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EUROMET Project 509: A comparison of platinum-iridium kilogram mass standards

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National Measurement System

EUROMET Project 509:
A comparison of platinum-iridium kilogram mass standards

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ABSTRACT

The kilogram is unique among the base SI units in being the only one defined by an artefact rather than with relation to naturally occurring physical constants [1]. This imposes a unique set of problems relating to the maintenance and traceability of the mass scale worldwide. All mass measurements must be ultimately traceable to the International Prototype of the Kilogram (K) held at the BIPM (*Bureau International des Poids et Mesures*). This traceability is achieved via copies of the Prototype held by National Measurement Institutes (NMIs) and maintained by the periodic re-verification of these copies by the BIPM [2]. A major problem with maintaining this traceability is the inherent instability of the kilogram artefacts. The national copies of K accrete surface contamination over time which leads to an increase in their mass values. Without reference to K it is difficult to assess the magnitude of this mass gain and the traceability of measurements is compromised to some extent.

The purpose of this project was to compare the values of the national copies of the prototype of 18 European NMIs. The comparison was piloted by NPL (UK) who circulated two platinum-iridium transfer standards using a petal type comparison, each petal consisting of three or four participants. While the results obtained can be used to demonstrate equivalence between the participants, the main objective of the work was to calculate the relative mass gains of the national copies, to analyse this data, and to draw conclusions about the relative stabilities of the kilograms. Each participating NMI uses an algorithm to predict the mass gain of their national standard. The results gained from this comparison have been used to evaluate the accuracy of these algorithms and also to recommend a best fit algorithm for the modelling of mass gain of national standard kilograms.

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Approved on behalf of NPLML by Dr Andrew Lewis, Science Area Leader.

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1 INTRODUCTION

The kilogram is unique among the SI base units in being the only one defined by an artefact rather than with relation to naturally occurring physical constants. This imposes a unique set of problems relating to the maintenance and traceability of the mass scale worldwide. All mass measurements must be ultimately traceable to the International Prototype of the Kilogram (K) held at the BIPM (*Bureau International des Poids et Mesures*). This traceability is achieved via copies of the Prototype held by National Measurement Institutes (NMIs) and maintained by the periodic re-verification of these copies by the BIPM. A major problem with maintaining this traceability is the inherent instability of the kilogram artefacts. The national copies of K accrete surface contamination over time which leads to an increase in their mass values. Without reference to K it is difficult to assess the magnitude of this mass gain and the traceability of measurements is compromised to some extent.

The purpose of this project was to compare the values of the national copies of the prototype of 18 European NMIs. While the results obtained can be used to demonstrate equivalence between the participants, the main objective of the work is to calculate the relative mass gains of the national copies, to analyse this data, and to draw conclusions about the relative stabilities of the kilograms. Each participating NMI uses an algorithm to predict the mass gain of their national standard. The results gained from this comparison have been used to evaluate the accuracy of these algorithms.

2 PARTICIPANTS

The Participating laboratories are listed in table 1.

Table 1: List of Participating Laboratories

Laboratory		Country
Bundesamt fur Eich- und Vermessungswesen	BEV	Austria
Metrology Division, FPS Economy	SMD	Belgium
Czech Metrological Institute	CMI	Czech Republic
Danish Institute of Fundamental Metrology	DFM	Denmark
Mittatekniikan keskus	MIKES	Finland
Institut National de Métrologie	BNM-INM	France
Physikalisch-Technische Bundesanstalt	PTB	Germany
National Office of Measures	OMH	Hungary
Istituto di Metrologia "G Colonnetti"	IMGC	Italy
Nederlands Meetinstituut-Van Swinden Laboratorium	NMi VSL	Netherlands
Justervesenet	JV	Norway
Central Office of Measures	GUM	Poland
Slovak Institute of Metrology	SMU	Slovakia
Centro Español de Metrologia	CEM	Spain
SP Measurement Technology	SP	Sweden
Swiss Federal Office of Metrology and Accreditation	METAS	Switzerland
Tübitak Ulusal Metroloji Enstitüsü	UME	Turkey
National Physical Laboratory	NPL	United Kingdom

The National Physical Laboratory acted as the pilot for this exercise. Additionally, measurements made by the BIPM provided traceability for the reference and travelling standards both before and after the comparison.

3 MASS STANDARDS

Two platinum-iridium kilograms were used as the travelling mass standards for this comparison; these had the designations 55 and 651. Kilogram 55 is an official copy of the International Prototype and was manufactured in 1950, calibrated as part of the second verification in 1953 allocated to the PTB in 1954. Kilogram 651 is an underweight copy produced in 1979 and calibrated and supplied to NPL in 1982. NPL platinum-iridium kilogram A was used as a reference standard against which to monitor the stability of the travelling standards.

4 COMPARISON PROTOCOL

The protocol followed was similar to that which has been adopted for CCM regional key comparisons in the EURAMET area. The two transfer standards were circulated among the participating laboratories, returning to NPL for stability checks after each series of measurements. Each measurement series comprised either three or four laboratories. Participants had one month in which to complete their measurements.

While being transported the transfer standards were housed in a sealed enclosure vented to the air through a micropore filter. Figure 1 shows a sealed kilogram enclosure similar to those used to transport the masses. The mass standards were hand carried between laboratories.

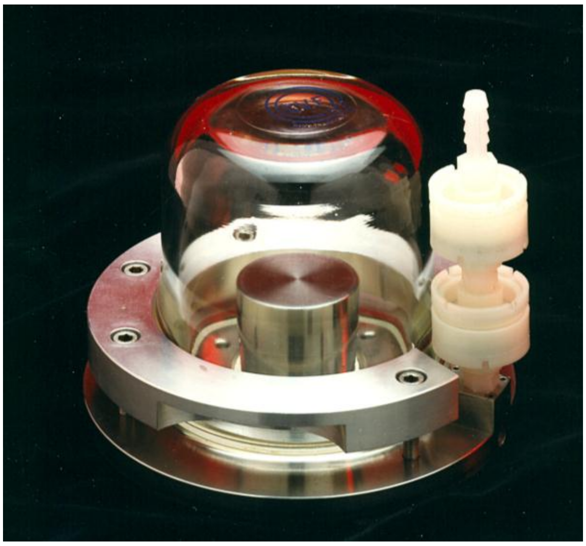

Figure 1: Kilogram Enclosure

5 PREPARATORY MEASUREMENTS

5.1 STABILITY

The stability of the transfer standards 55 and 651, and of the stability standard A, had been monitored at their respective laboratories since their allocation by the BIPM. Figures 2 to 4 show the stabilities of the three platinum-iridium mass standards prior to the start of the comparison in November 2000.

