

COMPARISON BETWEEN THE NATIONAL PROTOTYPE OF THE KILOGRAM AND STAINLESS STEEL MASS STANDARDS

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Abstract – In 2013, the National Prototype of the Kilogram (NPK) No.2 belonging to Romania, together with stainless steel kilogram standard Ni81, received an updated mass value from BIPM. Therefore, the first task after their receiving from BIPM was to perform comparisons between NPK and reference kilograms stainless steel standards. In the paper are described mass standards, weighing scheme used for comparisons, calculations of mass and associated uncertainties, as the mass change for all weights involved. It is also presented a comparison between Romanian CMC(s) and other countries for this important stage of dissemination of mass unit.

Keywords: national prototype of the kilogram, reference mass standards, weighing scheme, check standard.

1. INTRODUCTION

In 1889, at the First Conference on Weights and Measures (CGPM), the kilogram prototypes were shared - randomly - for each country. Romania received the "National Prototype Kilogram No. 2" (NPK 2). Now, it is maintained by the National Institute of Metrology and serves as a reference for the entire dissemination of the mass unit in Romania.

The link between the SI unit of mass and the Romanian national standard of mass is maintained through periodic calibrations of NPK at the BIPM. During its lifetime, the Romanian national standard of mass was calibrated at the BIPM six times: three "periodic verifications" occurred in 1899-1911, 1939-53, and 1988-92 and three additionally calibrations in 1976, 2005 and 2013.

The realization and dissemination of the mass unit by the Mass Laboratory of the Romanian National Institute of Metrology starts from the reference stainless steel standards (a set of three 1 kg mass standards and two sets of disc weights from 50 g to 500 g), which are traceable to the International Prototype Kilogram through the mass of the Romanian Prototype Kilogram No. 2. This is followed by dissemination to multiples and submultiples of the kilogram covering the range from 0.1 mg to 1000 kg.

In a schematic representation, in the Fig. 1 is presented this main stage of the Romanian dissemination mass unit from NPK until mass standards of class E_1 .

The first task after receiving the standards from BIPM was to perform comparisons between NPK and reference stainless steel standards. In the first stage, the reference kilogram standards marked with 656, 655 and Ni81 were

compared with NPK and, in a second stage, two sets of disc weights were compared with NPK. For both stages, Ni 81 (considered the most important standard after NPK) acted as check standard. In this paper, the mass comparisons between NPK No. 2 and the three stainless steel kilogram standards are presented. The mass standards, weighing instrument, weighing scheme used for comparisons, calculations of mass and associated uncertainties, as the mass change for all weights involved are described.

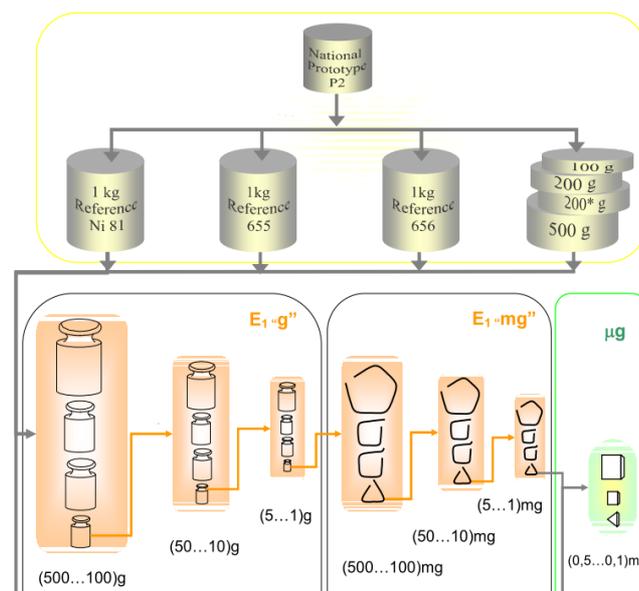


Fig. 1. Schematic representation of the main stage of the dissemination of mass unit

2. EQUIPMENTS AND STANDARDS INVOLVED IN MEASUREMENT

2.1. Mass comparator

An automatic mass comparator (AT 1006, manufactured by Mettler-Toledo) was available for the dissemination of mass unit from NPK to stainless steel mass standards. With this automatic mass comparator, batch of weights can be loaded in one step at the beginning and one unloading in the end of the process. The comparator is designed for mass determinations of high accuracy using substitution method. Errors due to operator during the determinations are practically eliminated by automatic operation mode. This comparator gives the possibility to perform measuring cycles ABA, ABBA or AB1 ... BnA, according to [1].

