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Evaluation of the parameters for weighing uncertainty estimation in radionuclide source preparation

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Abstract: In radionuclide metrology Pycnometer, Substitution, Elimination and Modified Elimination methods could be used for source preparation. In order to validate Modified Elimination method against the former ones supporting measurements should be performed. As a result, in considering these measurements for uncertainty evaluation the four methods based on carefully weighing were found compatible and complies with the requir In radionuclide metrology Pycnometer, Substitutio, Elimination and Modified Elimination methods could be used for source preparation. In order to validate Modified Elimination against the former ones supporting measurements should be performed. As a result, in considering these measurements for uncertainty evaluation the four methods based on carefully weighing were found compatible and complies with the required threshold uncertainty. ed threshold uncertainty.

Keywords. Radionuclide metrology, source preparation, weighing methods, uncertainty evaluation.

1. INTRODUCTION

In radionuclide metrology, quantitative source are prepared for activity measurements then serving as an activity concentration standard, in Bq per mass unit.

To high accuracy source standards, sampling from a master solution performed by drop deposition using a polyethylene pycnometer should be based on a weighing procedure able to achieve relative standard uncertainties below than 0.1% [1]. This requirement is very important when is required uncertainty in activity concentration between 0.05% to 0.1% [2] since activity uncertainty should be the dominant component.

The mass uncertainties from pycnometer and substitution methods were assessed in the uncertainty budgets for 4πβ-γ coincidence counting comparison CCRI(II)-S7. The reported results for mass uncertainties, a dominant component, mean 0.11% and standard deviation 0.06% showed non uniform and unrealiable proficiency in uncertaitny estimation

In order to provide guidance to achieve standard relative uncertainties below 0.1 %, Lourenço and Bobin has shown in a detailed way the uncertainty evaluation for elimination method as applied in LNHB.

A new method has been presented [3], namely modified elimination method, able to achieve in some circunstancies even lower uncertainties than the other methods by the determination of the repeatibility from weighing. The uncertainty evaluation for this method has been shown [4]. However in the validation of this method against ther former ones supporting measurements required for uncertainty estimation and mass of the drop determination should be detailed yet.

This work shows how measurements related to balance, environment and radionuclide solution were performed for validation purposes. From the results a comparison between the four methods is carried out to evaluate modified elimination performance.

2. MEASUREMENT

2.1. Experimental set up

In order to obtain the several parameters required for mass measurement and uncertainty estimation a full range Mettler Toledo XP56 balance was sensored as shown in Figure 1. The environmental conditions were recorded by temperature, relative humidity and pressure sensors integrated in a Arduino nano microcontroller board. Automatic data acquisition of indications provided from sensors and balance was carried out by a developed Labview application which trigger data communication via serial ports. The balance communication was implement by using specific Labview Vis for Mettler balances while libraries written in C or C++ were recorded in arduino processor to allow sensors reading. Data acquisition and reconding each 2 seconds allowed to evaluate checks for error results.

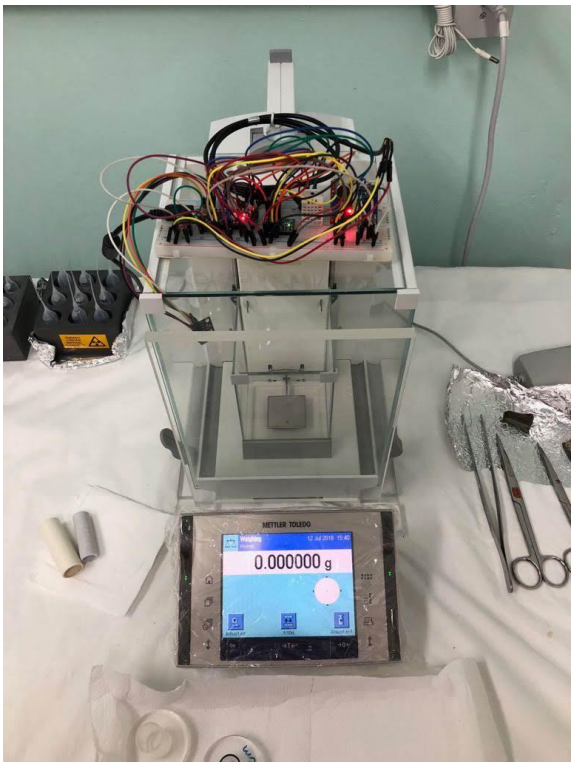

Figure 1 Mettler Toledo XP56 microbalance

This microbalance properties are maximum capacity $max = 52$ g, resolution $d_0 = 0.001$ mg and temperature sensitivity parameter $K_T = 1 \times 10^{-6}°C^{-1}$. Balance was not adjusted before measurements since it was not adjusted before in *loco* external calibration by a accreditated laboratory so preventing changes in calibration errors which could put calibration in check. Previously to performing weighing , balance was warm up and indications were taken when the stability indicator was displayed.

