Metrologia
Fortaleza - CE 2017

Uncertainty evaluation of a modified elimination weighing for source preparation

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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%.

Keywords: radionuclide metrology, source preparation; elimination weighing method; uncertainty evaluation.

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 ΔI_{1i} between the first weighing, that includes the conventional mass of the drop mc_d, and the i^{th} (2^{nd} or 3^{rd}) weighing with standard weights of conventional mass mc_{pi} can be written:

$$\Delta I_{1i} = mc_d - mc_{pi}$$

Here the difference ΔI_{1i} includes the balance readings for 1^{st} weighing R_1 and the i^{th} R_i, sensitivity error ΔS and the buoyancy correction [11] which take in account the air density ρ_a, the conventional air density ρ_0 (1.2 kg m^{-3}), density of the master solution ρ_S , density of balance reference standards ρ_R and the density of standards weighed together with the solution ρ_i:

$$\Delta I_{1i} = \left[(R_1 - R_i)\left(1 - \frac{(\rho_a - \rho_0)}{\rho_R}\right) + (\rho_a - \rho_0)\left(\frac{R_1}{\rho_S} - \frac{R_i}{\rho_i}\right)\right](1 - \Delta S)$$

From the two weighing differences the equation system in matrix form can be mounted:

$$\begin{bmatrix}\Delta I_{12}\\ \Delta I_{13}\end{bmatrix} = \begin{bmatrix}1 & -1 & 0\\ 1 & 0 & -1\end{bmatrix} \cdot \begin{bmatrix}mc_d\\ mc_{p1}\\ mc_{p2}\end{bmatrix}$$

The solution of this system, on the assumption of one standard reference with conventional mass mc_{p1} provides the measurement model for the conventional mass mc_{d1R} (1R means obtained by one reference), and mc_{p2}:

$$mc_{d1R} = \left[(R_1 - R_2)\left(1 - \frac{(\rho_a - \rho_0)}{\rho_R}\right) + (\rho_a - \rho_0)\left(\frac{R_1}{\rho_S} - \frac{R_2}{\rho_2}\right)\right](1 - \Delta S) + mc_{p1} - (e_1 - e_2)$$

$$mc_{p2} = \left[(R_3 - R_2)\left(1 - \frac{(\rho_a - \rho_0)}{\rho_R}\right) + (\rho_a - \rho_0)\left(\frac{R_3}{\rho_3} - \frac{R_2}{\rho_2}\right)\right](1 - \Delta S) + mc_{p1} - (e_3 - e_2)$$

When both standards are set as reference just one solution for the conventional mass of drop mc_{d2R} is possible:

$$mc_{d2R} = \left[\left(R_1 - \left(\frac{R_2 + R_3}{2}\right)\right)\left(1 - \frac{(\rho_a - \rho_0)}{\rho_R}\right) + (\rho_a - \rho_0)\left(\frac{R_1}{\rho_S} - \frac{R_2}{2\rho_2} - \frac{R_3}{2\rho_3}\right)\right](1 - \Delta S) + \frac{(mc_{p1} + mc_{p2})}{2} - e_1 + \left(\frac{e_2 + e_3}{2}\right)$$

In these equations, 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. This factor takes in account the conventional air density ρ_0, density of the master solution ρ_S and conventional standard weight density ρ_c (8000 kg m^{-3}):

$$F = \frac{\left(1 - \frac{\rho_0}{\rho_c}\right)}{\left(1 - \frac{\rho_0}{\rho_S}\right)}$$

3. ERRORS STRUCTURE

The errors in weighing (δ_1, δ_2, δ_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 any conclude about additional higher order systematic error as in mass comparisons [12]. The redefined values for mc_{d1R}, mc_{p2} and mc_{d2R} are:

$$mc_{d1R} = mc_{d1R} + (\delta_1 - \delta_2)$$

$$mc_{p2} = mc_{p2} + (\delta_3 - \delta_2)$$

$$mc_{d2R} = mc_{d2R} + \delta_1 - \left(\frac{\delta_2 + \delta_3}{2}\right)$$

For two references the errors difference (δ_3-δ_2) should be estimated from the difference between mc_{p2} and the calibration result mc_{p2C}, however if only one reference was used (δ_3-δ_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 by:

$$(\delta_3 - \delta_2)^* = mc_{p2} - mc_{p2C} \text{ (2 references)}$$

$$(\delta_3 - \delta_2)^* = mc_{p2} - mc_{p1} \text{ (1 reference)}$$

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

a) Constant ($\delta_1 = \delta_2 = \delta_3$), in this case the value (δ_3-δ_2) = 0 and (δ_1-δ_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 ($\delta_2 = \delta_1 + k$ and $\delta_3 = \delta_2 + k$), thus (δ_3-δ_2) = k and (δ_1-δ_2) = -k. Here $(\delta_3-\delta_2)^*$ should be add with changed signal to mc_{d1R} and to mc_{d2R} added as $1.5(\delta_3-\delta_2)^*$. 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 $-(\delta_3-\delta_2,)^*$ should be summed to mc_{d1R} and $-0.5(\delta_3-\delta_2)^*$ 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) ($\delta_2 = \delta_1 \neq \delta_3$), in this case ($\delta_1$-$\delta_2$) = 0 and the estimated value for (δ_3-δ_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 by Lourenço and Bobin was not taken.