The technical specifications for the comparator are:

- Maximum capacity: 1011g
- Readability: 1µg
- Repeatability:
 - (2...3) µg in the determinations with Pt-Ir standard,
 - (0.4...1) µg in the determinations with stainless steel mass standards

2.2. Reference kilograms

The Fig. 2 shows the weights involved in the main stage of the dissemination of mass unit:

- NPK is a cylinder with diameter and height of about 39 mm. It is made of an alloy of 90 % Platinum and 10 % Iridium.

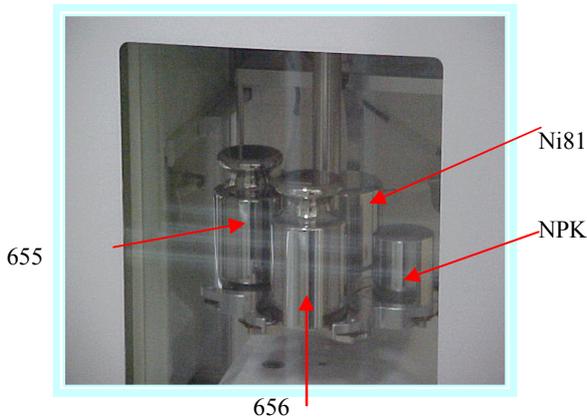


Fig. 2. Kilograms mass standards

- Nicral 81 (Ni81) was made by “Prolabo”- France in 1978 and received by INM in 1981. It is the most important standard after NPK and it is made of Ni-Cr, having a diameter approximately equal to the height (54 mm).

- The weights denoted with 655 and 656 are made from non-magnetic stainless steel, having a cylindrical form, according to OIML.

The main characteristics of the weights involved in measurements are listed in the Table 1.

Table 1. The characteristics of the weights involved in the measurements

Weight	Volume V cm ³	Density, ρ kg/m ³	U_V cm ³	U_ρ kg/m ³	α °C ⁻¹
VP2	46,4377	21534,22	0,0012	0,56	2,60E-05
V656	124,8407	8010,21	0,0011	0,07	4,80E-05
VNi	127,7398	7828,41	0,0012	0,07	4,59E-05
V655	124,8405	8010,22	0,0011	0,07	4,80E-05

2.3. Environmental conditions monitoring system

The mass comparator is equipped with an environmental conditions monitoring system, consisting in a precise “climate station”, model Klimet A30.

Apart from this, an instrument for determination of the carbon dioxide concentration from air, type CarboCap GMP343 is used. The instrument is necessary for measuring

the CO₂ concentration from air, in order to calculate air density and air buoyancy corrections during comparisons performed between the NPK and stainless steel mass standards.

Starting from environmental parameters, the air density is calculated using the formula recommended in [2].

3. COMPARISON SCHEME

The mass standards are compared between them in all possible combinations, as is presented in Fig. 3.

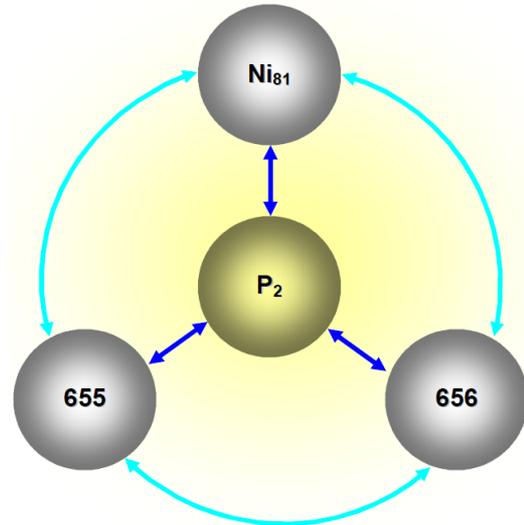


Fig. 3. Comparison scheme

In matrix form, the scheme is presented as follows:

$$X = \begin{matrix} & P_2 & Ni81 & 656 & 655 \\ \begin{matrix} P_2 \\ Ni81 \\ 655 \\ 656 \end{matrix} & \begin{vmatrix} 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 \\ 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & -1 \end{vmatrix} \end{matrix} \quad (1)$$

In the comparisons, Ni 81 acted as check standard.

