ESTIMATION OF UNCERTAINTY IN ANALYTICAL BALANCES - COMPARISON OF MASS MEASUREMENTS PERFORMED IN ANALYTICAL BALANCES (LATU-1999).

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The current paper provides the details of the main sources of uncertainty that occur when conventional mass determinations are performed in analytical balances.

The data presented correspond to the calibration of 18 analytical balances that belong to LATU, together with the detailed quantification of each of the sources of uncertainty.

The results of a comparison of conventional mass measurement performed in those balances with a Teflon sample are assessed, considering their uncertainty values. Conclusions are subsequently drawn on conventional mass measurement´s reproducibility in analytical balances in LATU.

1. INTRODUCTION

When mass determination is performed in an analytical balance, the reading value is usually taken as an estimate of the conventional mass of the sample. This estimation is affected by a series of sources of uncertainty that are detailed and assessed in the current document.

2. SCOPE

The estimation of uncertainty that is proposed is applicable to the electronic analytical balances that require a periodical sensitivity adjustment (either automatically, prior to usage, or with a periodicity established by the technical service or user).

3. ERRORS IN WEIGHING

"Weighing error" is defined as the difference between the balance's reading and the conventional mass value of the sample producing that reading. It may arise from various sources, which may be classified as:

- Sample - related
- Related to sample/balance interactions
- Related to sample/environment interactions.
- Balance - related.

Some in the latter category affect the balance sensitivity (ratio between the displayed reading and the conventional mass placed in the balance pan or relative reading) and others affect the absolute reading.

Therefore:

$$M + \varepsilon_m = P = \frac{L_i}{S} = \frac{L - \varepsilon_{mb} - \varepsilon_b}{(1+\delta_S)} \qquad \textbf{(1)}$$

where:

M- Conventional mass of the sample.
P- Reading of an ideal balance (with no reading or sensitivity errors, nor sample-interactions)
L_i- Reading of a balance with no reading errors nor interactions with the sample.
L- Reading of the balance.
S- Balance sensitivity (if the adjustment is adequately performed and there are no errors affecting sensitivity, then: S=1).
ε_m- sample- related errors.
ε_{mb}- errors derived from sample/balance interactions.
ε_b- errors affecting the absolute balance's reading.
δ_S- errors affecting the balance's sensitivity.

3.1. SOURCES OF SAMPLE - RELATED UNCERTAINTY

-INSTABILITY OF THE SAMPLE¨S MASS:

Instability may be due to oxidation, hygroscopicity, etc. It is very difficult to quantify error or to estimate uncertainty derived from this source; therefore, the weighing or sample preparation methods should tend to minimize these effects (e.g.: use of drying agents in the balance chamber).

3.2. SOURCES OF UNCERTAINTY RELATED TO SAMPLE-BALANCES INTERACTIONS.
-ELECTROMAGNETIC EFFECTS:

If the sample has an electrostatic charge, permanent magnetism or an important magnetic susceptibility, there may be electric and/or magnetic interactions between the sample and the balance's electrical and magnetic fields, resulting in weighing errors. Again, given that this source is very difficult to quantify, the weighing methods used must tend to minimize these effects (for example, by placing samples with high magnetic susceptibility as far away from the area with greater magnetic field in the balance as possible, in order to minimize magnetic forces).

3.3. SOURCES OF UNCERTAINTY RELATED TO SAMPLE- ENVIRONMENT INTERACTIONS
-DIFFERENCE BETWEEN THE DENSITY OF THE SAMPLE AND THE DENSITY OF THE WEIGHTS USED TO ADJUST THE BALANCE:

If the density of the sample being weighed differs from that of the balances adjustment weight(s), and the air density at the time of adjustment and weighing differ from standard air density (1.2 kg/m^3), an ideal balance's reading (P) will differ from the conventional mass of the sample (M).