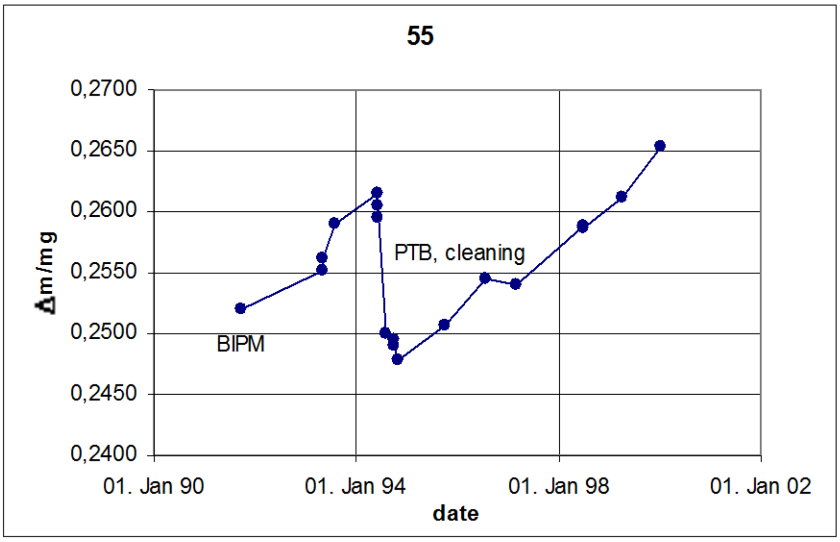

Figure 2: Stability of kilogram 55 from September 1991 to project start

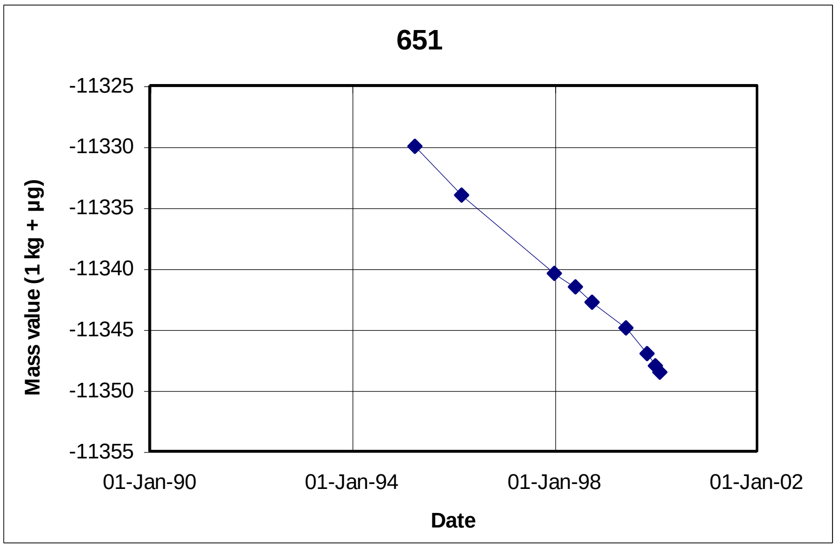

Figure 3: Stability of kilogram 651 from April 1995 to project start

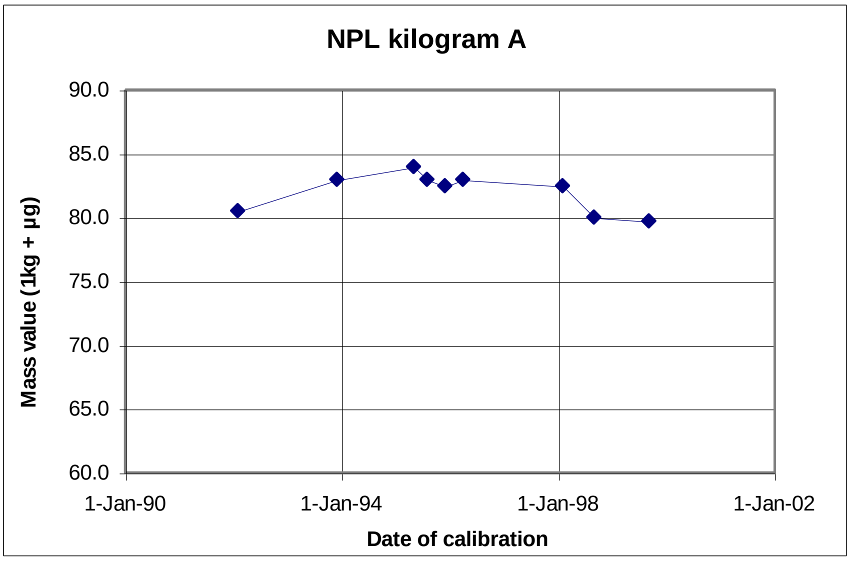

Figure 4: Stability of kilogram A from September 1991 to project start

Kilogram 55 shows a mass gain of approximately 2.5 micrograms per year, which is typical of a platinum-iridium kilogram. Unusually, kilogram 651 shows a loss in mass equal to about 4.5 micrograms a year. Although this behaviour is unusual, and no obvious explanation can be given for the weight loss, kilogram 651 has shown this behaviour over a number of years. While not ideal, the fact that the mass change in 651 is predictable means it was suitable for use in this comparison. Kilogram A can be seen to be extremely stable over the period prior to the start of the comparison, making it suitable as a reference standard against which to monitor changes in the transfer standards.

5.2 CALIBRATION OF STANDARDS

Prior to the start of the comparison both of the transfer standards and the stability standard were calibrated by the BIPM. The masses were returned to NPL, compared with each other and then transported to the first participating laboratory.

Between each series of three or four measurements by the participating laboratories the two travelling standards were returned to NPL where their stability was checked against the reference standard.

After the completion of the comparison the travelling standards were checked against the reference standard at NPL and all three masses were again calibrated by the BIPM.

6 RESULTS

The results of the participating laboratories, together with those of the pilot laboratory (NPL) and of the BIPM are given in Table 2.

Table 2: Comparison results reported by the participants

Date		Lab	Country	Measured mass value (1 kg +) / µg			
				651	u (*k*=1)	55(PTB)	u (*k*=1)
2000	Nov	BIPM	BIPM	-11395.0	5.0	269.0	5.0
2001	Jan	NPL	UK	-11392.6	6.0	270.1	6.0
	Feb	SMD	Belgium	-11378.0	11.0	275.0	11.0
	Mar	NMi	Netherlands	-11379.0	7.0	279.0	7.0
	Apr	CEM	Spain	-11400.0	5.0	223.0	5.0
	May	NPL	UK	-11399.4	6.0	234.2	6.0
	Jun	GUM	Poland	-11391.0	3.1	240.0	3.1
	Jul	CMI	Czech Rep.	-11418.0	50.0	234.0	50.0
	Aug	PTB	Germany	-11404.6	5.0	234.0	5.0
	Sep	SMU	Slovakia	-11433.0	5.0	216.0	5.0
	Oct	NPL	UK	-11410.0	6.0	237.2	6.0
	Oct	OMH	Hungary	-11397.0	8.0	237.0	8.0
2002	Feb	BEV	Austria	-11411.0	11.0	237.0	11.0
	Apr	METAS	Italy	-11418.9	3.7	229.5	3.7
	May	IMGC	Switzerland	-11400.4	12.6	248.6	12.6
	May	NPL	UK	-11416.2	6.0	233.3	6.0
	Jun	DFM	Norway	-11417.0	17.0	229.0	17.0
	Jul	JV	Denmark	-11421.5	5.4	229.9	5.3
	Aug	SP	Sweden	-11418.0	7.0	245.0	7.0
	Sep	MIKES	Finland	-11417.0	13.0	236.0	13.0
	Oct	NPL	UK	-11422.8	6.0	234.7	6.0
2003	Jan	BNM-INM	France	-11404.5	7.2	229.0	7.2
	Feb	UME	Turkey	-11400.0	5.5	241.0	5.5
	Mar	NPL	UK	-11425.8	6.0	236.2	6.0
	Apr	BIPM	BIPM	-11424.0	5.0	238.0	5.0

Results show reasonable consistency between participants except for a step change in the value of kilogram 55 between March and April 2001. On examination of the weight on return to NPL it was clear that the weight had been damaged.

7 ANALYSIS

7.1 REFERENCE VALUES

The results from the participants, from the NPL stability checks and from the BIPM calibration values were analysed. Three potential reference values were considered;

1. Using only the BIPM data
2. Using the BIPM and NPL data
3. Using all consistent data

Consistent data was regarded as that data having a normalised deviation from the reference value of less than 2.0 (calculated using standard uncertainties).

The step change noted in the value of kilogram 55 was taken into account when calculating the reference value for this weight.

