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Report on

A bilateral comparison of a 1 kg platinum standard

by

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Abstract:
A bilateral comparison on the measurement of mass has been carried out between the national measurement institutes INM, Romania and DFM, Denmark. The transfer standard was a 1 kg platinum standard, which was calibrated directly against the national prototypes held by INM and DFM. The purpose of the comparison was to assess the models used by DFM and INM to predict the change in mass of the prototypes over time due to the adsorption of hydrocarbons or other airborne pollutants. The results of the comparison indicate that the current mass values assigned to the prototypes are slightly inconsistent. As the Danish prototype was recalibrated at BIPM in 2001 and provided consistent results in a similar comparison in EUROMET Project 509 in 2002, it is most likely the drift model assigned to the Romanian prototype that is less accurate than assumed.

1 Introduction

This report describes a bilateral comparison of a 1 kg platinum weight between the National Institute of Metrology (INM), Romania and the Danish Institute of Fundamental Metrology (DFM). The comparison was carried out under a contract (Ref.: RO0006.02.05) with Deutsche Gesellschaft für Zerstörungsfreie Prüfung (DGZfP) and was financed by the European Community.

INM and DFM are both participating in the key comparison EUROMET.M.M-K4 (EUROMET Project 510) in which two 1kg standards of stainless are calibrated. The preliminary analysis of this comparison indicates that the results of DFM are consistent with the key comparison reference values whereas the results of INM deviates significantly from the key comparison reference value compared to the uncertainty claimed in the Romanian CMC table recently submitted to EUROMET. DFM

Romania holds the national prototype no. 2, which was last calibrated at BIPM during the Third Periodic Verification of National Prototypes of the Kilogram (1988-1992). The prototype has not been calibrated at BIPM since then, but the laboratory has applied a drift model that takes into account the possible change in mass value since the verification.

DFM holds prototype no 48, which was last calibrated at BIPM in July 2001. The value assigned to no. 48 based on a drift model was verified to be consistent to reference values assigned to two prototypes compared in EUROMET Project 509 taking into account the estimated uncertainty (k=1) of 0.005 mg on the results reported by DFM.

The purpose of the bilateral comparison between DFM and INM is to test the consistency of the drift models applied by DFM and INM for the change in mass values of the national prototypes.

2 Transfer standard

The transfer standard selected as the measurement object, identified as DFM 251, is an old platinum 1 kg weight named "Schumacher" after the Danish astronomer, who bought it in 1835 as a copy of the French Archive Kilogram. The weight DFM 251 has been compared to the Danish prototype since 1907 and seems to be reasonably stable although the surface finish is rather poor compared to that of the prototypes.

The quantity to be measured in the comparison is the mass value m of the DFM 251 weight (not the conventional value). The volume of the weight DFM 251 is $V = 47.188\ 0\ \text{cm}^3$ (at 20 °C) with standard uncertainty $u(V) = 0.005\ 0\ \text{cm}^3$. The volume temperature expansion coefficient is $\alpha = 27 \cdot 10^{-6}\ \text{K}^{-1}$.

3 Participants

The participants of the bilateral comparison were INM, Romania and DFM, Denmark. DFM was the pilot laboratory for the comparison. The addresses of the participants are given in Annex 1.

4 Circulation scheme and time schedule

The weight DFM 251 was calibrated first at DFM, then at INM and finally at DFM again. The weight was transported by airplane (in the cabin) forth and back between DFM and INM. During transport the weight was kept in its original wooden case inside a waterproof box. The agreed time schedule of the comparison is given in Annex 1.

5 Measurement protocol

The agreed measurement protocol is given in Annex 1.

6 Results

The values of the mass m (expressed in terms of the correction $\Delta m = m - 1$ kg) of the weight DFM 251 measured in the comparison are shown in Table 1, column 4 "Results". The table includes two mass values measured in the spring 2002, when the DFM 251 weight was used as a check standard in the comparison between the Danish prototype and two Pt/Ir mass standards circulated in the EUROMET project 509.

