative standard uncertainties and errors are presented.

Table 2: Errors and uncertainties (µg).

| Errors                  | (δ₁ – δ₂)* | md₁R | mc₂ | md₂R |
|-------------------------|------------|------|-----|------|
| Values                  | (δ₁₀δ₂₀δ₃₀) | u    | u(%)| u    | u(%)|
| δ₁₀δ₂₀δ₃₀                | 6.1        | 10.8 | 0.05| 6.5  | 0.03|
| δ₁ = 10 δ₂ = 0 δ₃ = 0   | 6.1        | 10.8 | 0.05| 6.5  | 0.03|
| δ₁ = 10 δ₂ = 20 δ₃ = 30 | 6.1        | 10.8 | 0.05| 6.5  | 0.03|
| δ₁ = 10 δ₂ = 20 δ₃ = 10 | 6.1        | 6.5  | 0.03| 6.5  | 0.03|
| No Error                | 6.5        | 0.03 | 6.5 | 0.03|

By Table 2, the relative uncertainty to 20 mg is always lower than the limit for relative standard uncertainty, i.e., 0.1%. The higher than 6.5 µg uncertainty of md₁R and md₂R for cases with error zero means the correlation effect which arises from the sum of (δ₁ – δ₂)* to the mass. As previously, the higher uncertainty in error linearly increasing means the correlation effect from the added corrections (δ₁ – δ₂)* for md₁R and 1.5 x (δ₁ – δ₂)* for md₂R. Otherwise, for errors just in the second weighing the correlation in md₁R and md₂R is reduced due to correction, respectively, −1 x (δ₁ – δ₂)* and −0.5 x (δ₁ – δ₂)*. If it was not regard the error, the lowest uncertainty for mass is obtained. Just in this case the usage of two mass standards would be justified.
5. Conclusion
The uncertainty calculation achievable for a modification in elimination weighing method was performed. This modification, in contrast to the standard elimination weighing, allows correcting the common errors in weighing of radioactive source and provide information for variability studies, thus improving the reliability of elimination weighing.

By the results, the relative standard uncertainty complies with the limit for relative standard uncertainty of the drop mass and the usage of additional standard weights is not fundamental.

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