From these assumptions, some conclusions can be taken about the applicability of the estimate (δ_3-δ_2)* and its uncertainty u(δ_3-δ_2)*:

1. (δ_3-δ_2)* < u(δ_3-δ_2)*: Cases **a** (δ_1=δ_2=δ_3=0), **b** (δ_1=0 and k= 0) and **c** ((δ_3-δ_2) = (δ_1-δ_2) =0) are the fundamental hypothesis to a carefully weighing practice, for a trained staff, so (δ_3-δ_2)* < u(δ_3-δ_2)* accomplishes it and no correction should be applied but the uncertainty should be applied. If there some evidence that had occurred case **e**, uncertainty should be taken in the same way.

2. (δ_3-δ_2)* > u(δ_3-δ_2)*: Case **b** can occur even for a carefully weighing so (δ_3-δ_2)* and the uncertainty should be applied to the mass of the drop. Case **c** and **d** relies on the technician judgment. For case **c** applies the correction and uncertainty, however for case **d** no correction is applied but the uncertainty will be.

Due to errors structure, (δ_3-δ_2)* is correlated with mc_{d1R} and mc_{d2R} thus, in according to the multiplicative term for (δ_3-δ_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 (δ_3-δ_2)*, mass corrected m_{d1R}, mass corrected m_{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 1×10^6 trials.

The environmental conditions taken in these calculations are: temperature variation within 21.5 °C ≤ T ≤ 22.5 °C, pressure variation is 995 hPa ≤ p ≤ 1005 hPa, relative humidity variation within 40% ≤ h ≤ 60%. By these values, the air density value is (Euramet, 2015) 1,181 (12) kg m^{-3}. 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 (δ_3-δ_2)* and mass corrected md_{1R}, mc_{p2} and md_{2R}.

Table 1: Uncertainty components for mass.

Uncertainty component	Distribution	Unit	Parametersa a
Readability (zero)	R(-a,a)	μg	a= 1
Readability (load)	R(-a,a)	μg	a= 1
Repeatability	N(μ,σ^2)	μg	μ= 0 σ= 4
Sensitivity tolerance	R(-a,a)		a= 1.5 × 10^{-6}
Temperature sensitivity	R(-a,a)		a= 5.8 × 10^{-7}
Air density	N(μ,σ^2)	kg m^{-3}	μ= 1.181 σ= 0.012
Solution density	N(μ,σ^2)	kg m^{-3}	μ= 1000 σ= 3
Balance standard density	R(-a,a)	kg m^{-3}	a= 200
Standard weights 1 density	N(μ,σ^2)	kg m^{-3}	μ= 8000 σ= 15
Mass instability of weight 1	R(-a,a)	μg	a= 6
Mass weights 1 20 mg E_2	N(μ,σ^2)	μg	μ= 20 × 10^3 σ= 1.5
Standard weights 2 density	N(μ,σ^2)	kg m^{-3}	μ= 8000 σ= 15
Mass instability of weight 2	R(-a,a)	μg	a= 6
Mass weights 2 20 mg E_2	N(μ,σ^2)	μg	μ= 20 × 10^3 σ= 1.5

Additional parameters	Value	Unit
R1= R2= R3	2000	mg
ρ_2=ρ_3	1.095	kg m^{-3}

ρ_0	1.2	kg m^{-3}
ρ_c	8000	kg m^{-3}

Table 2 shows the uncertainty for $(\delta_3\text{-}\delta_2)^*$ and of the mass corrected md_{1R}, mc_{p2} and md_{2R}. Additionally, the non-corrected mass uncertainty, relative standard uncertainties and errors are presented.

Table 2: Errors and uncertainties (µg).

Error values $u_r(\%)$	$(\delta_3\text{-}\delta_2)^*$ u	md_{1R} u		mc_{p2} $u_r(\%)$	u	md_{2R} $u_r(\%)$	u
δ_1=0 δ_2=0 δ_3=0	6.1	10.8	0.05	6.5	0.03	8.1	0.04
δ_1 = 10 δ_2 = 20 δ_3 = 30	6.1	10.8	0.05	6.5	0.03	11.6	0.06
δ_1 = 10 δ_2 = 20 δ_3 = 10	6.1	6.5	0.03	6.5	0.03	6.3	0.03
No Error	----	6.5	0.03	6.5	0.03	5.4	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 md_{1R} and md_{2R} for cases with error zero means the correlation effect which arises from the sum of $(\delta_3\text{-}\delta_2)^*$ to the mass. As previously, the higher uncertainty in error linearly increasing means the correlation effect from the added corrections $(\delta_3\text{-}\delta_2)^*$ for md_{1R} and $1.5(\delta_3\text{-}\delta_2)^*$ for md_{2R}. Otherwise, for errors just in the second weighing the correlation in md_{1R} and md_{2R} is reduced due to correction, respectively, $-(\delta_3\text{-}\delta_2)^*$ and $-0.5(\delta_3\text{-}\delta_2)^*$. 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. CONCLUSIONS

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.

ACKNOWLEDGEMENTS

One of the authors wishes to thank IRD/CNEN and Pronametro/Inmetro for the financial scholarship sponsor.

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