$$M = P\frac{\left(1-\dfrac{\rho_a}{\rho_P}\right)\left(1-\dfrac{\rho_o}{\rho_M}\right)}{\left(1-\dfrac{\rho_o}{\rho_P}\right)\left(1-\dfrac{\rho_a'}{\rho_M}\right)} \quad \textbf{(2)}$$

$$\varepsilon_{m.d.} = P - M = P\left[\frac{\left(1-\dfrac{\rho_a}{\rho_P}\right)\left(1-\dfrac{\rho_o}{\rho_M}\right)}{\left(1-\dfrac{\rho_o}{\rho_P}\right)\left(1-\dfrac{\rho_a'}{\rho_M}\right)} - 1\right] \cong$$

$$\cong L\left[\frac{\left(1-\dfrac{\rho_a}{\rho_P}\right)\left(1-\dfrac{\rho_o}{\rho_M}\right)}{\left(1-\dfrac{\rho_o}{\rho_P}\right)\left(1-\dfrac{\rho_a'}{\rho_M}\right)} - 1\right] \quad \textbf{(3)}$$

where:
$\varepsilon_{m.d.}$: Error due to the difference between the sample density and the density of the adjustment weights.
ρ_a : Air density at the time of adjustment of balance
ρ_a' : Air density at the time of weighing
ρ_0 : Air standard density (1. 2 kg / m^3)
ρ_P: Adjustment weight density
ρ_M : Sample density

NOTE: M=P and $\varepsilon_{m.d.}$=0 in any of the following situations:
- The sample density is the same as the adjustment weight density and the air density is the same at the time of adjustment and weighing.
- The air density at the time of adjustment and weighing are equal to standard density.
For instance, if no corrections are made for this source and highly accurate mass measurements are required, the conditions at the laboratory where weighing is performed should ensure an air density as close to standard density as possible.

3.4.- BALANCE- RELATED SOURCES OF UNCERTAINTY
- Unsatisfactory Repeatability:

This source affects the balance reading. Variations in reading occur when one same load is repeatedly placed in the center of the balance pan. These variations are due to the balance electronics and the loading cell itself. The uncertainty component due to these variations depends on the load. The dependence function depends on the balance but in every case it is monotonous increasing with the load. Consequently, we will conservatively consider that it is constant in the value that corresponds to the maximum capacity:

$$u_{rep.} = s_{rep.} \quad \textbf{(4)}$$

where:
$u_{rep.}$: Uncertainty due to the unsatisfactory repeatability
$s_{rep.}$: Standard deviation resulting from a series of weighing of a load with a conventional mass close to the balance's maximum capacity performed under repeatability conditions.

3.4.1.-SOURCES OF UNCERTAINTY THAT AFFECT THE SENSITIVITY OF THE BALANCE:

a) Adjustment:

-Systematic adjustment error:

A systematic error may occur when adjusting the sensitivity of the balance, usually owing to a drift in the conventional mass value of the adjustment weight.

This error may be estimated and corrected by performing a series of weighings (n) with a conventional mass load with a nominal value equal to that of the adjustment weight ($M_{aj.}$), centered in the balance pan, immediately after the adjustment.

$$\delta_{sist.aj.} \cong \frac{\overline{L}_{aj.} - M_{aj.}}{M_{aj.}} = \frac{\overline{L}_{aj.}}{M_{aj.}} - 1 \cong \frac{\overline{L}_{aj.}}{\hat{M}_{aj.}} - 1 \quad \textbf{(5)}$$

where:

$\delta_{sist.aj.}$: Estimation of the sensitivity error due to inadequate adjustment of the balance's sensitivity

$\bar{L}_{aj.}$: Mean reading of the weighing series.