4. PROCESSING DATA OBTAINED IN COMPARISONS

The mathematical model of the comparison can be represented as follow:

$$Y = X\beta + e \quad (2)$$

where

$Y(n,1)$ is the vector of the n observations (including buoyancy corrections);

$\beta(k,1)$ the vector of the k mass values of the standards;

$X(n, k)$ design matrix; entries of the design matrix are +1, -1, and 0 according to the role played by each of the parameters (from the vector β) in each comparison;

$e(n,1)$ vector of the deviations

Each element of the vector Y is calculated using formula:

$$y = \Delta m + \rho_a(V_j - V_t) \quad (3)$$

y the corrected indication;

Δm difference of balance readings calculated from weighing cycles (ABBA);

ρ_a air density at the time of the weighing;

V_t, V_j volumes of the standards involved in a measurement

If the temperature during the measurements is different than 20°C, the volume of the weights is corrected using the formula:

$$V_t = V_{20} \cdot [1 + \alpha_t \cdot (t - 20)] \quad (4)$$

where:

V_t is the volume of the standard at the working temperature;

V_{20} volume of the standard at 20°C;

t temperature during calibration;

α_t the coefficient of cubic expansion of the material from which the weights are made.

At each difference calculated, was added the correction due to the difference between the centers of gravity of the weights.

The results of the calibration are obtained with the aid of least squares adjustment which also provides the variance-covariance matrix of the calculated mass values.

The mass of the weights was calculated using the formula [3]:

$$\langle \beta \rangle = (X' \cdot X')^{-1} X' \cdot Y' \quad (5)$$

where

$$X' = G \cdot X \quad \text{and} \quad Y' = G \cdot Y \quad (6)$$

G is a diagonal matrix containing the diagonal elements:

$$g_{ii} = n_i \cdot (s_{bal}^2 / s_i^2), \quad i = 1 \dots n \quad (7)$$

n_i is the ABBA cycles number,

s_{bal} standard deviation of the balance, determined from a complete comparison,

s_i standard deviation of each determination, from a complete comparison.

$X' \cdot X'$ transpose of X and

$(X' \cdot X')^{-1}$ is the inverse of $(X' \cdot X')$.

5. ESTIMATING UNCERTAINTY

In evaluating standard uncertainty associated with the results of calibration, the following contributions have to be taken into account:

- type A uncertainty, evaluated by statistical analysis of series of repeated observations;
- type B uncertainty, evaluated by scientific judgment based on all of the available information on the possible variability of an input quantity that has not been obtained from repeated observations, such as:

- reference standard,

- resolution of the weighing instrument;

- sensitivity of the weighing instrument;

- effect of the air buoyancy

- the difference between the heights of the centers of gravity of the weights.

The uncertainty components can be graphically represented in an Ishikawa (Fishbone) diagram [4], as shown in Fig. 4.

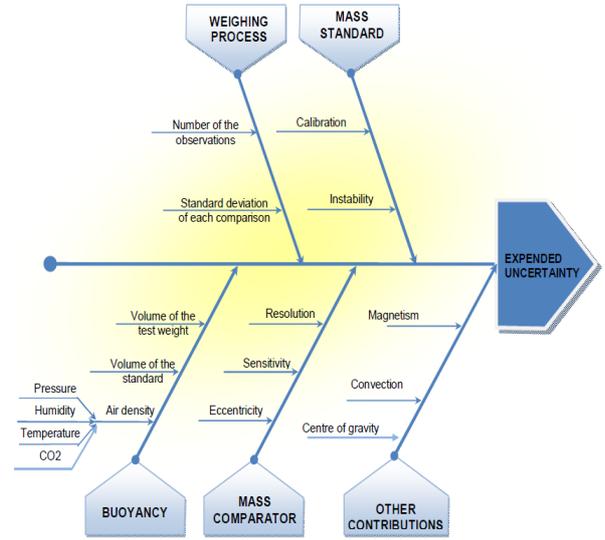


Fig. 4 Ishikawa diagram of uncertainty components

6. FINAL RESULTS OBTAINED FROM THE COMPARISONS

The results obtained for the three mass standards calibrated are presented in the Table 2.