Meas. No.	Lab ID	Date	Result		Reference value		Norm.dev.	Included?
i		t/day	Δm/mg	$u(\Delta m)$/mg	Δm_r/mg	$u(\Delta m_r)$/mg	d	(y/n)
1	DFM-DK	2002-05-24	-2.8643	0.0082	-2.8784	0.0091	1.7	y
2	DFM-DK	2002-06-15	-2.8647	0.0080	-2.8784	0.0091	1.7	y
3	DFM-DK	2003-08-20	-2.8794	0.0081	-2.8784	0.0091	-0.1	y
4	INM-RO	2003-09-15	-2.905	0.013	-2.8784	0.0091	-2.0	y
5	DFM-DK	2003-10-08	-2.8800	0.0080	-2.8784	0.0091	-0.2	y

Table 1. Results of the comparison. Δm is the mass correction of the weight DFM 251 measured by the specified participant at the specified date, Δm_r is the corresponding reference value, and d is the normalised deviation defined as the difference $D = \Delta m - \Delta m_r$ divided by the standard uncertainty of that difference. The last column indicates if a result is included in the calculation of the reference value or not (y=yes, n=no).

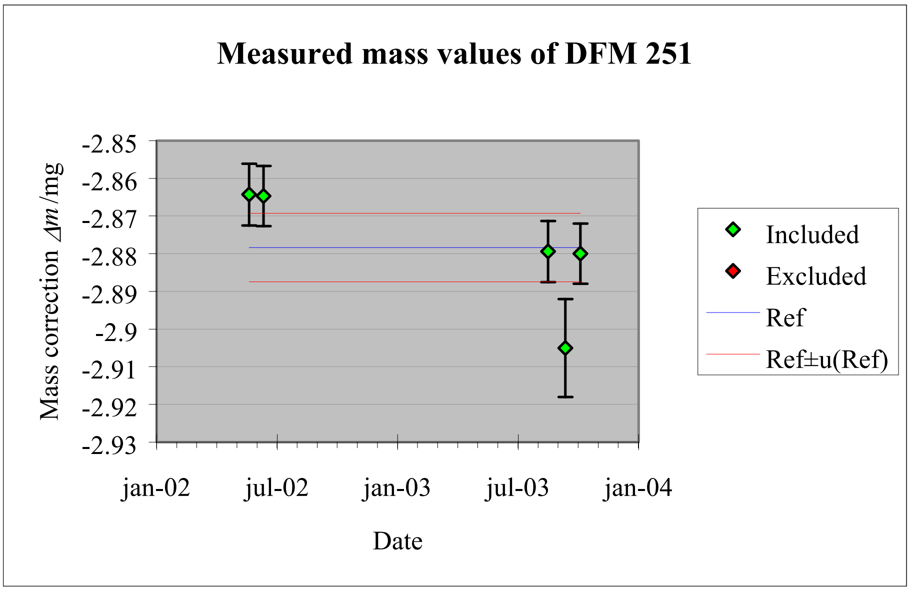

Figure 1. The results provided by the participants. The errors bars indicate the stated standard uncertainties ($k = 1$) associated with the results. The lines represent the reference values calculated from the results marked "Included" together with the associated standard uncertainty.

The following general model for the change in the actual correction Δm of the DFM 251 weight during the comparison has been used[1]:

$$\Delta m = a_1 + a_2 t + \delta m \,, \qquad (1)$$

where t is the time of measurement, a_1 and a_2 are constants, and δm is a time dependent random variable with expectation 0 and variance σ^2, which describes random changes in the mass of DFM 251 over time. The constant a_2 describing a deterministic drift in time is assumed to be negligible. Based on this model, the reference values Δm_r have been calculated by the method of least squares taking into account the claimed uncertainties and covariances of the measurement results[2]. The calculated reference values are given in Table 1 and plotted in Figure 1 as a solid line.

As the four results provided by DFM are directly traceable to the Danish prototype No. 48, there is a significant covariance between the results; this covariance is equal to $u^2(m_{48}) = (0.0055 \text{ mg})^2$, where $u(m_{48})$ is the standard uncertainty associated with the mass value m_{48} assigned to the prototype, cf. section 7.1.

In order to improve the consistency of the highly correlated results of DFM, a standard deviation $\sigma = 0.0065$ mg of the random changes δm has been introduced. This uncertainty component is included in the uncertainty of the reported reference values.