Since the NPL reference standard A and the travelling standards were calibrated at the BIPM before and after the comparison there is a strong correlation between the stability measurements made at NPL and the calibration of the weights at the BIPM. For this reason a correlation coefficient of r=0.9 between the NPL and the BIPM measurements has been assumed. Additionally, since each participating laboratory is directly traceable to the BIPM there can be assumed to be some correlation between the measured values and the BIPM value (and between individual measured values). However, this correlation will depend on a number of factors, such as when the national standard of each participant was calibrated. For this reason no correlation coefficient for the participants' data was included.

The results of these analysis methods in calculating reference values for the two travelling standards are shown in figures 5 and 6.

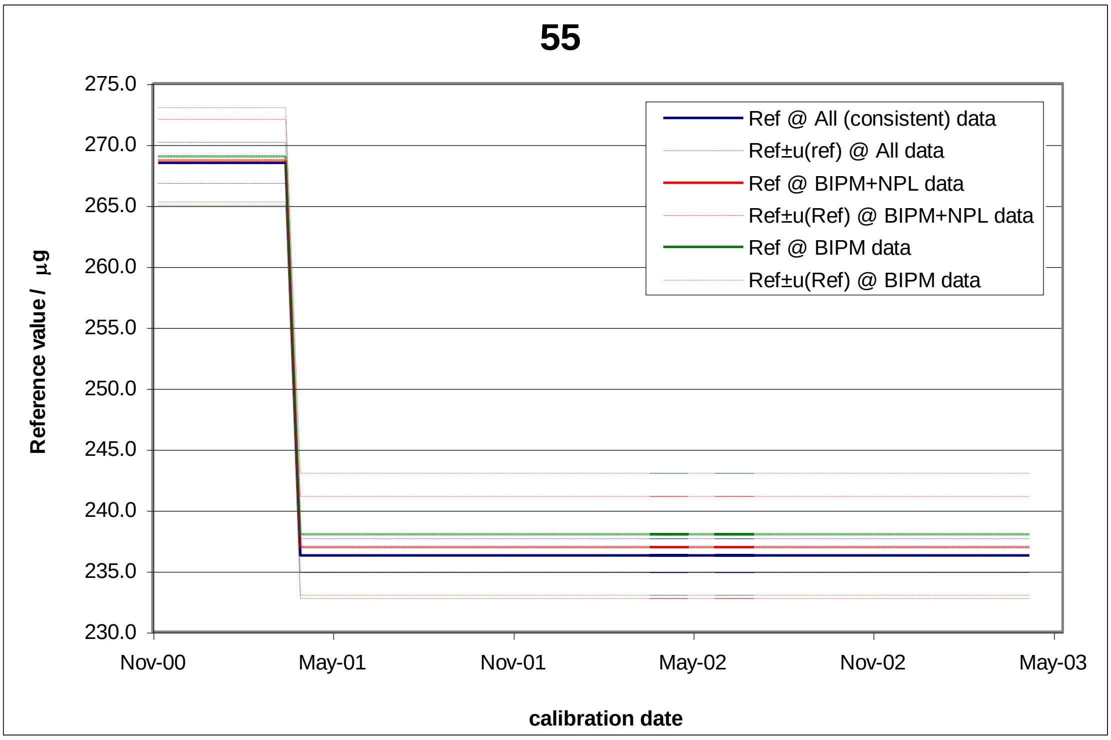

Figure 5: Potential reference values for kilogram 55

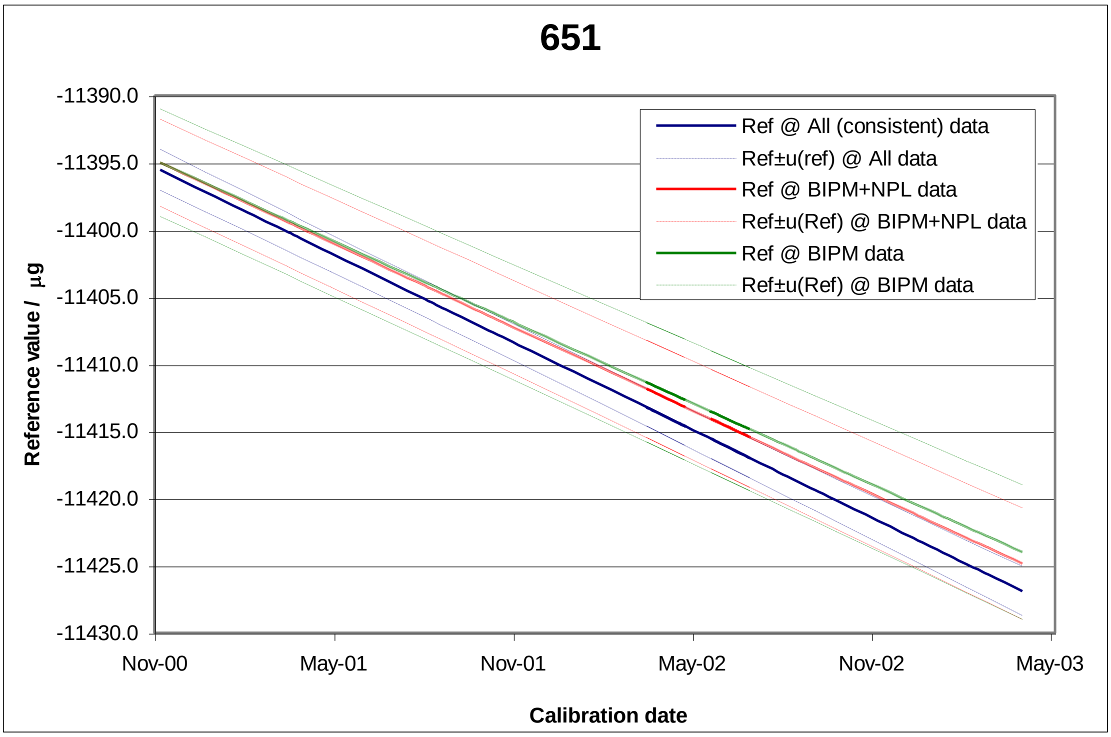

Figure 6: Potential reference values for kilogram 651

The three analysis methods give very consistent reference values both in terms of the absolute value and in terms of any calculated drift, the agreement being within the smallest uncertainty calculated. Apart from the step change in kilogram 55 previously discussed the value of the weight was stable during the period of the comparison. As expected the value of kilogram 651 showed some drift during the comparison. The drift calculated by the three analysis methods is almost identical and equal to about 1 microgram per month mass loss. Interestingly this is much higher than the drift previously measured in 651 (4.5 micrograms per year) but appears to have been consistent throughout the period of the comparison. It can be seen that in terms of the uncertainties in the reference values, as the number of results included increases the uncertainty in the value becomes less. Since there is little significant difference between the reference values, the values calculated from just the BIPM measurements were used. These reference values are shown in Figures 7 and 8.