Three sensors were employed to measurements a BME280, for enviromental conditions measurements inside of weighing chamber and a DHT22 for humidity together with a BMP180, for temperature and pressure outside. These sensor were calibrated at hygrometry and pressure laboratories from Inmetro. The environmental sensors resolution are 0.1°C, 0.1% and 0.01 hPa.

The density determinations of samples were performed on a Mettler Toledo DA-310M digital densimeter, installed at Inmetro's fluids laboratory. As calibration report, this densimeter is properly for neutral or acid sample with densities in range of 0.7 g cm^{-3} to 1.6 g cm^{-3} at temperatures from 15°C to 25°C. Indications with resolution 1×10^{-5}°g cm^{-3} were obtained at sound indication. The samples were in the form of liquid hydrochloric acid in concentrations of 0.1 mol L^{-1}, 0.5 mol L^{-1} and 1 mol L^{-1} as they are required for the most accurated standardized radionulides ^{60}Co, ^{68}Ge, ^{137}Cs and ^{241}Am at LNMRI. Carriers and radionuclides was not used because its concentration in radioactivity solutions is too low to appreciably change the diluent density. Sampling was performed with the aid of a syringe. Between different concentration of sample measures the densimeter was cleaned with distilled water and isopropyl alcohol to prevent cross contamination.

The 5ml pycnometers manufactured to order are made of polyethylene with chemical composition ^{6}C(96.3%) ^{8}O(3.3%), ^{24}Cr (0.1%), ^{55}Fe (0.1%) and ^{11}Na (0.1%) checked by X-ray fluorescence. The density is in the range from 0.88 g cm^{-3} to 0.91 g cm^{-3}as determined by hydrostatic weighing. These

pycnometers were employed in evaporation test and for weighing methods and they were prepared by stretching the stem, warming and gently rotating the pycnometer, while the tip of the stem is pulled with tweezers to form a capillary so its tip is cut.

Pycnometers were filled with deionized water in evaporation test, repeatibility test and in execution of weighing methods.

In performing tests based on weighing two set of stainless standards weights were used. A OIML F_1 set of two individual weights 20 g and 50 g was used to eccentricity tests and repeatability measurement required to non linearity determination at *max*. The other set a 1 mg to 50 g E_2 accuracy class was employed to differential non linearity, method repeatibility, drift measurements and in perfoming weighing methods. These set was calibrated twice in mass laboratory of Inmetro. The two set are maintained at the weighing room to achieve thermal stabilization. Handling of mass standards was performed with properly for weight tweezers, gloves and lint-free tissue paper.

2.2. Environmental parameters

The environmental parameters were taken during about an year and a 3 milion data set includes data when air conditioning system was off. The maximum variations of temperature, humidity and air density in Figure 2 were Δt=5.7 °C, Δhr = 47 % and $\Delta\rho_a$ = 0.04 kg m^{-3}.

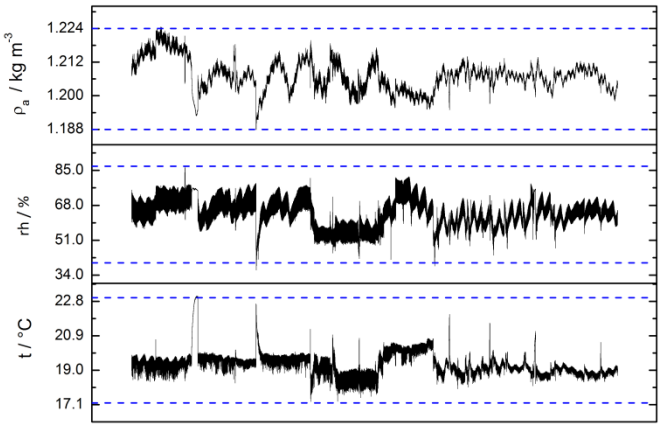

Figure 2 Environmental parameters changing

The calibration results for sensors inside weighing chamber were –1.9(0.2)°C, 11(2)%, –1.3(0.2)hPa and for the outside sensors were –0.4(0.2)°C, 3(2)%, –2.4(0.2)hPa. The uncertainties include stability component yet. From these results for humidity and pressure sensors, neither correction either uncertainty should be accounted. However the correction for temperature should be applied. The temperature gradient measured at the weighing chamber was 0.5°C, thus the uncertainty estimated by $\Delta t/2$ covers gradient and traceability uncertainty sources.