In order to test the overall consistency of the results, the observed chi-square value χ^2 of the least square analysis,

$$\chi^2_{\text{Obs}} = 7.1$$

is compared to the expectation value

$$\nu = 4.$$

As the probability p,

$$p = P\{\chi^2(\nu) > \chi^2_{\text{Obs}}\} = 12.9\%,$$

is larger than 5%, the overall consistency of the results can not be rejected at a 5% level of significance.

In order to identify potentially discrepant results[3], the normalised deviations are calculated:

$$d = \frac{\Delta m - \Delta m_{\text{r}}}{u(\Delta m - \Delta m_{\text{r}})}. \quad (2)$$

A result is classified as discrepant at a 5% level of significance, if $|d| > 2$. The values of d shown in Table 1 and Figure 2 indicates that result no 4 is marginally discrepant.

The degree of equivalence between the results and corresponding reference values are shown in Figure 3. Also this figure indicates that result no. 4 is marginally discrepant.

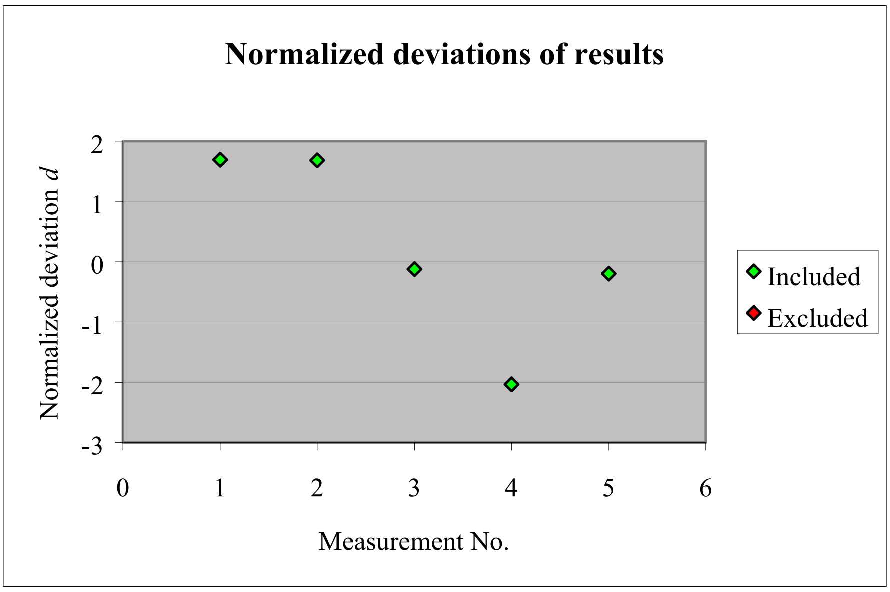

Figure 2 The normalised deviations d of the results. Results with $|d| > 2$ are classified as discrepant results.