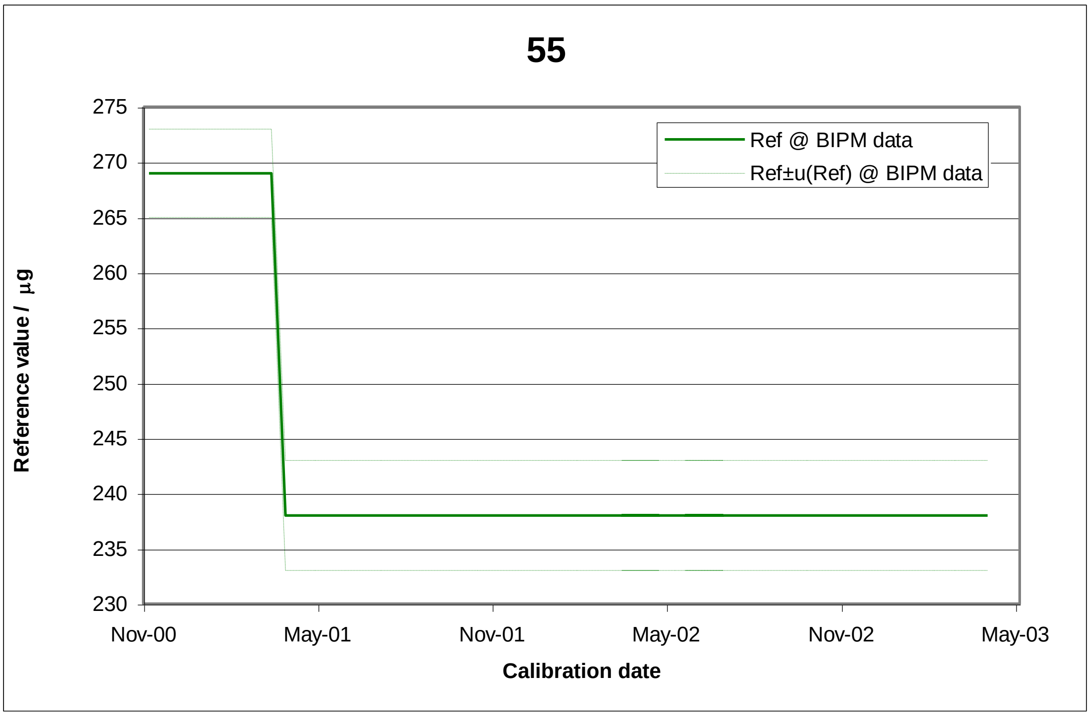

Figure 7: Reference values for kilogram 55 based on BIPM calibration data

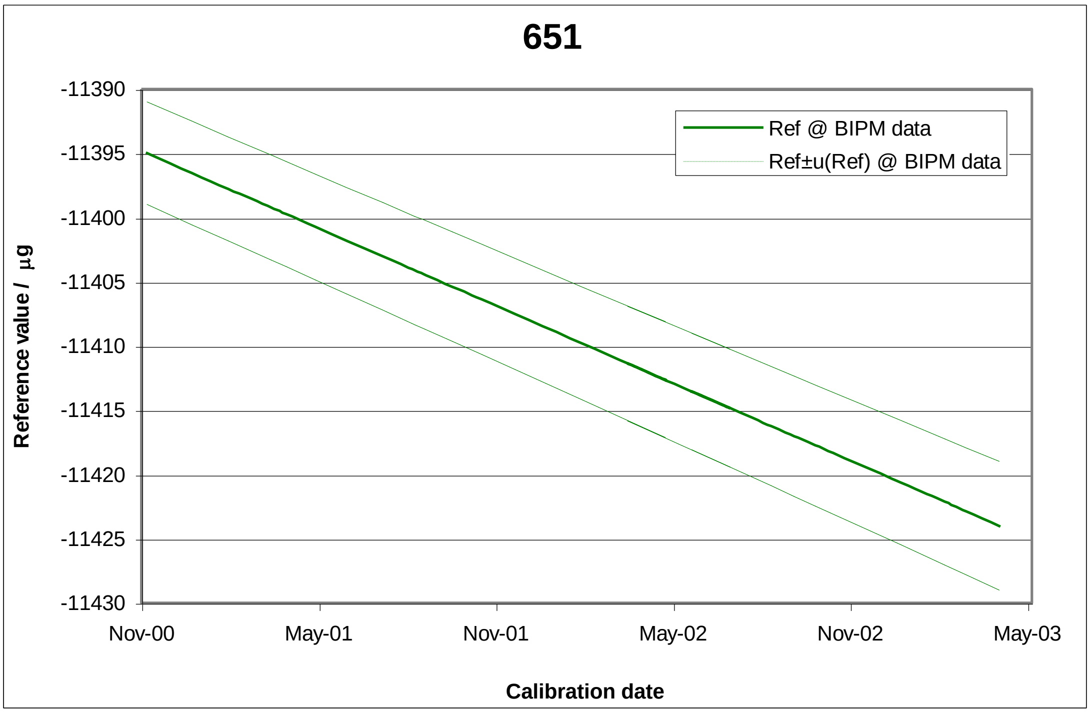

Figure 8: Reference values for kilogram 651 based on BIPM calibration data

7.2 PARTICIPANTS' DATA

The participants' results and uncertainties (k=1) with relation to the reference values are shown in figures 9 and 10. Values have been "excluded" where the result had a normalised deviation from the reference value of greater than 2.0 (calculated using standard uncertainties).