$\hat{M}_{aj}$ - Estimation of the conventional mass of the standard used in the assessment as per its calibration certificate. The estimation of the error due to the incorrect adjustment of the balance's sensitivity for the equation (5) is associated to an uncertainty that may be evaluated with the following equation:

$$u_{sist.aj.} = \sqrt{\left(\frac{u_{\overline{L_{aj}}}}{\hat{M}_{aj.}}\right)^2 + \left(\frac{u_{patron.aj.}}{\hat{M}_{aj}} \cdot \frac{\overline{L_{aj.}}}{\hat{M}_{aj}}\right)^2} \cong$$

$$\cong \frac{1}{\hat{M}_{aj.}} \sqrt{\frac{s_{rep.}^2}{n} + u_{patron.aj.}^2} \quad \textbf{(6)}$$

where:

$u_{sist.aj.}$: Estimation of the uncertainty associated to the error resulting from an incorrect adjustment of the balance's sensitivity.

$u_{\overline{L_{aj}}}$: Uncertainty in the mean reading.

$u_{patrón.aj}$: Uncertainty in the estimation of the conventional mass of the standard used in the assessment as per its calibration certificate.

- Error resulting from lack of reproducibility in the mechanism of adjustment:

The reading when the adjustment weight (internal or external) is placed on the balance presents random variations between the adjustments. The uncertainty component caused by this factor may be estimated from the historical values of the readings resulting from the verification of the adjustment with a standard weight (with a nominal value equal to the adjustment weight). The weight must be placed on the balance pan immediately after the adjustment is performed, and the reading on the balance must be recorded. The readings variance equals the addition of the variances resulting from the lack of reproducibility in the mechanism of adjustment and the unsatisfactory repeatability of the balance.

$$u_{rep.aj.} \cong \frac{\sqrt{s_{p.aj.}^2 - s_{rep.}^2}}{\hat{M}_{aj.}} \quad \textbf{(7)}$$

where:

$u_{rep.aj.}$: Estimation of the uncertainty component in the sensitivity resulting from a lack of reproducibility in the adjustment.

$s_{p.aj.}$: Standard deviation of the historical values of the readings resulting from the verification of adjustment.

b) Difference in temperature between the times of adjustment and weighing

The sensitivity of the electronic balances is a function of temperature, being its coefficient usually reported by the manufacturer.

This source is not to be considered if the balance is adjusted automatically, as required by variations in temperature, or if the balance is always adjusted by the user prior to each weighing. If the balance is adjusted for the technical service or by the user at defined intervals, the error due to this source is estimated with the following equation:

$$\delta_{T.} = \frac{\partial S}{\partial T} \Delta T \quad \textbf{(8)}$$

where:

$\delta_{T.}$: Estimation of the sensitivity error due to the variation in temperature between the time of adjustment and the time of weighing

ΔT :Difference between the weighing temperature and the adjustment temperature.

$\delta S/\delta T$: coefficient of variation of the balance sensitivity with respect to temperature.

If the correction for this source is not desired, it is possible to estimate uncertainty resulting from it, assuming a rectangular distribution for temperature, centered in the adjustment temperature with limits in $\pm \Delta T_{MÁX.}$

$\Delta T_{MÁX.}$: Greater variation in temperature expected at the site where the balance is usually used, since the adjustment was performed.

$$\mu_{T.} = \frac{\partial S}{\partial T}\frac{\Delta T_{MAX}}{2\sqrt{3}}$$

(9)

$\mu_{T.}$: Estimation of the uncertainty component due to the variation in sensitivity caused by the difference in temperature between the time of adjustment of sensitivity and the time of weighing

3.4.2.- SOURCES OF UNCERTAINTY THAT AFFECT READING.

a) Unsatisfactory Repeatability: described above.

b) Eccentricity of the load:

Variations in the balance readings may occur when a sample is placed in different points of the balance pan.