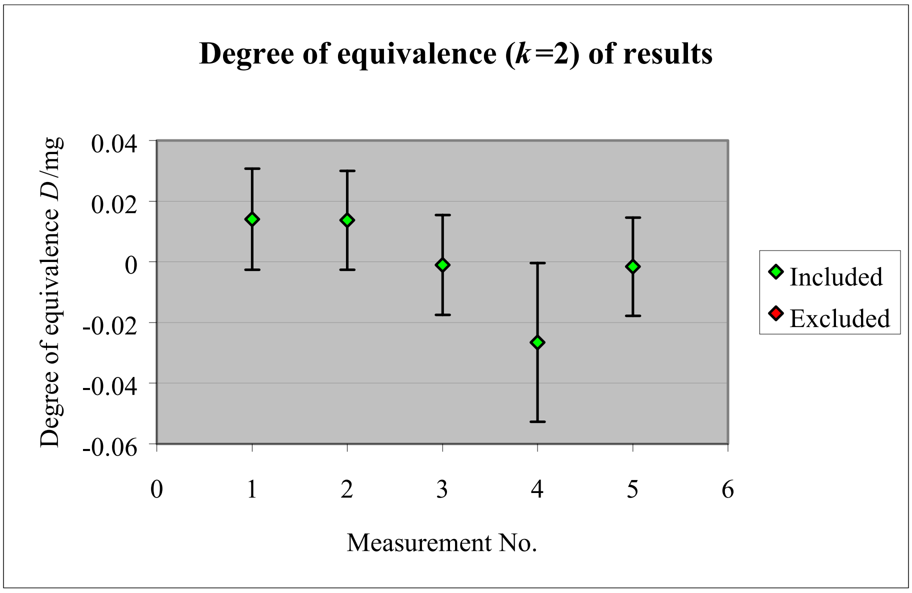

Figure 3. The degree of equivalence expressed as the deviation $D = \Delta m - \Delta m_r$ and the expanded uncertainty ($k = 2$) of that deviation.

7 Assignment of mass values to prototypes

The dominant source of uncertainty in the measurements performed in the comparison is the limited knowledge about the current value of the national prototype used as reference standard. It is therefore essential to assess how the current values and the associated uncertainties of the prototypes have been assigned from the calibration history available.

7.1 Danish prototype (No. 48)

The mass $m_{48} = 1\,\text{kg} + \Delta m$ of prototype no 48 of the kilogram is changing as a function of time t. The change in mass can be split up into two terms: 1) Change in mass of the prototype in its cleaned state, and 2) change in mass due to adsorption of "dirt" (hydrocarbons from the air) since last cleaning. Whereas the first change is assumed to be linear in time t, the second change is assumed to be proportional to $\sqrt{t - t_0}$, where t_0 is the time of last cleaning:

$$\Delta m = \Delta m_0 + \gamma_1 (t - t_0) + \gamma_2 H(t - t_0) \sqrt{t - t_0} \qquad (3)$$

where $H(x)$ is the Heaviside step function. The constants Δm_0, γ_1 and γ_2 and the associated covariance matrix are determined by fitting the model (3) to the set of calibration points (t, Δm) obtained from the BIPM. The fitting is performed by the method of least squares taking into account the uncertainties of the calibrations performed by BIPM. The mass predicted by equation (3) and the associated standard uncertainty is shown in Figure 4 as a function of time. The preliminary results of EUROMET 509 indicate that the drift model (3) was valid up to June 2002.

The value assigned to the Danish prototype by DFM in this comparison is:

m_{48} = 1 kg + 0.1291 mg, $u(m_{48})$ = 0.0055 mg (2003-08-15)