Table 2. The final results obtained for mass standards

Standard	Mass	Uncertainty U mg
Ni 81	1 kg + 0.113 mg	0.042 mg
655	1 kg - 0.293 mg	0.042 mg
656	1 kg - 0.203 mg	0.042 mg

7. STATISTICAL CONTROL REGARDING QUALITY ASSESSEMENT OF THE CALIBRATION

To see if the mass value obtained for Ni 81 are consistent with previous value received from BIPM, it was calculated the normalized error E_n , which takes into account the result and its uncertainty from the last calibration. The calibration certificate from BIPM gives for Ni 81 the value:

$$1 \text{ kg} + 0.119 \text{ mg with } u_c = 0.015 \text{ mg (k=1)}$$

By calculating the normalized error, it can be seen that the consistency of the results is demonstrated.

$$E_n = \frac{\delta_{INM} - \delta_{BIPM}}{\sqrt{U_{INM}^2 + U_{BIPM}^2}} = 0.12 \quad (8)$$

8. MASS CHANGE OF STAINLESS STEEL STANDARDS

8.1. Kilogram Ni81

Analysis of the behaviour in time for the standard Ni81 presented in the Table 3 and Figure 4 was performed using only the mass values obtained at BIPM.

Table 3. Mass change of Ni 81

Data	Mass error mg	Uncertainty U mg	Drift mg
1981	0.123	0.023	
Sept. 2005	0.130	0.014	0.007
Sept. 2012	0.177	0.030	0.047
Oct. 2012	0.123	0.030	-0.056
Nov. 2012	0.120	0.030	-0.003
May 2013	0.119	0.030	-0.001

One can observe a good stability of this standard. It is noted the fact that, the values obtained starting with October 2012 were given after the cleaning of the standard.

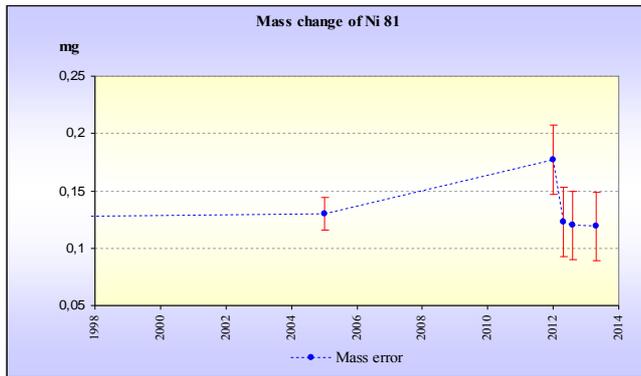


Fig. 5 Mass change of Ni 81

8.2. Kilogram 655

Table 4. Mass change of 655

Data	Mass error mg	Uncertainty U mg	Drift mg
Mar.1999	-0.14	0.150	
Dec.2002	-0.184	0.043	-0.044
Nov.2003	-0.211	0.064	-0.027
Dec.2006	-0.194	0.054	0.017
Ian.2010*	-0.271	0.070	-0.077
Feb.2011	-0.285	0.070	-0.014
Dec.2011	-0.384	0.070	-0.099
Dec.2011**	-0.330	0.070	+0.054
July 2012	-0.316	0.070	0.014
Dec. 2013	-0.293	0.070	+0.023

* It was determined the density of the weights
 **These values are obtained after corrections

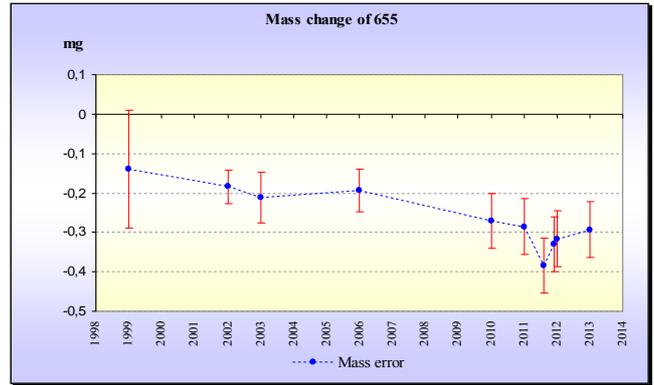


Fig. 6 Mass change of 655

8.3. Kilogram 656

Table 5. Mass change of 656

Data	Mass error mg	Uncertainty U mg	Drift mg
Mar.1999	-0.19	0.15	
Dec.2002	-0.187	0.048	0.003
Nov.2003	-0.257	0.046	-0.070
Dec.2006	-0.142	0.026	0.115
Ian.2010**	-0.224	0.070	-0.082
Feb.2011	-0.250	0.070	-0.026
Dec.2011**	-0.287	0.070	-0.037
Feb. 2012	-0.241	0.070	+0.046
Dec. 2013	-0.203	0.070	+0.038