2.3. Radionuclide solution parameters

2.3.1 Density. Previously to carry density measurements ambar glasses filled with the different concentrations acid samples were shaked to homogenize. Measurements were performed at 19°C , 20°C and 21°C, about of work temperature range in drop depositions. Due to the bias resulting in

executing density measures in only increasing or decresing temperature, temperature point order was chosen in a random way. Three cycles of three repeated density measuring were obtained at temperature point for each sample. Regardless of temperature, the density values varied linearly with concentration and are in the range of 1.004(4) g cm^{-3} to 1.020(4) g cm^{-3}. The density thermal expansion coefficient was –2(2) × 10^{-4}°g cm^{-3} $°C^{-1}$ thus no significative in temperature work range. For buoyancy correction purposes a density ρ = 1.00 g cm^{-3} limited by ± 0.02 g cm^{-3}, is enough for working concentrations and temperatures. Thus, density standard uncertainty is $u(\rho)$=0.01 g cm^{-3}. These density results covers deionized water density also measured to the same temperature range 1.002(4) g cm^{-3}.

2.3.2 Evaporation. The evaporation rate of the pycnometer filled with deionized water were evaluated by weighing. Water was used because has an average evaporation rate close to HCl in concentration range from 0.1 mol L^{-1} to 1 mol L^{-1}. The filled pycnometer was mainted in weighing room so in thermal stability with ambient air. As shown in Figure 3, no correlation between readings with temperature or relative humidity was observed. The mesured evaporation rate was –0.0003 mg min^{-1} , so in a 7 min drop deposition the evaporation error is δR_{evap} = –0.002 mg. However, due to the very low error value it is assumed in mean δR_{evap} = 0 mg with a standard uncertainty $u(\delta R_{evap})$= 0.002 mg.

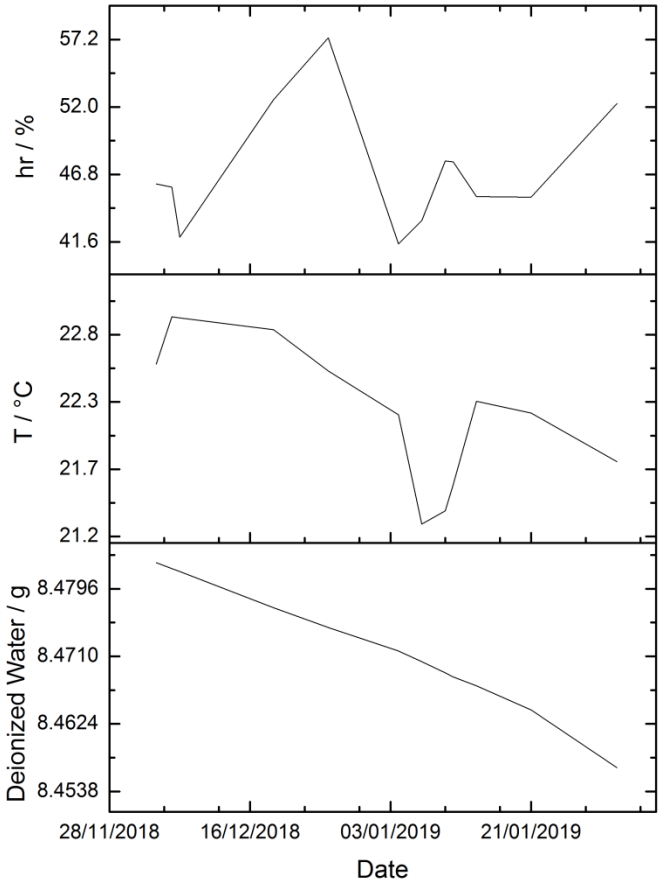

Figure 3 Comparison of evaporation and temperature and relative humidity changes

2.4. Balance parameters

2.4.1 Standard weights. For each set of standards in the the expanded uncertainty (k=2) for individual standards were close to the maximum for its accuracy class, equal to one third of the maximum permissible error according to OIML R-111.The standard uncertainty $u(m_s)$ was obtained as the half of this value. Table 1 provides data for standards obtained from calibration.

