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Extension of dissemination of mass unit below 1 mg in Romania

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Abstract. The determination of mass influences a vast range of activities and is the dominant factor in the conduct of trade. Many chemical reference methods rely on gravimetric determinations. Health, safety and business costs may be vitally dependent on the accurate determination of mass which it's an important source of errors in any analysis. In addition, a wide range of derived SI units (Flow, Volume, Force, Pressure, Humidity, Density) is based on mass determination for traceability [1]. An improvement in the realization and dissemination of the mass scale lead to an improvement of measurement uncertainty in these areas. Some of the needs for reduced uncertainties at small mass (milligram and below) exist in pharmaceutical, health, defence and biotechnology industries. Similarly, in nanotechnology, micro-mass standards can provide traceability for a range of measurements of mass, force and density. In the last period, the dissemination of mass unit below 1 mg has seen a continuous development, the main applications of the micro-mass being in the small force measurements and also for determination of sensitivity error of mass comparators with high accuracy. Considering all these aspects, the mass laboratory of Romanian National Institute of Metrology (INM) considered necessary to extend the dissemination of mass unit below 1 mg using micro-mass standards, with nominal values between (100...500) µg.

1 Introduction

Measurements play a key role in modern life, in industry, commerce and generally in society, in quality assurance and safety, in establishing the prices. In addition, it is an increasing need in science and technology to continuously improve the measurement accuracy and complexity. That is the reason why "the metrologists" are permanently involved in the development of new measurement standards, new technical methods of measurement, to conceive new tools and procedures to meet the growing demands in improving accuracy, increasing trust and speed of measurements [2].

In this way, the mass laboratory of INM considered necessary to extend the dissemination of mass unit below 1 mg, in order to address the emerging needs.

Although these weights are not identified in [3].only in the description of the subdivision method, their calibration gives the possibility to extend the mass scale below this limit.

The extension of dissemination of mass scale below 1 mg represents the basis of micro/nano force measurements, being required by industries such as pharmaceutical, defense, environmental monitoring, energy production and transportation, etc.

The calibration of micromass standards having nominal values between (100…500) µg was carried out for the first time in Romania, at INM.

In a first stage, was calibrated two sets of micromass standards belonging to INM (having foil shape) with a sequence of (5, 2, 1) for each set and after that, in a second stage, some of these weights were used as check standards for calibration of wire shape micro masses, with a classical sequence of (5, 2, 2, 1) , belonging to clients.

The article is divided into 5 sections as follows: introduction, measurement instruments used for comparison, calibration of the micro-standards using weighing designs, quality assessment of the calibration, conclusions.

2 Measurement instruments used for comparison

The comparator used for the measurements was an UMX 5 balance with 0.1µg resolution, installed at INM in 2008. Fig. 1 shows this mass comparator.

For accurate determination of the air density an environmental monitoring system was used, consisting in a precise "climate station", Klimet A 30.

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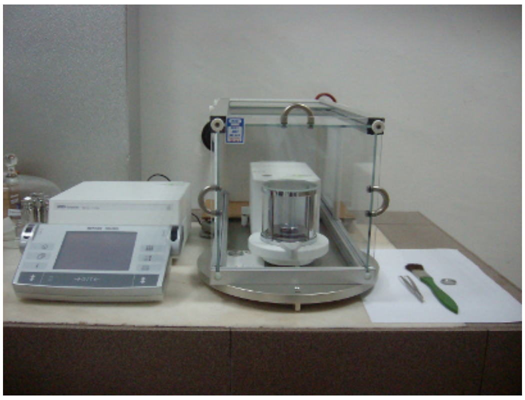

Figure 1. Mass comparator used in calibration

All the unknown micro standards are made of aluminum alloy.
Figure 2 shows the handing tools and storage boxes for the micro masses foil shaped.

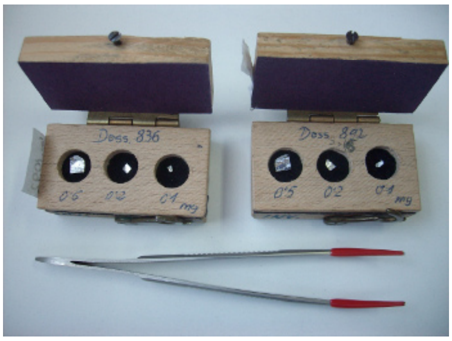

Figure 2. Boxes containing micro masses foil shape

The weights belonging to clients are wire shaped, Fig. 3.

