Standards fabrication to providing metrological traceability in micromass and nanoforce measurements results

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Abstract: Some of the more sensitive weighing equipment available nowadays has its repeatability close to tenth of microgram. OIML characterize mass standards bigger than 1 mg, so in this range doesn’t exist direct traceability to the kg prototype. The ASTM has a characterization of mass standard 50, 100, 200 e 500 micrograms. This work have a purpose of providing traceability to mass measurement in microgram scale (nanonewton scale in force) with the confection and calibration of a standard weights collection. At this time were studied two materials, Tungsten and MetGlass2705M (MetGlass), and produced 12 mass standards.

1. Introduction
The American Society for Testing and Materials (ASTM) recognized the advances in the area of weighing equipments that currently can achieve less than one microgram in the repeatability. The ASTM has specifications for precision mass standards (ASTM E617-13 revised in 2013 for including definition of weight specifications sub milligrams with maximum permissible error.

“Weight manufacturers must be able to provide evidence that all new weights comply with specifications in this standard (material, density, magnetism, mass values, uncertainties)” [1].

In Brazil, specialized metrology regulations for the manufacturing and use of standard weights N°. 233/1994 [2] don’t exist in 50 µg up to 500 µg range (500 nN up to 5 µN in the force case). The OIML R-111, specifies the format, dimensions, nominal values, nature of the material used in mass standards construction and assigns accuracy classes, has international classification and definitions related to mass standards and in this recommendation mass standards have their nominal value starting in 1 mg.

The US government is the most invests in micro and nanotechnology. In 2000, the Institute of Technology of the National Initiative of Nanotechnology was created, with initial investments of United State of American $ 495 million and continues being the country that invests more in this area. The science current state increasingly requires traceability in the microgram range, being relevant for balances sensitivity determination, in nanotechnology, in biotechnology, in fine chemistry, and others.

Researches in the Chemical, Biological, Biotechnology, Pharmaceutical and Materials areas often involve weighing-based measurement processes whose results must be traceable to mass units in order to ensure, in micro scale, the quality of their measurement results. Usually gravimetric measurements have the small uncertainties involved in this process.
This paper shows the process of choosing the adequate material for mass standards and stability monitoring. Was used aluminum to make the mass standards, as it is recommended in OIML to nominal values in milligram range, and testing the manufacturing with other materials, MetGlass and tungsten, which showed good stability during the monitoring tests.

2. Material characteristics
The manufacture of microgram standards requires proper material and precise production. It's hard to manipulate these mass standards, the size and shape are critical characteristics of these standards. Was used Aluminum (Al), MetGlass2705M and Tungsten, but we will describe just the MetGlass (MG) and Tungsten (W) characteristics because Aluminum is already recommended for use in standard weights.

2.1. Tungsten characteristics
The Tungsten was confirmed [3] by determining its specific mass. The value of its mass was obtained from weighing, and its dimensions determined by an optical measurement system [4] and tungsten wire diameter is 0.0767 mm obtained by optical device (figure 1.a), as shown in table 1.

| Tungsten | Tabulated value | Measured value |
|----------|----------------|----------------|
| Density  | 19.2 g/cm³      | 19.1 g/cm³    |
| Elastic Modulus | 400 GPa | -- |

2.2. MetGlass characteristics
Amorphous metal alloys, MetGlass, are a new class of material, are composed of atoms, molecules or ions that don’t have a long range ordering. The MetGlass properties are direct related with its homogeneous structure, thus allowing a different behavior of the amorphous alloys in relation to the crystalline alloys.

These alloys are produced by the fast cooling of their liquid phase (glasses), therefore metals without crystalline structure are called "metallic glasses" [5, 6, 7]. MetGlass used was the MetGlass2705M and have a chemical composition of 69% Co, 12% B, 12% Si, 5% Ni and 2% Mo [8]. And it has the following properties [9] as shown in table 2:

| Density (g/cm³) | Vicker’s hardness (50 g load) | Tensil strength (GPa) | Elastic Modulus (GPa) |
|-----------------|-------------------------------|----------------------|----------------------|
| 7.80            | 900                           | 1 – 2                | 100 – 110            |

2.3. Stability
An important step in this research is mass monitoring and stability after six months the weighs collection has the following distribution, table 3.

| Amount | Mass value (µg) |
|--------|----------------|
| 4      | 50             |
| 4      | 100            |
| 2      | 200            |
| 2      | 500            |
We currently manufacture a weights collection of nominal values outside the OIML recommendation, but which can be very useful for calibrating scales in the micromass range because it preserves the regularity of the intervals between each calibration point and also because it is easier to apply the subdivision calibration method to these weights. This weighs collection has the following distribution, table 4.

| Amount | Mass value (µg) |
|--------|----------------|
| 3      | 250            |
| 6      | 500            |
| 2      | 750            |
| 1      | 1000           |

Table 4. Standards mass in microgram.

Was obtained from weighing of first standards the following results, show in table 5.

| Standards Identification | Mean Value (µg) | Standard deviation (µg) |
|--------------------------|-----------------|-------------------------|
| 1 (MG)                   | 47.00           | 0.87                    |
| 2 (Al)                   | 47.50           | 0.58                    |
| 3 (MG)                   | 50.00           | 1.04                    |
| 4 (MG)                   | 52.50           | 2.18                    |
| 5 (MG)                   | 96.50           | 1.60                    |
| 6 (MG)                   | 97.50           | 0.76                    |
| 7 (MG)                   | 99.00           | 0.76                    |
| 8 (MG)                   | 102.50          | 1.29                    |
| 9 (MG)                   | 201.00          | 1.92                    |
| 10 (MG)                  | 201.00          | 3.21                    |
| 11 (W)                   | 497.50          | 1.80                    |
| 12 (MG)                  | 499.50          | 2.32                    |

Table 5. Standards mass in microgram.