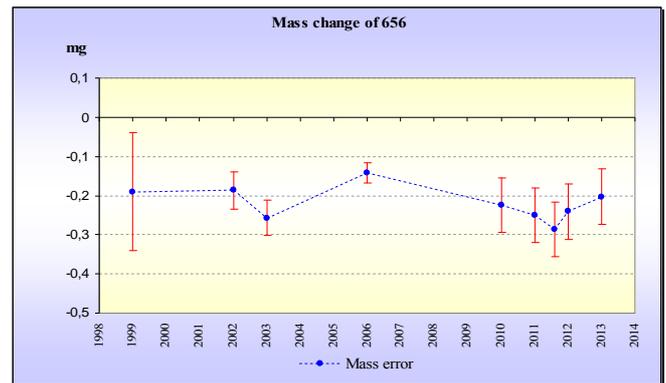


Fig. 7 Mass change of 656

If for the standards 655 would be eliminated the measurement performed in December 2011 (when a correction was necessary), it can be observed a satisfactory stability of this mass standard.

It is considered that, it would be necessary for the next period that the standards be recalibrated at an interval of 2 years.

9. COMPARISON BETWEEN CMC(S) AT 1 kg LEVEL

In Figure 7 is presented a comparison between Romanian CMC(s) and other countries for this important stage of dissemination of mass unit.

The Figure shows the current stage of our CMC and the new position of Romania if the results from the Table 2 would be confirmed.

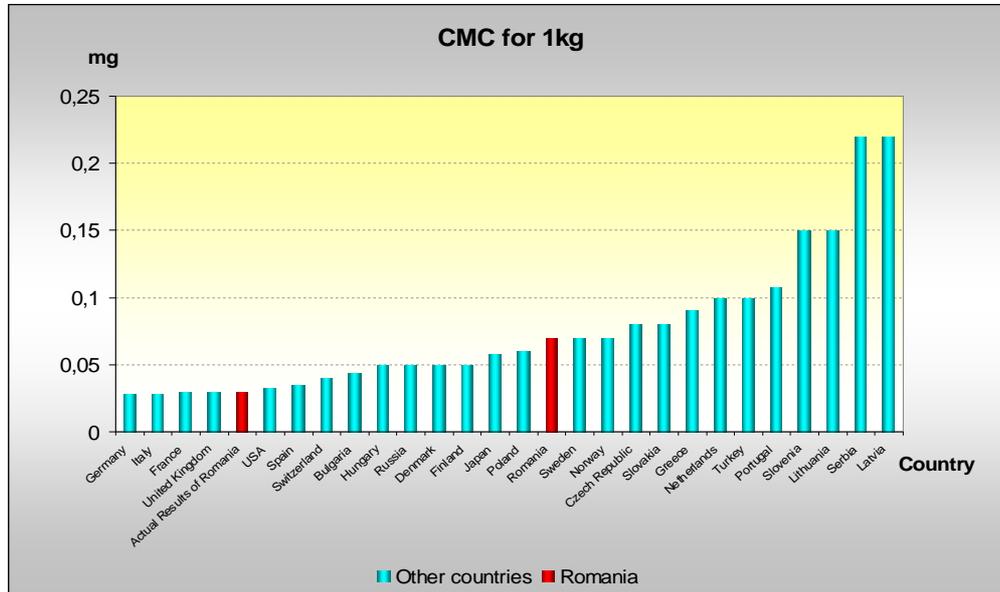


Fig. 7 Comparison between CMC(s) at 1 kg level

10. CONCLUSIONS

The paper presents the comparison between the Romanian National Prototype of the Kilogram and three stainless steel mass standards marked as: Ni 81, 655 and 656.

In the comparisons, the mass standard Ni 81 acted as check standard. The analyzed results using the normalized error showed a good consistency.

From the analysis of mass change made for the standards 655 and 656, it was concluded that they should be recalibrated at 2 years.

Although for expanded uncertainty were obtained the values from Table 2, in the calibration certificate was recorded the value covered by CMC, namely $U = 0.07$ mg.

REFERENCES

- [1] OIML, "International Recommendation No 111, Weights of classes E1. E2. F1. F2. M1. M2. M3", 2004, pp. 5-71.
- [2] A. Picard, R. Davis, M. Glaser and K. Fujii, "Revised formula for the density of moist air", CIPM-2007.
- [3] R. Schwartz, "Guide to mass determination with high accuracy", *PTB MA-40*, pp. 3 and pp. 54-58, 1995.
- [4] A. Vălcu, "Extension of dissemination of mass unit below 1 mg in Romania", *Proceedings of International Metrology Congress*, Paris, 2013 and "Metrologie Revue", Vol.LX n°. 2-3/2014, pp.21-28, 2014.