Some standard weights do not have errors limited by OIML E_2 or F_1 class. However, there no problem since this errors are considered in mass values determinations and the mass drift is maintained unde control.

Table 1 Errors and uncertainties for weights

Nominal value	E ± $U(k=2)$/ µg	Nominal value	E ± $U(k=2)$/ µg
1mg	–2 ± 3	200mg**	–7 ± 6
2mg	–42 ± 3	1g	–8166 ± 12
10mg	–14 ± 3	2g	–13455 ± 14
20mg	–3 ± 3	2g*	–10259 ± 14
20mg*	–16 ± 3	5g	–11810 ± 20
20mg**	–327 ± 3	10g	–30 ± 20
50mg	5802 ± 5	50g	–150 ± 30
100mg	–64 ± 5	20g F_1	–73810 ± 90
200mg	–8 ± 6	50g F_1	–78230 ± 120
200mg*	–3 ± 6		

Figure 4 shows the normalized deviation between calibrations of the mass standards. This consistency evaluation took in account the covariance introduced by the same reference standards used

in both calibrations. The covariance term for each standard was considered as one third of the overall variance for mass, according to OIML one third rule.

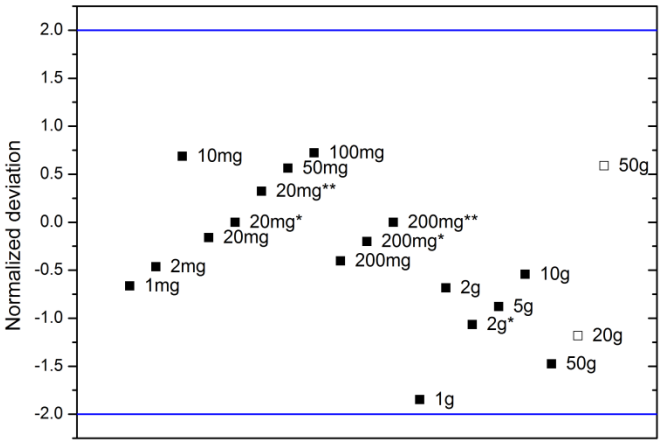

Figure 4 Normalized deviations

Indeed, consistency is confimed since all normalized deviations are in the range ± 2. Furthermore, negative drift is the predominant observed trend and may be due to wear in using weights. However, the calibration frequency of one year seems sufficient when all standard weight tests presented in this work are executed.

2.4.2 Eccentricity test. The eccentricity of the balance was measured by the four methods specified by Euramet, by weighing a load of L_{ecc} = 20 g at the five points indicated in Figure 5. Among the four methods the the maximum difference in off-centre indication was $|\Delta I_{ecc}|_{max}$ = 0.036 mg. The difference from this maximum and those obtained by other three methods was about 0.016 mg, so no significative for weighings in range of 10 mg to 200 mg.

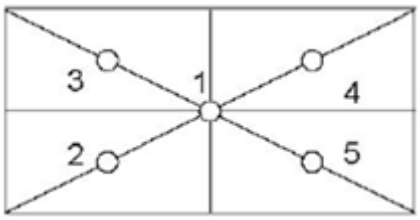

Figure 5 Eccentricity test scheme

2.4.3 Non linearity checks. In order to determine linearity error at *max* =50 g and the differential errors on miligram range balance calibrations were performed according to specified by Euramet.

Figure 6 shows the largest difference in calibration errors at the maximum capacity as required to adjustment drift uncertainty estimation. The largest difference value is $|\Delta E(max)|$ = 0.23 mg. This value is expected since periodic internal adjustment was not trigged.