3. Traceability
The traceability to the SI unit mass, the kilogram, is widely used and established in all countries. In Brazil, the mass measurements results are traceable of 1 mg up to greater nominal values. A lot of the modern weighing equipment has resolution much less than 1 milligram, in fact 0.1 microgram. In this case the traceability can be reached by interpolation (or extrapolation) [10] to determine the corrections and the respective measurement uncertainties [11]. Thus to provide a better reliability and reach lower uncertainties (Type A) is necessary to provide traceable standards weights in the microgram range.
3.1 Equipments and materials

The following materials were used in the standards mass production:

![Wire tungsten magnification in system optical](image1)

![MetGlass strip](image2)

![Aluminum strip](image3)

**Figure 1.** a) Wire tungsten magnification in system optical. b) MetGlass strip. c) Aluminum strip.

The equipments used are:

i) Mass comparator (ultramicro). Used in the samples mass determination and stability monitoring, resolution 0.1 μg.

ii) Standard weight collection PP016, 1 mg up to 20 mg [12]. To perform the mass comparator linearity e sensitivity.

iii) Digital caliper with 0.01 mm resolution. Just to samples length measurements.

iv) Optical dimensional system. 0.001 mm of resolution [3]. To determine the volume of tungsten used in calculating density.

4. Measurements and monitoring

To improve the measurements results reliability was made a mass comparator linearization in nominal value below 20 mg. The measurements points (table 6) were verified using the E₁ accuracy class standard weight collection PP016.

|   | 1 mg  | 2 mg  | 5 mg  | 10 mg  | 20 mg  |
|---|-------|-------|-------|--------|--------|
| 1 | 0.9885| 2.0003| 4.9987| 10.0087| 19.9890|
| 2 | 0.9887| 2.0008| 4.9988| 10.0109| 19.9909|
| 3 | 0.9887| 2.0006| 4.9985| 10.0086| 19.9897|
| 4 | 0.9889| 2.0014| 4.9984| 10.0092| 19.9901|
| 5 | 0.9895| 2.0005| 4.9981| 10.0098| 19.9896|

| $\bar{m}$ | 0.9888| 2.0007| 4.9985| 10.0094| 19.9898 |

Where, $\bar{m}$ is the mean mass value.

Using the Calibration Certificate [12] we obtain the corrected values, table 7.
Table 7. Mass corrected measurement results.

| Nominal value (mg) | Mean value (mg) | Corrected values (mg) |
|-------------------|-----------------|-----------------------|
| 1                 | 0.9888          | 0.9904                |
| 2                 | 2.0007          | 2.0006                |
| 5                 | 4.9985          | 4.9995                |
| 10                | 10.0094         | 10.0083               |
| 20                | 19.9898         | 19.9932               |

In figure 2 are shows the plotted data of table 7 (corrected values) and calculate the mass comparator angular $a$ coefficients (sensitivity).

\[ a = 0.9998 \text{ mg/mg} \]

Figure 2. Nominal value vs. measurement result.

5. Conclusion
Nowadays, scientific researchers have greater requirements for traceability at lower mass values, lower than OIML R-111 recommendation provides. This lack accuracy in all fields that requires measurements results in micro or nanoscale in mass or force measurements.

This research has the purpose of determining the methodology of mass standards production, including the material choice and its metrological characterization.

The initial results point out that in this range of mass all of materials (Tungsten, MetGlass and Aluminum) are stable at least in these months of monitoring. Aluminum is already recommended by OILM as a material for mass standards, especially for its low density which allows better handling of the standards. Tungsten has very high density, creating a difficulty for its handling despite its advantages of homogeneity and chemical stability. The MetGlass alloy has an intermediate density, but it is very versatile and can be manufactured in very thin strips which allows for better standards
manipulation, the disadvantage are its magnetic properties, in many cases the cutting process already cause magnetization, what is a factor against its use. The next steps Calibrate standards by subdivision method and continuous evaluation of the long term stability.

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6. References

[1] NCSLI 2013 Standard Specifications for Laboratory Weights and Precision Mass Standards Nashville
[2] Inmetro 1994 Portaria 233 - Regulamentação Metrológica Instrumentos de Medicação e Medidas Materializadas (Brasil: Inmetro)
[3] AZoM 2012 Tungsten - Mechanical Properties and Material Applications Azo Materials
[4] Optical Grade Calibration Certificate DIMCI 0926/2016 Lamed/Inmetro
[5] HOLT, M. L. 1956 Less-common Metals and Alloys Metal Finish pp 48-55
[6] NAGEL, S. R. 1982 Advanced chemical physics Wiley pp. 227-275 New York
[7] SEARSON, P. C.; NAGASKAR, P. V.; LATANISION, R. M. In: WHITE, R. E.; BOCKRIS, J O. M.; CONWAY, R. B. 1990 Modern aspects of electrochemistry Plenum Press N° 20 pp 121-161 New York
[8] MATERIALS 1996 Conference proceedings. Technology & Engineering. Volume II SPE/ANTEC pp 1769
[9] Technical Bulletin Ref: 2705M08022014 - MAGNETIC ALLOY 2705M Metglass
[10] EURAMET 2015 Guidelines on the calibration of non-automatic weighing instruments: Version 4.0 (11/2015) (Braunschweig: EURAMET)
[11] BIPM, IEC, IFCC, ILAC, ISSO, IUPAC, IUPAP and OIML 2008 Guide to Expression of Uncertainty in Measurement (GUM: 1995 with Minor Corrections) JCGM 100:2008 (Sèvres: Bureau International des Poids et Mesures)
[12] Standards Weighs Calibration Certificate (PP016) DIMCI 1247/2015 Lamas/Inmetro