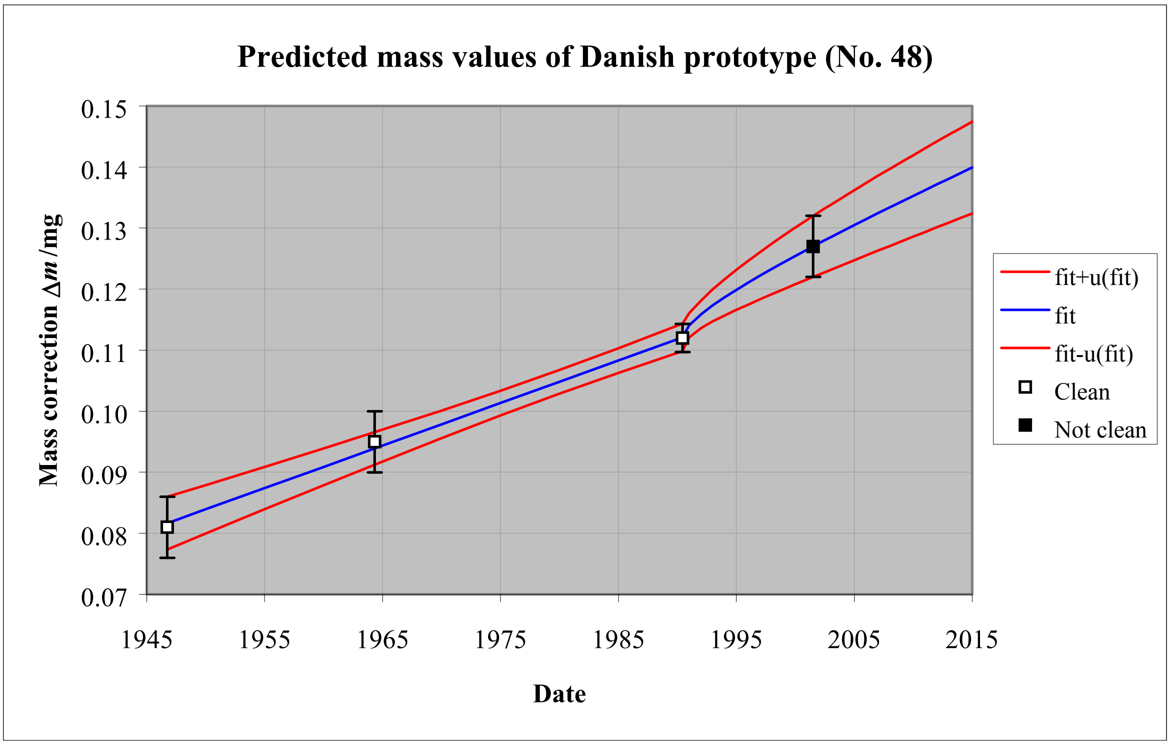

Figure 4. The predicted mass values of prototype no. 48 as a function of time. The error bars of the calibration points indicate the standard uncertainties ($k = 1$) associated with the points. Up to 1992, the calibration points refer to the mass after cleaning, whereas the last calibration point refers to the mass with no cleaning since 1992. After 1992, the curve "fit" describes the predicted value of the prototype since the last cleaning. The curves "fit±u(fit)" indicates the standard uncertainty of the prediction.

7.2 Romanian prototype (No. 2)

The calibration history of the Romanian prototype No. 2 is shown in Figure 5. In the time interval from the calibration of the cleaned weight in 1976 to the calibration of the not-cleaned weight in 1991, the change in the mass of the prototype was –1.71 µg/year. INM has assumed the same annual change in mass since the cleaning in 1992 with a standard uncertainty of 11 µg. The value assigned to the Romanian prototype by INM in this comparison is therefore:

$$\boldsymbol{m_2 = 1\ \text{kg} - 1.146\ \text{mg}, \quad u(m_2) = 0.011\ \text{mg} \quad (2003)}$$