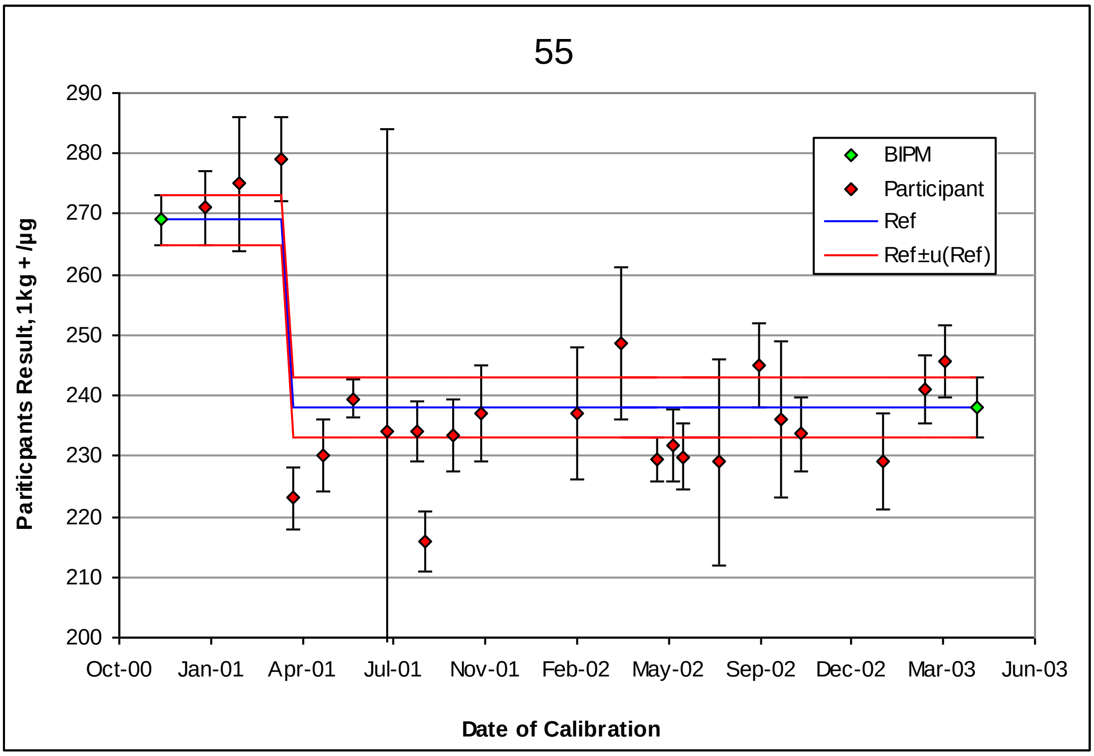

Figure 9: Participants' results relative to the reference value for kilogram 55

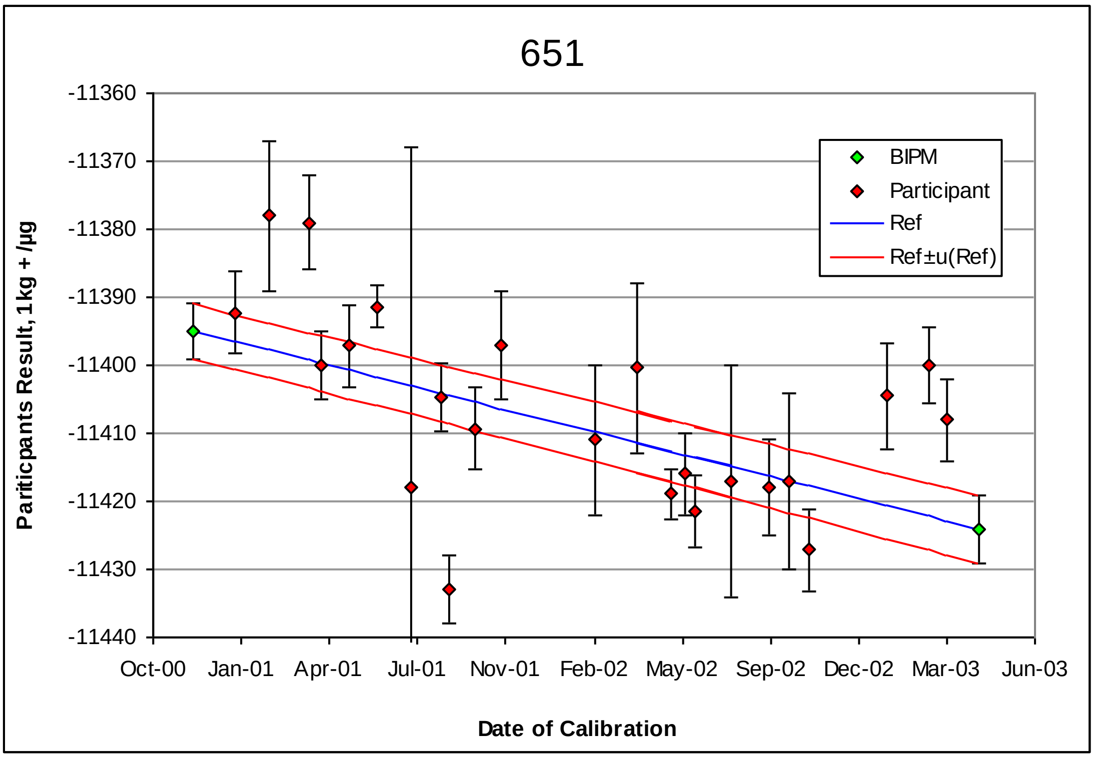

Figure 10: Participants' results relative to the reference value for kilogram 651

It can be seen that the majority of the results are in agreement with the reference value (when the results are expressed at k=2 uncertainty). More of the measurements of kilogram 651 disagree with the reference value. The most obvious explanations for this are either that the relatively large discrepancy of the weight from nominal (over 11 mg) made it difficult for some laboratories to calibrate or that the model for the drift is in error. Figure 6 shows the reference value for 651 (including a linear drift coefficient) calculated in three ways. The fact that the reference values calculated by all three approaches (including one using all the measured values) agree so well suggests that the drift model is valid (providing a linear drift can be assumed). It is, however, interesting to note that the last three participant measurements, including one at NPL, show a marked discrepancy from the calculated reference value but relatively good agreement among themselves. Table 3 summarises the results shown in the two graphs above.

Table 3: Participant results and uncertainties compared with calculated reference values

Participant	Cal. date	Kilogram 55					Kilogram 651				
		Mass Value (µg)	u (*k*=1) (µg)	Ref. Mass (µg)	u (*k*=1) (µg)	Diff (µg)	Mass Value (µg)	u (*k*=1) (µg)	Ref. Mass (µg)	u (*k*=1) (µg)	Diff (µg)
BIPM	Nov-00	269.0	4.0	269.0	4.0	0.0	-11395.0	4.0	-11395.0	4.0	0.0
NPL	Jan-01	270.9	6.0	269.0	4.0	-1.9	-11392.7	6.0	-11396.5	4.0	-3.9
SMD	Feb-01	275.0	11.0	269.0	4.0	-6.0	-11378.0	11.0	-11397.8	4.1	-19.8
Nmi	Mar-01	279.0	7.0	269.0	4.0	-10.0	-11379.0	7.0	-11399.2	4.1	-20.2
CEM	Apr-01	223.0	5.0	238.0	5.0	15.0	-11400.0	5.0	-11399.7	4.1	0.3
NPL	May-01	229.6	6.0	238.0	5.0	8.4	-11397.3	6.0	-11400.7	4.1	-3.4
GUM	Jun-01	239.5	3.1	238.0	5.0	-1.5	-11391.4	3.1	-11401.8	4.1	-10.4
CMI	Jul-01	234.0	50.0	238.0	5.0	4.0	-11418.0	50.0	-11403.0	4.2	15.0
PTB	Aug-01	234.0	5.0	238.0	5.0	4.0	-11404.6	5.0	-11404.1	4.2	0.5
SMU	Sep-01	216.0	5.0	238.0	5.0	22.0	-11433.0	5.0	-11404.4	4.2	28.6
NPL	Oct-01	232.0	6.0	238.0	5.0	6.0	-11410.5	6.0	-11405.4	4.3	5.1
OMH	Oct-01	237.0	8.0	238.0	5.0	1.0	-11397.0	8.0	-11406.4	4.3	-9.4
BEV	Feb-02	237.0	11.0	238.0	5.0	1.0	-11411.0	11.0	-11409.8	4.4	1.2
METAS	Apr-02	248.6	12.6	238.0	5.0	-10.6	-11400.4	12.6	-11411.4	4.5	-11.0
IMGC	May-02	229.5	3.7	238.0	5.0	8.5	-11418.9	3.7	-11412.6	4.5	6.3
NPL	May-02	231.3	6.0	238.0	5.0	6.7	-11416.7	6.0	-11413.2	4.5	3.5
DFM	Jun-02	229.9	5.4	238.0	5.0	8.1	-11421.5	5.4	-11413.5	4.5	8.0
JV	Jul-02	229.0	17.0	238.0	5.0	9.0	-11417.0	17.0	-11414.8	4.6	2.2
SP	Aug-02	245.0	7.0	238.0	5.0	-7.0	-11418.0	7.0	-11416.2	4.6	1.8
MIKES	Sep-02	236.0	13.0	238.0	5.0	2.0	-11417.0	13.0	-11417.0	4.7	0.0
NPL	Oct-02	235.7	6.0	238.0	5.0	2.3	-11424.9	6.0	-11417.7	4.7	7.1
BNM-INM	Jan-03	229.1	7.8	238.0	5.0	8.9	-11404.5	7.8	-11420.6	4.8	-16.1
UME	Feb-03	241.0	5.5	238.0	5.0	-3.0	-11400.0	5.5	-11422.1	4.9	-22.1
NPL	Mar-03	243.9	6.0	238.0	5.0	-5.9	-11409.6	6.0	-11422.9	4.9	-13.2
BIPM	Apr-03	238.0	5.0	238.0	5.0	0.0	-11424.0	5.0	-11424.0	5.0	0.0

Looking at the measurements as a whole only one laboratory can be said to have results that are systematically different to the reference values by more than the combined uncertainty. Table 4 summarises the deviations of the individual measurements and, were provided by the participants, indicates the algorithm which the individual laboratories use to account for drift in the values of their national standard.