The uncertainty due to this factor is considered lineal with the load and with the distance from the mass center of that load and the center of the balance pan. It is estimated from the data from the eccentricity test. A triangular, cero-centered distribution is assumed for the possible values for the position of the sample with respect to the center of the balance pan (the density of probability of weighing a sample at an r distance from the center decreases with r, tending to cero on the edge of the balance pan).

$$u_{\text{exc.}} = \frac{\varepsilon_{\text{exc.}}}{\hat{M}_{exc}\, 2\sqrt{6}} L \quad \textbf{(10)}$$

where:

$u_{\text{exc.}}$: Estimation of the uncertainty component resulting from the eccentricity of the load

$\hat{M}_{exc}$ - Estimation of the conventional mass of the weight(s) used for the eccentricity test as per the calibration certificate.

$\varepsilon_{\text{exc.}}$: Maximum difference between two readings obtained in the eccentricity test.

c)Rounding:

This source is due to the discontinuous division of the balance. The uncertainty associated to it is independent of the load and it can be estimated by assuming the reading has a rectangular distribution between two divisions:

$$u_{\text{red.}} = \frac{d}{2\sqrt{3}} \quad \textbf{(11)}$$

where:

$u_{\text{red.}}$: Estimation of the uncertainty component in the reading due to rounding

d : Balance resolution

d) Lack of linearity:

The function that correlates the reading data in the balance as a function of the load can separate from the lineal function. This introduces a new source of uncertainty.

The mean of a sufficient number of readings ($\bar{L}$) performed immediately after the adjustment with a standard weight of a conventional mass M, centered on the balance pan permits to estimate the balance's accuracy error for that load:

$$\varepsilon_{exact.} = \bar{L} - M = \bar{L} - \left(\hat{M} - \varepsilon_{patron}\right) \cong \bar{L} - \hat{M} \quad \textbf{(12)}$$

where:

$\varepsilon_{\text{exact.}}$ – Accuracy error in L.

$\hat{M}$ - Estimation of the conventional mass of the standard weight as per the calibration certificate.

$\varepsilon_{\text{patrón}}$ - Error in the estimation of the conventional mass of the standard.

The linearity error measures the bias in the mean reading with respect to the S slope straight line defined by the cero and the coordinates (load, reading) corresponding to the point of adjustment:

$$\varepsilon_{lin} = \bar{L} - \left(\hat{M} - \varepsilon_{patron}\right) S$$

$$S \cong 1 + \delta_{\text{sist.aj.}} = \frac{\bar{L}_{\text{aj.}}}{\hat{M}_{\text{aj.}} - \varepsilon_{patron.aj.}}$$

so:

$$\varepsilon_{\text{lin.}} = \bar{L} - \frac{\hat{M} - \varepsilon_{patron}}{\hat{M}_{aj.} - \varepsilon_{patron.aj.}} \bar{L}_{aj.} \quad \textbf{(13)}$$

$$\varepsilon_{lin.} \cong \bar{L} - \frac{\hat{M}}{\hat{M}_{aj}} \bar{L}_{aj.} = (\bar{L} - \hat{M}) + \hat{M}\left(1 - \frac{\bar{L}_{aj.}}{\hat{M}_{aj}}\right) \cong$$

$$\cong \varepsilon_{exact.} - \hat{M}\,\delta_{sist.aj.} \quad \textbf{(14)}$$

We can thus estimate the error because of a lack of linearity in each load, with the possibility of correcting it.

In the cases in which the correction of this error is not desired, the uncertainty associated to the non linearity can be estimated (assuming that the correction of the adjustment systematic error is performed). That requires considering the data collected from the balance's accuracy test. This test implies recording the readings when calibrated and uniformly distributed loads within their own range, are centered on the balance balance pan.To estimate the uncertainty due to non linearity, the accuracy error for each load($\hat{\varepsilon}_{exact.}$), is approximated to the total error for that load. Then:

$$u_{lin.} \cong \frac{\sum_{i=1}^{n} (\hat{\varepsilon}_{exact.} - \hat{M}\,\delta_{sist.aj.})^2}{n} \quad \textbf{(15)}$$

where:

$u_{lin.}$: Uncertainty resulting from the lack of linearity

n : Number of weights performed in the accuracy test.