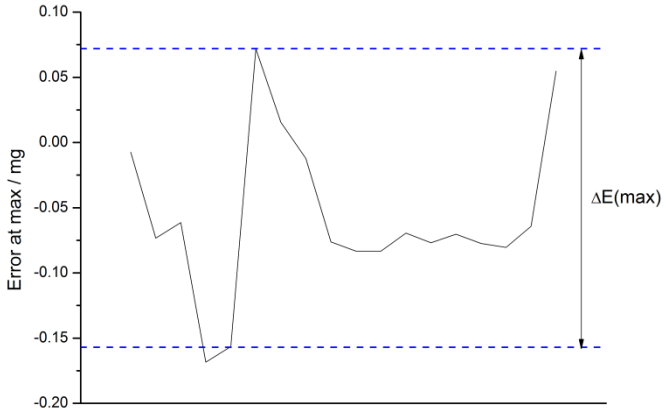

Figure 6 Non linearity changes at 50 g

In drop deposition pycnometer weighs about 3 g, so calibration was perfomed in the range of 10 mg to 100 mg with balance no loaded and also loaded with standard weights in the range from 1 g to 10 g. As is shown in Figure 7, mean differential linearity varies very little with load and calibration point.

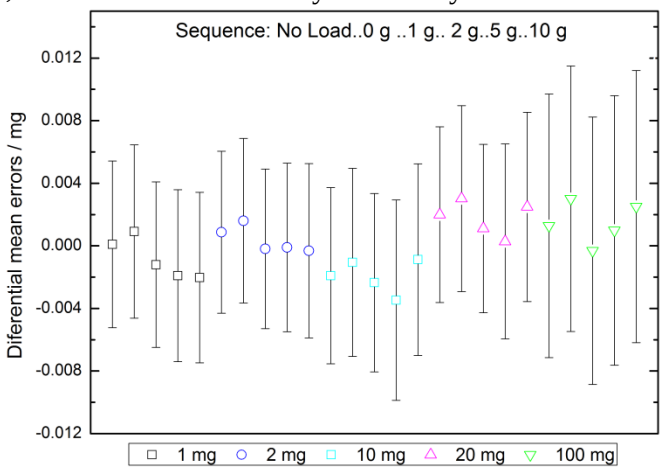

Figure 7 Differential non linearity errors

The differential linearity error is δR_{NL} = 0.000 mg and its standard uncertainty is $u(\delta R_{NL})$ = 0.002 mg.

2.4.4 Drift avoiding procedures. Drift elimination is carried by two procedures applied in sequence: zeroing between each weighing and not zeroing, but recording reading with balance no load before and after weighing. They were performed to some weighing used to determine differential errors in last section. In first procedure the indication is that obtained with balance loaded, in the second one the indication is the resul of the difference between the reading when balance is loaded and the average of the two recorded no load readings. The difference between indications obtained by each procedure is showed in Figure 8.

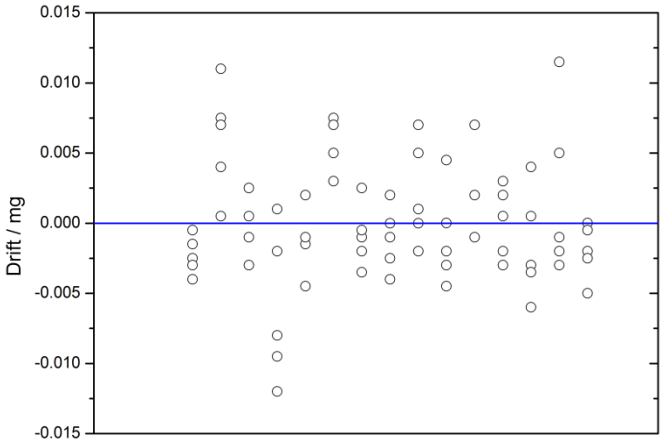

Figure 8 Drift changing around the average

The average of indications difference is null, so both eliminations procedures are so effective to avoid drift. The standard deviation of these differences is 0.004 mg which is equal to the pooled standard deviation of typical repeatibilities shown in Figure 9 obtained from tests performed by each avoiding drift procedure as is.

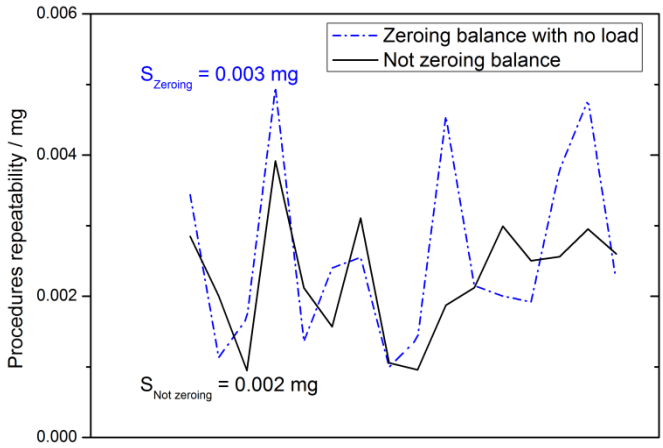

Figure 9 Repeatability at different elimination drift methods

2.4.5 Weighing methods repeatability. Repeatability tests were performed in order to achieve typical repeatability and maximum standard deviation variation. All weighing were carried out with a pycnometer filled whose mass was about 3 g.