Table 4: Participant results and uncertainties and mass gain algorithms used

Participant	National std. No.	Diff. from ref. 55 (µg)	Diff. from ref. 651. (µg)	u (*k*=1) (µg)	Date of cal.	Algorithm
BIPM	K	0.0	0.0	4.0		
NPL	18	-1.9	-3.9	6.0	Oct-91	$m=m_{(1991)}$ + 0.356 097 x $t^{0.511\ 678}$ µg (t in days)
SMD	37	-6.0	-19.8	11.0	Feb-91	$m=m_{(1991)}$ + 3.0 µg/year
NMi	53	-10.0	-20.2	7.0	Jan-97	Data fit - approximates $m=m_{(1997)}$ + 1.2 µg/year
CEM	24	15.0	0.3	5.0	May-93	Note 1
NPL	18	8.4	-3.4	6.0	Oct-91	As above
GUM	51	-1.5	-10.4	3.1	Jun-90	$m=m_{(1990)}$ + 2.2632 µg/year
CMI	67	4.0	15.0	50.0	Feb-99	none
PTB	52	4.0	0.5	5.0	1996	$m=m_{(1996)}$ + 3.064 µg/year
SMU	65	22.0	28.6	5.0	1991	none
NPL	18	6.0	5.1	6.0	Oct-91	As above
OMH	16	1.0	-9.4	8.0	Jun-90	$m=m_{(1990)}$ + 1 µg/year + 0.0368 µg/day
BEV	49	1.0	1.2	11.0	Jun-90	$m=m_{(1990)}$ + 10 µg + (n - 1) x 1.4 µg (n in years)
IMGC	62 76	8.5	6.3	3.7	Feb-93 Feb-99	Compromise between estimated drift and consistency of two standards
METAS	38	-10.6	-11.0	12.6	Feb-91	$m=m_{(1991)}$ + 0.037 µg/day (first 18 months) + 1.205µg/year (subsequent)
NPL	18	6.7	3.5	6.0	Oct-91	As above
JV	36	9.0	2.2	17.0	Jan-01	$m=m_{(2001)}$ + 10 µg + 1 µg/year
DFM	48	8.1	8.0	5.4	Jul-01	Note 2
SP	40	-7.0	1.8	7.0	Feb-91	$m=m_{(1991)}$ + 3.2 µg + (n - 0.25) x 1 µg (n in years)
MIKES	23	2.0	0.0	13.0	Feb-01	$m=m_{(2001)}$ + 6 µg (year 1) + 5 µg/year (subsequent)
NPL	18	2.3	7.1	6.0	Oct-91	As above
BNM-INM	35	8.9	-16.1	7.8	Apr-02	none
UME	54	-3.0	-22.1	5.5	May-93	$m=m_{(1993)}$ + 10 µg
NPL	18	-5.9	-13.2	6.0	Oct-91	As above
BIPM	K	0.0	0.0	5.0		

Note 1: CEM algorithm

$m(t)$ - calculated mass
m - mass at last calibration
m_1 - mass loss due to cleaning (last calibration)
m_2 - mass diff. between last two calibrations (after cleaning)
m_3 - 10 µg (first year mass gain)
n - years since last calibration
n_1 - years between last two calibrations

$$m(t) = m(t_0) + \gamma_1 (t - t_0) + \gamma_2 \sqrt{t - t_0}$$

Note 2: DFM algorithm

$m(t)$ - calculated mass at time t
$m(t_0)$ - mass at last cleaning
γ_1 - 1.91 x 10^{-6} mg/day
γ_2 - 1.13 x 10^{-4} √mg/day
$t - t_0$ - days since last cleaning

7.3 ANALYSIS OF ALGORITHMS

In order to check the accuracy of the algorithms used by the individual laboratories to predict the mass gain of their national prototype, the results of the comparison were analysed with respect to the time elapsed since the national prototype was last calibrated. Table 5 summarises the participants' results (with respect to the reference value), corrected using the individual drift algorithms, in temporal order. The uncertainty values quoted are the combined uncertainties from the uncertainty quoted by the participant and the uncertainty in the reference value (see Table 3).

Table 5: Time between national prototype calibration and participation in the comparison (results corrected by participants for the drift in their national prototype)

Laboratory	Date of calibration	Date of calibration of national standard	Date of last nettoyage-lavage cleaning (if performed)	Days since clean	Deviation from ref. value 55 (µg)	Deviation from ref. value 651 (µg)	Combined Unc. *k*=1 (µg)
BIPM	Nov-00				0.0	0.0	5.7
NPL	Jan-01	Oct-91	Oct-91	3381	-1.9	-3.9	7.2
SMD	Feb-01	Feb-91	Feb-91	3661	-6.0	-19.8	11.7
NMi	Mar-01	Jan-97	Jan-97	1545	-10.0	-20.2	8.1
CEM	Apr-01	May-93	Sep-92	3143	15.0	0.3	6.5
GUM	Jun-01	Jun-90	Jun-90	4030	-1.5	-10.4	5.2
CMI	Jul-01	Feb-99	Dec-97	1327	4.0	15.0	50.2
PTB	Aug-01	Jun-96	Not cleaned		4.0	0.5	6.5
SMU	Sep-01	Jun-91	Jun-91	3745	22.0	28.6	6.5
OMH	Oct-01	Jun-90	Jun-90	4170	1.0	-9.4	9.1
BEV	Feb-02	Jun-90	Jun-90	4275	1.0	1.2	11.8
METAS	Apr-02	Feb-91	Feb-91	4078	-10.6	-11.0	13.4
IMGC	May-02	Feb-99	Feb-93	3386	8.5	6.3	5.8
DFM	Jun-02	Jul-01	Not cleaned		8.1	8.0	7.1
JV	Jul-02	Jan-01	Jan-01	563	9.0	2.2	17.6
SP	Aug-02	Feb-91	Feb-91	4228	-7.0	1.8	8.4
MIKES	Sep-02	Feb-01	Feb-01	599	2.0	0.0	13.8
BNM-INM	Jan-03	Apr-02	Not cleaned		8.9	-16.1	9.2
UME	Feb-03	May-93	Feb-91	4490	-3.0	-22.1	7.4
BIPM	Apr-03				0.0	0.0	7.1

Note: Where the national standard is identified as "not cleaned" this indicates that it did not undergo the nettoyage-lavage cleaning process as part of its last calibration at the BIPM

The results of the participants' measurements on the two transfer standards, with respect to the time since their national prototype was calibrated, are plotted in Figures 11 and 12. Only results from participants who had the national standards cleaned before they were last calibrated are included.

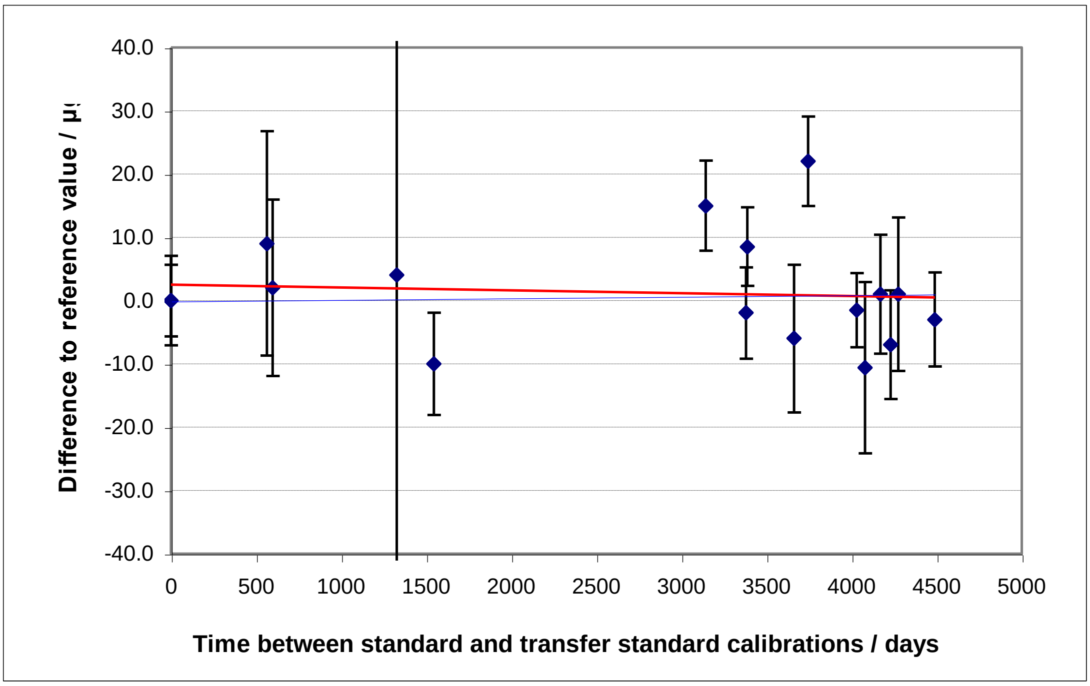

Figure 11: Results for kilogram 55 with respect to time since national prototype calibration (values corrected by participants for drift in national prototype)