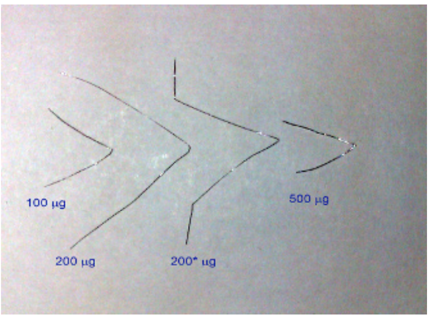

Figure 3. Micro masses wire shape

3 Calibration of the micro-standards using weighing designs

3.1 Calibration of the micro standards (belonging to INM) having foil shape

In the first part of the calibration, using as reference standard a mass of 1 mg, made of stainless steel, six unknown micromass standards (foil shaped) are calibrated according to the weighing matrix presented in the Table 1. As check standard is used a mass of 1 mg, made of aluminium alloy.
The calibration data used are obtained from 6 weighing cycles ABBA for each comparison.

Table 1. Weighing matrix for the first stage of the calibration.

Obs. No.	Mass (mg)							
	1	1*	0,5	0,5*	0,2	0,2*	0,1	0,1*
	R	C	T	T	T	T	T	T
1	1	-1	0	0	0	0	0	0
2	1	0	-1	-1	0	0	0	0
3	0	1	-1	-1	0	0	0	0
4	0	0	1	-1	0	0	0	0
5	0	0	1	0	-1	-1	-1	0
6	0	0	0	1	-1	-1	0	-1
7	0	0	0	0	1	-1	0	0
8	0	0	0	0	1	0	-1	-1
9	0	0	0	0	0	1	-1	-1
10	0	0	0	0	0	0	1	-1

The third row of the table identifies the function of the weight in the weighing design, using the following abbreviations:

R = reference standard
T = (unknown) test weight
C = check standard.

In the Table 2 are presented the volumes and densities (together with associated uncertainties) for all the weights involved in the calibration.

TABLE 2. Volumes V_i, densities ρ_i and their associated uncertainties for all the weights

Nominal mass mg	***V*** **cm³**	***U(V)*** **cm³**	***ρ*** **kg/m³**	***U(ρ)*** **kg/m³**
1	0.00013	$2 \cdot 10^{-6}$	7950	140
1*	0.00038	$2 \cdot 10^{-5}$	2650	130
0,5	0.00019	$9 \cdot 10^{-6}$	2650	130
0,5*	0.00019	$9 \cdot 10^{-6}$	2650	130
0,2	0.00008	$4 \cdot 10^{-6}$	2650	130
0,2*	0.00008	$4 \cdot 10^{-6}$	2650	130
0,1	0.00004	$2 \cdot 10^{-6}$	2650	130
0,1*	0.00004	$2 \cdot 10^{-6}$	2650	130

The least squares method using weighing designs was used to determine the conventional mass for each micro-standard.
In the Table 3 are presented the measurement results obtained by subdivision method for sub-milligram weights belonging to INM.

Table 3. Measurement results obtained for sub-milligram weights belonging to INM (first stage of the calibration).

Nominal value (mg)	Conventional mass (mg)	Uncertainty *U* (mg)
1*	1,0031	0,0012
0,5	0,5183	0,0007
0,5*	0,5141	0,0007
0,2	0,2017	0,0004
0,2*	0,1742	0,0004
0,1	0,0993	0,0003
0,1*	0,0934	0,0003

3.2 Calibration of the micro weights (belonging to clients) having wire shape

In the second part of the calibration, the set of wire shape micromass standard belonging to a client, having a classical sequence of (5, 2, 2, 1), was calibrated. As reference standard was used a mass of 1 mg, made of stainless steel and as check standards were used some of the micro weights (belonging to INM) calibrated before.
The weighing matrix used for the measurements is presented in the Table 4.

Table 4. Weighing matrix for the second stage of the calibration.

Obs. No.	Mass (mg)							
	1	1*	0,5	0,5	0,2	0,2	0,1	0,1
		INM	INM	Λ	Λ	Λ	INM	Λ
	R	C	C	T	T	T	C	T
1	1	-1	0	0	0	0	0	0
2	1	0	-1	-1	0	0	0	0
3	0	1	-1	-1	0	0	0	0
4	0	0	1	-1	0	0	0	0
5	0	0	1	0	-1	-1	-1	0
6	0	0	0	1	-1	-1	0	-1
7	0	0	0	0	1	-1	0	0
8	0	0	0	0	1	0	-1	-1
9	0	0	0	0	0	1	-1	-1
10	0	0	0	0	0	0	1	-1

Taking into account that all the unknown micro standards are made of aluminum alloy their volumes and densities (together with associated uncertainties) are the same from the Table 2.
The measurements results obtained in the second part of the calibration are presented in the Table 5.

Table 5. Measurements results obtained for sub-milligram weights belonging to a client (second stage of the calibration).

Nominal value (mg)	Conventional mass (mg)	Uncertainty *U* (mg)
1* (INM)	1,0030	0,0012
0,5 (INM)	0,5184	0,0007
0,5 Λ	0,5001	0,0007
0,2 Λ	0,2010	0,0004
0,2 Λ	0,2006	0,0004
0,1*(INM)	0,0935	0,0003
0,1 Λ	0,0998	0,0003

3.3 Estimating measurement uncertainty

In evaluating expanded uncertainty (from the Table 3 and Table 5), the following contributions were taken into account:

- type A uncertainty;
- type B uncertainty given by:
    - reference standard,
    - resolution of the weighing instrument;
    - sensitivity of the weighing instrument;
    - effect of the air buoyancy.