3.5. CALCULATION OF UNCERTAINTY FOR AN ANALYTICAL ELECTRONIC BALANCES

The following mathematical model corresponding to the equation (1)is proposed:

$$M + \varepsilon_{.m.} = \frac{L_i}{S} = \frac{L - \varepsilon_{m.b.} - \varepsilon_{rep} - \varepsilon_{exc} - \varepsilon_{red} - \varepsilon_{lin}}{(1 + \delta_{sist.aj.} + \delta_{rep.aj} + \delta_T)} \quad \textbf{(16)}$$

If $\epsilon_{.m.}$ and $\epsilon_{m.b.}$. are neglectable, combined uncertainty in M can be evaluated by:

$$u_M = \frac{1}{S}\sqrt{u_{Li}^2 + \left(\frac{L_i}{S}\right)^2 u_S^2} \quad \textbf{(17)}$$

as $S \approx 1$ and $L_i \approx L$ then:

$$u_M \approx \sqrt{u_{Li}^2 + L^2 u_S^2} =$$

$$= \sqrt{u_{rep.}^2 + u_{exc.}^2 + u_{red.}^2 + u_{lin.}^2 + u_{m.d.}^2 + L^2\left(u_{sist.aj.}^2 + u_{rep.aj.}^2 + u_T^2\right)}$$

Evaluating expanded uncertainty (U_{exp}) requires evaluating the coverage factor (k) according to the effective degrees of freedom.

$U_{exp} = k\, u_M$

In general, k=2 may be assumed as an approximation.

4. CALCULATION OF TOTAL EXPANDED UNCERTAINTY DERIVED FROM THE CALIBRATION DATA OF THE ANALYTICAL BALANCES AT LATU.

A study was performed of the different sources of uncertainty in weighing for a set of 18 electronic analytical balances that belong to LATU. The set includes balances of different trademarks and length of service.

An analysis was conducted of the contribution of the various sources of uncertainty to the overall uncertainty, as a function of load. The results obtained are shown in Table 1:

Table 1:

Source	Mean contribution in L = 40 g	Mean contribution in L = 200 g
Adjustment error (g)	11×10^{-5}	55×10^{-5}
Lack of repr. at adjustment (g)	4×10^{-5}	22×10^{-5}
Uncertainty in correction due to the systematic error of the adjustment (g)	1×10^{-5}	4×10^{-5}
Difference between density of sample(2g/cm^3) and adj. weighs (g)	2×10^{-5}	90×10^{-5}
Repeatability (g)	11×10^{-5}	11×10^{-5}
Eccentricity (g)	6×10^{-5}	29×10^{-5}
Rounding (g)	3×10^{-5}	3×10^{-5}
Linearity (g)	26×10^{-5}	26×10^{-5}
Total expanded uncertainty (g) (if the adjustment error is adjusted)	59×10^{-5}	203×10^{-5}

As can be seen in the case of low loads, the controlling sources of uncertainty are the ones related to the lack of linearity and repeatability, while with higher loads the controlling sources of uncertainties relate to the difference between the density of the sample and the adjustment weights and load eccentricity.

NOTES:
a) The uncertainty due to the density of the sample was estimated on the basis of the following assumptions:
- Average environmental conditions at the laboratory: T= (20±3) C, P= (760 ± 10)mmHg, H=(50 ± 20) %
- Average density of the samples handled (chemistry laboratory) = 2g/cm3
b) The mean contribution of each source was calculated as the arithmetical mean corresponding to the balances under analysis.

5.-MASS COMPARISON PERFORMED IN ANALYTICAL BALANCES AT THE VARIOUS SECTIONS AT LATU.

A comparison was done in 1999 to determine the conventional mass of a sample in analytical balances of various laboratories in LATU.