In repeatability test for pycnometer method the first weighing was with pycnometer together a 20 mg weight simuling a drop and the second the pycnometer alone. In elimination method the first weighing was only the pycnometer and the second was the pycnometer with a 2 mg weight, simulating a possible diference between the two indications required for this method. Modified elimination method repeatability test was carried out in the same way of elimination method just with an addition weighing of pycnometer together with the weight. For substitution method the first weighing is of the pycnometer alone and the second one is of a set of standards who weighing reading is close to the first.

Figure 10 shows the repeatability values obtained from tests for each method. Blue segment lines indicates the typical repeatability, in general a little more than balance repeatability. Substitution

method shows higher typical repeatability and maximum reatibility among the methods due to the handle of several weights required by this method.

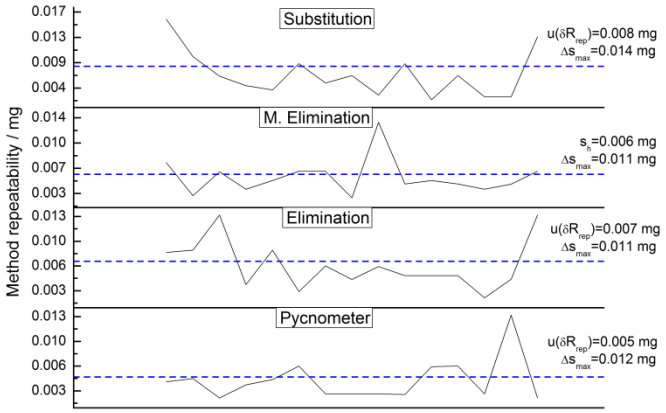

Figure 10 Repeatability for each weighing method

Repeatability test only in 20 mg is justified because there are no procedural difference in perfoming any deposition method in the range from 10 mg to 200 mg. Also, is expected in this range a single typical repeatability that characterizes each method, since, as already mentioned, the repeatability of the method is a consequence of the repeatability of the balance and the latter is unique in this range.

In contrast to other methods modified elimination allows to determine repeatibiity from its application, so typical repeatibility means the historical one which is required for checking errors in weighing.

3. PERFORMANCE OF MODIFIED ELIMINATION METHOD

3.1 Weighing

In order to evaluate the compatibility between the mass values of the aliquots deposited by modified elimination and the other methods, the weighing sequence shown in Figure 11 was executed and it allowed to determine the mass from the same aliquoting of solution. The complete execution of the weighing sequence take around 7 min.

The weighing were performed using deionized water once density and evaporation properties are close to liquid hydrochloric acid very used to source preparation tasks. Furthermore water usage complies with Alara's principle. A fifteen minutes wait time was applied for thermal stabilization between balance, pycnometer, environment and technician. Balance was zeroed before each weighing.

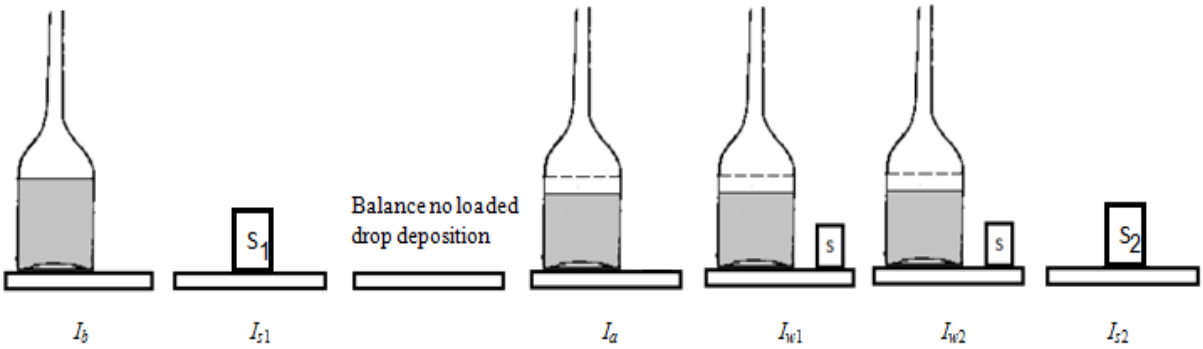

Figure 11 Weighing sequence

Table 3 shows the set of mass standards applied to substitution, elimination and modified elimination methods. The set used to form the mass of standars after deposition m_a is given from the set before deposition m_b including (+) or excluding (–) standards. The same set of standards was used to perform elimination m_E or modified elimination m_{EM} methods.