All these components can be graphically represented in an Ishikawa (Fishbone) diagram, as is shown in the Figure 4.

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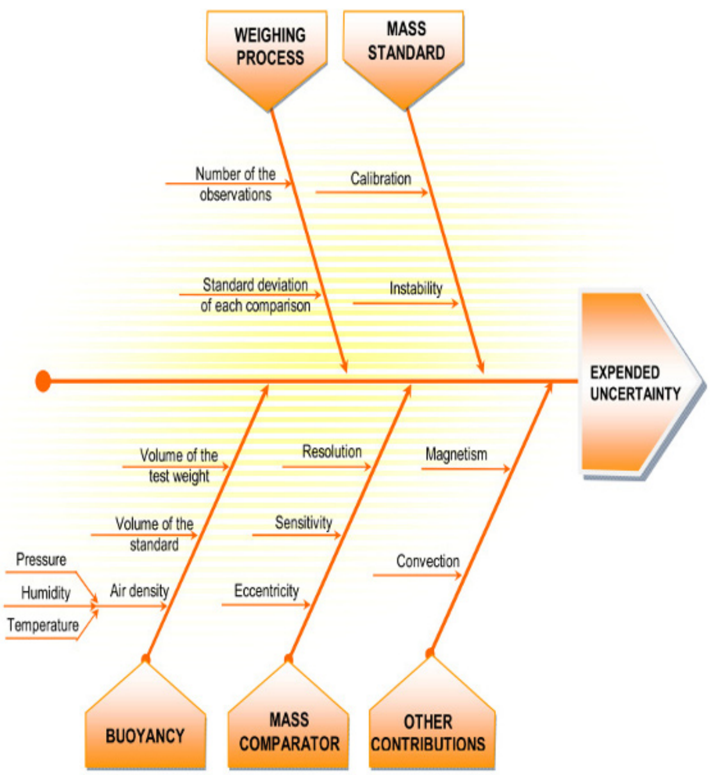

Figure 4. Ishikawa diagram of uncertainty components in micro masses determination

4 Quality assessment of the calibration

As shown, for calibration of micro weights belonging to a client, micro mass standards of 1 mg, 0,5 mg and 0,1 mg from INM were used as check standards.

To see if the mass values obtained for check standards are consistent with previous values, it is necessary to perform a statistical control. The purpose of the check standard is to assure the validity of individual calibrations. A history of values for these weights is required for this purpose [3]. Considering that for the micromass standard foil shape there are no sufficient calibration data to perform a statistical control according to [3], the method of normalized error E_n was chosen, which takes into account the result and its uncertainty from the last calibration [4].

The results obtained for the check standards in this subdivision procedure are compared with data from their calibration certificates (mass values obtained in the previous calibration). The differences in values are normalized using the formula [5]:

$$E_n = \frac{\delta_{II} - \delta_{certif}}{\sqrt{U_{II}^2 + U_{certif}^2}} \qquad (1)$$

where:

δ_{II} represents the mass error of the check standard obtained in the second stage of the calibration;

δ_{certif} the mass error of the check standard from the calibration certificate, obtained in the first stage of the calibration;

U_{II} the expanded uncertainty of the check standard obtained in the second stage of the calibration;

U_{certif} the expanded uncertainty of the check standard from the calibration certificate, obtained in the first stage of the calibration;

Using this formula, the measurement and the reported uncertainty are acceptable if the value of E_n, is between -1 and +1. Table 6 presents the results obtained for the normalized errors, E_n.

Table 6. Comparison of measurement results of check standards obtained by subdivision method (second stage) and results from the calibration certificate.

Nominal mass of check standard	**Results obtained in the second stage of the calibration**		**Calibration certificate (results obtained in the first stage of the calibration)**		**E_n**
mg	δ mg	U mg	δ mg	U mg	
1	0,0030	0,0012	0,0031	0,0012	-0,1
0,5	0,0184	0,0007	0,0183	0,0007	0,1
0,1	-0,0065	0,0003	-0,0066	0,0003	0,2

4 Conclusion

The paper focused on the calibration of weights below 1 mg, carried out for the first time in Romania, at INM.

The comparison of results obtained for the check standards using the normalized errors E_n, confirms the consistency of the results.

The micro-standards can be used in improving uncertainty in determining the indication error and sensitivity error of weighing instruments of special accuracy (micro and ultra-micro balances).

Also, the extension of dissemination of mass scale below 1 mg represents the basis of micro/nano force measurements being required by industries such as pharmaceutical, defense, environmental monitoring, energy production and transportation, etc. In this way, the extension of the mass unit till 100 µg can lead to an extending of force unit till 1µN.

References

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