The comparison was aimed at the following:
- To conduct a control of the process of conventional mass determination in the analytical balances used in the various sections in LATU and to evaluate the efficiency of the methods of control of weighIngs used.
- To evaluate the procedure for calibrating balances of the Metrology section in LATU, applied to the analytical balances.
- To evaluate the method for estimating uncertainty in the determinations of the conventional mass of the samples.

5.1. METHODOLOGY:

A teflon cylindrical sample was used with a conventional mass of approximately 40 g. The idea of introducing a teflon sample arises from the fact that its density (2.17 g/cm^3) is closer to the density of the materials typically used in the chemistry laboratory than that of stainless steel. This contributes to better assess the errors resulting from the difference between the sample density and the adjustment weights.

The conventional mass of the sample was determined in the analytical balances of the sections involved in the comparison, by their own staff, who applied the methods usually employed at each section.

The balances that participate in the comparison meet the following conditions:
- they have Calibration Certificates in force (the re-calibration period of the balances is one year).

- they are adjusted and verified by the user. The control method used consists of conducting the sensitivity adjustment (with an internal or external weight, depending on the type of balance) and its verification with an external control weight. A control graph with determined limits is plotted with the readings obtained for the control weight. If it falls outside those limits, the adjustment is repeated.

The following data were reported for each balance:
- the balance reading (s) when the weight is placed
- the room conditions at the time of determination (pressure, temperature and humidity)
- the uncertainty estimated for the weighing.

5.2. RESULTS:

The room conditions remained within the following limits in all cases:
Temperature: between 18 and 25 °C
Atmospheric pressure: between 757 and 774 mm Hg
Humidity: between 44 and 73 %

The results obtained are presented in Table 2. The table shows the errors obtained in each balance.
Error = Reported value – value of the Conventional Mass determined by Mass Metrology Section.
This value was determined through the double replacement method of comparison performed in a mass comparator with a division of 0.01 mg (standard deviation=0.012 mg). These measurements correspond to runs # 1 and # 19 in the table.

NOTES:
- the errors in the second column were calculated from the values reported for the conventional mass in direct reading
- the errors in the third column were calculated from the values of the conventional mass corrected for the adjustment errors in each balance, as reported in its calibration certificate.

Table 2:

SECTOR CODE	ERROR (direct reading) /mg	ERROR (reading corrected for the adjustment error)	UNCERTA-INTY (reading corrected for the adjustment
1	0	0	0,015
2	0,3	0,3	0,37
3	0,1	0,1	0,34
4	0,1	0,1	0,66
5	-0,2	0,1	0,82
6	-0,1	-0,1	0,34
7	-0,4	-0,5	0,46
8	0	0	0,45
9	-0,1	-0,1	0,38
10	0,5	0,6	0,57
11	0	0,2	0,1
12	0,2	0,2	0,47
13	0	-0,1	0,44
14	-0,4	-0,1	0,14
15	-0,3	-0,3	0,6
16	-0,1	-0,2	0,69
17	0,4	0,4	0,32
18	-0,1	0	0,89
19	0	0	0,015
20	-0,2	0,2	0,27
AVERAGE (ABS.VAL.)	0.11	0,1	0,58

5.3. CONCLUSIONS:

If the values falling outside the declared uncertainty interval are excluded, we observe that:

- the errors in the direct reading for the teflon sample do not exceed 0.4 mg.
- the errors with a corrected adjustment error do not exceed 0.3 mg.
- the errors observed are compatible with the uncertainties under evaluation.

It can generally be concluded that:

- in no cases do the errors in mass determinations at the sectors of LATU that conduct control of their balances exceed 0.3 mg if weighing is done with the load well centered on the balance pan and if corrections are made using the Calibration Certificate.
- the methods used for Control and Calibration of the balances do not suffice to ensure the above.

6.-REFERENCES:

- Calibration of non-automatic electronic weighing instruments-DKD- R-7-1, Issue 98.
- OIML R 76/1-2, 1992, 1993
- OIML R 111- Draft 2, February 2, 2000.
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