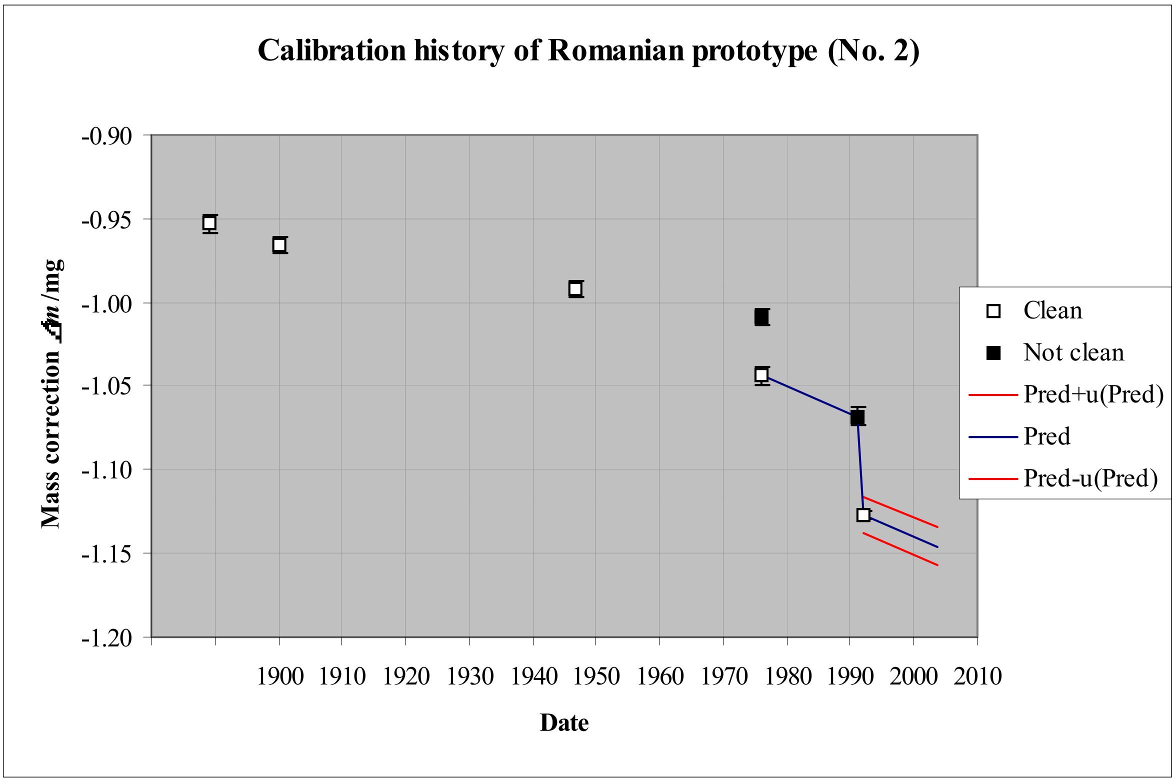

Figure 5. The calibration history of prototype no. 2. The full line "Pred" is shows how the mass of the prototype is assumed to have changed since the cleaning in 1976 and is used to predict the mass since the last cleaning and calibration in 1991-1992. The lines "Pred±u(Pred)" indicates the standard uncertainty of that prediction.

8 Discussion

Considering the unpredictable behavior of the Romanian prototype, even in its cleaned state, it may be argued that the claimed standard uncertainty of 11 µg for the predicted mass value is too small. If a straight line is fitted to the mass of the cleaned prototype, the standard deviation of the fit is 33 µg.

Even for a prototype that is predictable in its cleaned state, the adsorption of "dirt" on the surface is rather unpredictable. As a rule of thumb[4], the increase in mass of a prototype after cleaning is 10 µg within the first year plus 1 µg/year. From the observed variation in removable "dirt" from the different prototypes cleaned at BIPM, the uncertainty associated with this rule of thumb is estimated by DFM to be on the order of 20 µg. A smaller uncertainty of the predicted mass of the prototype in the not-cleaned state can only be achieved by monitoring the change in mass by recalibrations at BIPM (without cleaning) and frequent comparisons with one or several similar standards.

The mass value of the weight DFM 251 reported by INM is 33 µg lower than the average of the values reported by DFM. Assuming that the values reported by DFM can be trusted as indicated by the preliminary results of EUROMET Project 509, this means that the mass of the Romania prototype in 2003 is 33 µg higher than the value currently assigned by INM with a standard uncertainty of 9 µg. That is:

Hypothesis 1: $m_2 = 1\ \text{kg} - 1.113\ \text{mg}$, $u(m_2) = 0.009\ \text{mg}$ (2003)

If it is assumed that the annual change of –1.7 µg/year of the cleaned prototype observed between 1899 and 1992 continues, and the rule of thumb for the change due to adsorption of "dirt" is applied, then the following mass value of the Romanian prototype is predicted:

Hypothesis 2: $m_2 = 1\ \text{kg} - 1.125\ \text{mg}$, $u(m_2) = 0.020\ \text{mg}$ (2003)

Note that these two hypotheses are mutually consistent taking into account the uncertainties. That indicates that a drift model for the Romanian prototype based on BIPM's rule of thumb is a better choice than the drift model applied by INM in the comparison.

9 Conclusion

The results provided by DFM and INM are marginally inconsistent. The reason for the discrepancy is most probably due to the fact that the national prototypes change their mass due to adsorption of hydrocarbons from the air in a more or less unpredictable way. As the model for predicting the mass of the Danish prototype is confirmed by the preliminary results of EUROMET Project 509, it is most likely the model for predicting the mass of the Romanian prototype that is less accurate than assumed. It is therefore recommended that the uncertainty of the predicted value is increased, or that the prototype is recalibrated at BIPM, preferably without prior cleaning.

10 References

[1] Lars Nielsen, Evaluation of the calibration history of a measurement standard, DFM-01-R25 (2001).

[2] Lars Nielsen, Evaluation of measurement intercomparisons by the method of least squares, DFM-99-R39 (2001)

[3] Lars Nielsen, Identification and handling of discrepant measurements in key comparisons, DFM-02-R28 (2002).