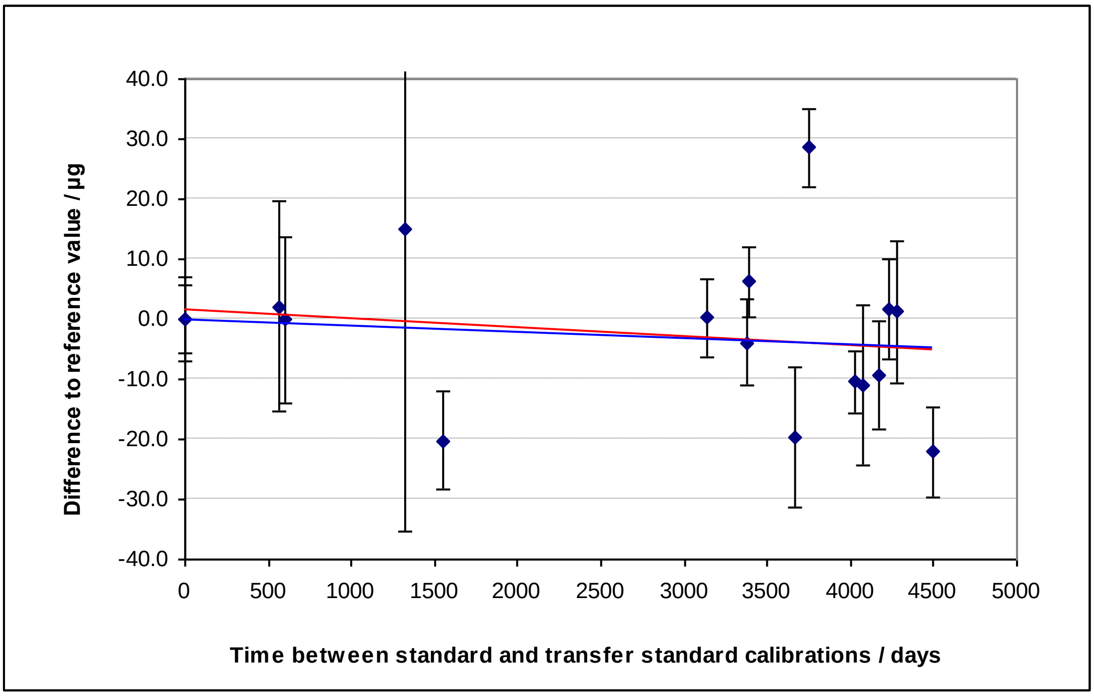

Figure 12: Results for kilogram 651 with respect to time since national prototype calibration (values corrected by participants for drift in national prototype)

The results broadly confirm that the algorithms used by the participants model the mass gain of their national prototypes correctly. While there is a reasonably large spread on the drift compensated results (particularly for kilogram 651), fitting both sets of data gives a drift co-efficient which is very small, indicating that there is minimal error on the collective algorithms. Linear best-fit lines have been added to the graphs and these show negligible departure from the expected result (along the y axis). The red lines represent the fit of all the data; the blue lines have been constrained to go through the origin. There is a small slope on the fitted line for kilogram 651 (equal to -0.4 micrograms per year). It is probable this is a function of the difficulty of calibrating this weight (it was significantly under 1 kilogram in nominal mass) and thus of the larger spread in the measurement data.

The results of the participants have also been analysed without the individual corrections for drift for their National Standards (*i.e.* the corrections calculated using the algorithms in Table 5). Theoretically, this data should give an indication of the (average) rate of mass gain for the national prototypes with respect to time since cleaning. Table 6 summarises the uncorrected results of the participants arranged with respect to the time of the last calibration of the national prototype.

Table 6: Time between national prototype calibration and participation in the comparison (results uncorrected for drift in national prototypes)

National prototype cal. date	Days since calibration	Laboratory	Dev. from ref. value		Unc. (k=1) (µg)
			55 (µg)	651 (µg)	
Apr-02	272	BNM-INM	8.9	-16.1	9.2
Jul-01	374	DFM	21.0	15.5	17.6
Jan-01	509	JV	9.0	7.6	7.1
Feb-01	585	MIKES	12.0	10.0	13.8
Feb-99	881	CMI	4.0	15.0	50.2
Feb-99	1142	IMGC	20.4	18.8	13.4
Jan-97	1518	NMi	-6.0	-16.2	8.1
Jun-96	1909	PTB	20.1	16.6	6.5
May-93	2879	CEM	35.2	20.5	6.5
Nov-00	3358	NPL	23.1	23.5	7.2
May-93	3571	UME	7.0	-12.1	7.4
Feb-91	3637	SMD	24.0	10.2	11.7
Jun-91	3745	SMU	14.0	20.6	6.5
Jun-90	4017	GUM	28.3	19.4	5.2
Feb-91	4092	METAS	26.0	25.0	5.8
Jun-90	4153	OMH	16.0	5.6	9.1
Feb-91	4203	SP	7.4	16.2	8.4
Jun-90	4263	BEV	26.0	26.2	11.8

The results of the uncorrected participants' measurements on the two transfer standards, with respect to the time since their national prototype was calibrated, are plotted in Figures 13 and 14.

Two best-fit models have been added to the graphs. The first (green line) is of the form;

$$m(t) = m(t_0) + A + B(t)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots\ldots\ldots\ldots\ldots(1)$$

where A is the initial rapid mass gain of the national standard and B is a constant representing the subsequent linear mass gain as a function of time t. This is the form of model used by the majority of participants.

The second (red line) is of the form;

$$m(t) = m(t_0) + A(t)^B \qquad (2)$$

where A and B are constants and t is the time since the calibration of the national prototype.