Table 2 Mass Standards used for weighing

#	m_b	m_a	m_E, m_{EM}
4	2g*,1g,,200mg*,100mg,20mg**	m_b – 20mg**	20mg**

The indications obtained in this weighing sequence are shown in Table 4.

Table 3 Parameters obtained from weighing sequence

Order#	I_b /g	I_{s1} /g	I_a /g	I_{w1} /g	I_{w2} /g	I_{s2} /g	p /hPa	hr /%	t /°C
1	3.319494	3.301197	3.293126	3.312796	3.312790	3.281514	1014.5	52	21.1

3.2 Mass comparison

Table 4 shows the uncertainty budget for the weighing sequence in Table 3. All values are in milligram except for covariance in squared milligram and buoyancy effect in "unit".

*Table 4 Uncertainty Budget**

	Pycnometer		Elimination		M. Elimination		Substitution			
							before		after	
Quantity	Value	u	Value	u	Value	u	Value	u	Value	u
Resol at 0	0	0.0003	0	0.0003	0	0,0003	0	0,0003	0	0,0003
Resol at *L*	0	0.0003	0	0.0003	0	0,0003	0	0,0003	0	0,0003
Eccentricity	0	0.0000	0	0.0000	0	0,0000	0	0,0000	0	0,0000
Repeatability	0	0.0050	0	0.0070	0	0,0035	0	0,0080	0	0,0080
Temp sensit	0	0.0000	0	0.0000	0	0,0000	0	0,0000	0	0,0000
Adj buoy	0	0.0001	0	0.0000	0	0,0000	0	0,0001	0	0,0000
Adj drift	0	0.0001	0	0.0000	0	0,0000	0	0,0000	0	0,0000

Evaporation	0	0.0021	0	0.0021	0	0,0021	0	0,0021	0	0,0021
Balance drift	0	0.0003	0	0.0003	0	0,0003	0	0,0003	0	0,0003
Repeat drift	0	0.0069	0	0.0064	0	0,0064	0	0,0081	0	0,0081
Linearity	0	0.0020	0							
Linear drift	0	0.0121	0				*not applicable*			
Std weight	*not applicable*		19.6730	0.0017	19.6730	0.0017	3301.1807	0.0102	3281.5076	0.0101
Meth result	26.3680		6.700		6.7020		18.297		11.612	
Weigh result	26.3680	0.0151	26.3730	0.0098	26.3752	0.0077	3319.4777	0.0154	3293.1196	0.0154
Cov/mg2	not applicable							0.0001		
	Bu=1.00105 u(Bu)=0.00002									
Drop mass	26.396	0.015	26.401	0.010	26.403	0.008		26.386	0.016	
Rel uncert		0.06%		0.04%		0.03%			0.06%	

*Unless otherwise stated, all values are in milligrams.

Some uncertainties components are negligeble due to low values of the differential method results such as eccentricity, temperature sensitivity and adjustment buoyancy and drift.

For pycnometer method assurance uncertainty components are the most significative. Also for elimination, modified elimination and substituion methods repeatability drift is a important uncertainty contribution. In this last, mass standards uncertainty is the harder contribuition. Different from the others methods where improve uncertainty means reduce confiability in results, in substitution method thechnical changes as reducing the amount of weights by using mass with not standardize nominal values should be improve uncertainty. Altough the reached uncertainty for elimination and modified elimination appear to be the lower uncertainty bound attainable by non-automatic weighing.

4. CONCLUSION

The supporting measurements required to validation and uncertainty estimation for Pycnometer, Substitution, Elimination and Modified Elimination metthods has been detailed. Further the results of these measurements were used to performance evaluation of Modified Elimination Method.

The results of performance evaluation shows compatibility between mass of the drop determined by all methods and Elimination Method shows lower uncertainty than the others.

ACKNOWLEDGMENTS

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