[4] G. Girard, The third periodic verification of national prototypes of the kilogram (1988-1992), *Metrologia*, 1994, **31**, 317-336

Annex 1

Bilateral comparison of mass

Measurement protocol

This protocol specifies the conditions of a bilateral comparison of a mass between Denmark and Romania. The comparison aims at serving as a supplement to the research project EUROMET 509 “Intercomparison of platinum-iridium kilogram standards” thus connecting the Romanian national prototype with those kept at other EUROMET institutes. The pilot laboratory (DFM) has participated in EUROMET 509 and will thus provide the link.

1. General information:

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2. Transfer standard:

The transfer standard used for the comparison will be a 1 kg platinum weight DFM 251 called “Schumacher” after the Danish astronomer, who bought it in 1835 as a copy of the French Archive Kilogram. The weight DFM 251 has been compared to the Danish platinum-iridium kilogram prototype since 1907 and is still used by DFM as a check standard for monitoring changes in the prototype..

The volume of the weight DFM 251 is $V = 47.188\ 0\ \mathrm{cm}^3$ (at 20 $^{\circ}$C) with standard uncertainty $u(V) = 0.005\ 0\ \mathrm{cm}^3$. The volume temperature expansion coefficient is $\alpha = 27 \cdot 10^{-6}\ \mathrm{K}^{-1}$.

3. Schedule and Transportation:

Preliminary schedule:

Measurements at DFM:	11 August to 22 August 2003.
Transport to INM, Bucharest:	26 August 2003.
Measurements at INM, Bucharest:	28 August to 28 September 2003.
Transport to DFM:	30 September 2003.
Measurements at DFM:	6 October to 17 October 2003.

Draft report is expected 14 November 2003.

The schedule allows for repeat measurements at INM, Bucharest, if preliminary results reported to the coordinator indicates significant deviations from the pilot results. However, no measurement values will be communicated between the participants until the draft report is issued.

The device is transported by courier between the participating laboratories. The device is shipped in a plastic transport case.

The coordinator has drawn up travel insurance for the transfer instrument.

4. Customs procedures:

An ATA-Carnet will be provided for clearance of customs. The recipient must ensure that the proper forms are filled at receipt and return shipment.

5. Measurements:

The quantity to be measured is the mass (not conventional value) of the transfer standard DFM 251.

In order to maintain the mass value of the transfer standard, it shall be handled with the tongue normally used for handling the prototype. The chamois leather pads of this tongue should be covered by clean lens paper wrapped around the pads and fixed with rubber bands or tape. If the weight is placed on a table, the table surface should be clean and covered by lens paper. Any accident during handling of the transfer standard should be reported to the pilot laboratory.

Upon arrival, the transport case shall be brought to the mass laboratory where it shall be kept closed for 24 hours for acclimatisation. After acclimatisation, the transport case should be opened and the wooden case with the weight DFM 251 should be taken out and inspected for damages. Any observed damage of the transport case as well as the wooden case shall be reported immediately to the pilot laboratory.

The transfer standard should be compared directly against the national prototype of the participant using a clean, high resolution mass comparator. Before starting the measurements, the standards to be compared shall be cleaned carefully by brushing with a clean, soft brush. After visual inspection for dust particles on the surface, the weights should be placed in the weighing chamber of the comparator. After 24 hours of acclimatisation in the weighing chamber, the measurements may be started.

6 Reporting:

A measurement report must be submitted to the pilot laboratory within **three weeks** after the completion of the measurements and should include:

a) The mass of the transfer standard DFM 251 and the associated standard uncertainty
b) A description of the measurement procedure
c) Date and result of the last calibration of the national prototype at BIPM
d) The value and standard uncertainty currently assigned to the mass of the national prototype
e) The value and standard uncertainty of the volume of the national prototype
f) Manufacture, model and resolution of the comparator used
g) Specification of instruments used for measurement of temperature, pressure, humidity and CO_2 content of the air.
h) Environmental conditions during the measurements.
i) An uncertainty budget that as a minimum includes the uncertainty of
    1) the mass of national prototype
    2) the weighing process
    3) the volumes of DFM 251 and the national prototype
    4) the air density

The coordinator will provide a first draft of the comparison report within **four weeks** after the receipt of the measurement report.

Protocol prepared by
Lars Nielsen, July 2003.