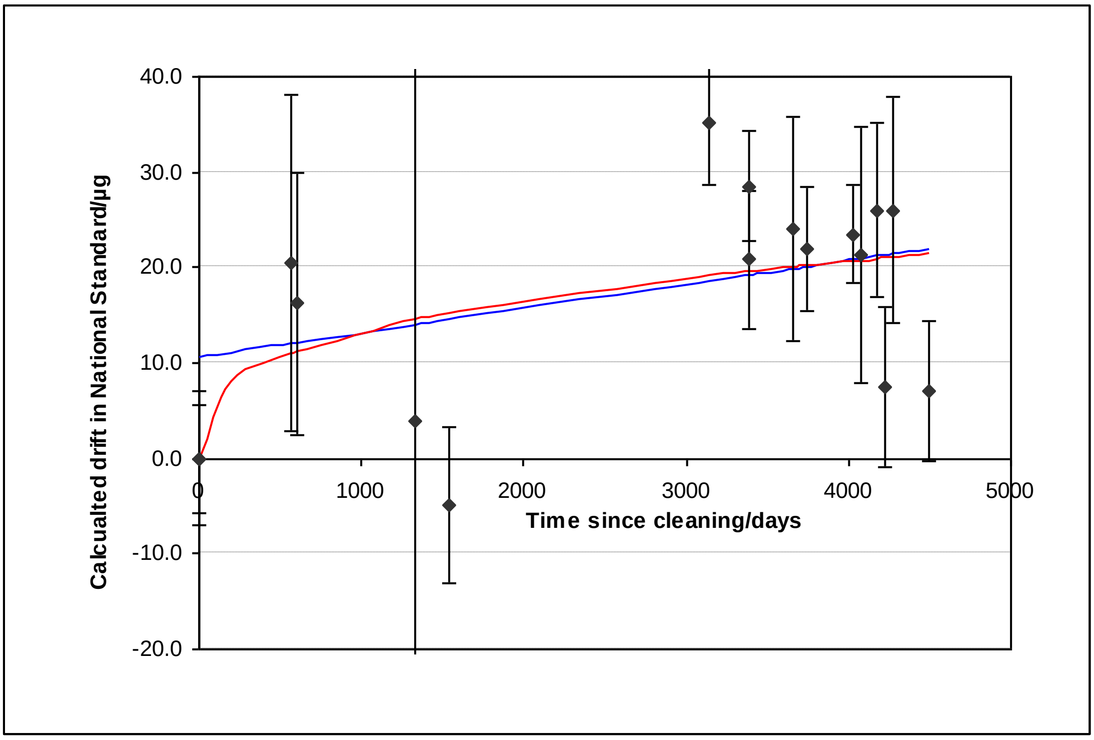

Figure 13: Results for kilogram 55 with respect to time since national prototype cleaning (results uncorrected for drift in national prototype)

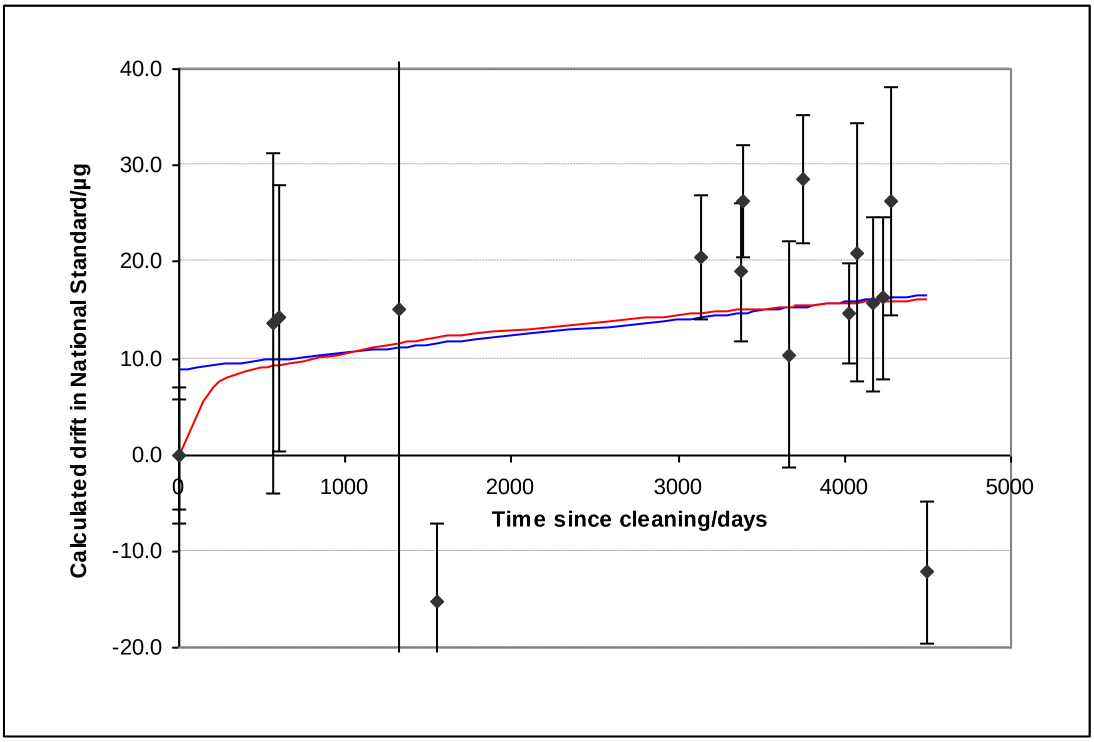

Figure 14: Results for kilogram 651 with respect to time since national prototype calibration (values uncorrected for drift in national prototype)

It can be seen that after a year the two models produce very similar solutions for the mass gain of the kilogram. It is probable that the second (red) model produces a better fit for the mass gain over the first year. This model was produced by NPL based largely on data gathered over the first two years after the cleaning of the kilogram.

With the value of t in days the solutions for equations (1) and (2) are given in Table 7. To allow comparison with the algorithms reported in Table 4 the solutions for equation 2 are also reported with the timescale in years. The root sum squares of the residual values (the differences between the modelled value and the measured value) have been calculated. These residual RSS values give an estimate of the goodness of fit of the algorithms shown. It can be seen that the residuals are the same for both algorithms indicating an equally good (although not the same) fit to the data.

Table 7: Best fit algorithms for mass gain of national prototype kilograms

Transfer standard	Linear gain model (µg)	Residual RSS (µg)	Exponential gain model (µg)	Residual RSS (µg)	Linear gain model (years)
55	10.6 + 0.002 55 t	2.5	$1.512\,8\ t^{0.315\,259}$	2.5	+10.6 µg + 1.9 µg/year
651	8.9 + 0.001 72 t	3.1	$1.641\,5\ t^{0.272\,362}$	3.1	+8.9 µg + 0.6 µg/year

Interestingly each model gives a significantly different solution for each of the two transfer standards, but looking at the spread on the data for the two standards this is not unexpected.

Combining the data gives the following solutions for the two mass gain models outlined;

Mass gain = $1.562\,0\ t^{0.295\,992}$ (with t in days)……………………….………(3)

for the exponential model and

Mass gain = 9.7 μg + 0.8 μg/year……………………………………….(4)

for the linear model.

These, in effect, represent the best-fit solutions for all the available data and so is the best estimate for the mass gain algorithms (taking the mass gain of all the cleaned kilograms of the participants). Both models give an average residual of 2.0 micrograms (difference between the fit and the measured value). For a number of participants the linear model is reassuringly near the most popularly adopted mass gain algorithm (+10 μg for the first year followed by a subsequent gain of + 1 μg/year).

8 CONCLUSIONS

Although the main aim of the comparison was not a demonstration of the participating laboratories ability to calibrate platinum-iridium kilogram mass standards there is generally good agreement between the results of the participants. Individual laboratories will be able to draw their own conclusions about their results.

Examining the algorithms used by the individual NMIs to correct for the mass gain of their national prototype kilograms shows that there is no bias to the data and that, taken as a whole, the various algorithms used represent good models of the mass gain of the respective national prototypes. Again, individual laboratories can draw conclusions regarding their own algorithms. Looking at the data uncorrected for the changes in the national prototypes, the results can be modelled using the widely accepted algorithm of rapid mass gain, after cleaning and BIPM, over the first few months followed by a linear mass gain model. From the analysis of this data, the values calculated are 8.4 micrograms for the rapid mass gain after cleaning followed by 1.1 microgram per year linear mass gain.

9 ACKNOWLEDGEMENTS

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10 REFERENCES

[1] Davis R 2003 The SI unit of mass *Metrologia* **40** 299-305

[2] Girard G 1994 International Report: The Third Periodic Verification of National Prototypes of the Kilogram (1988-1992) *Metrologia* **31** 317-336