EMRP SIB-05 Work Package 2
Deliverable 2.3.2

Report on the assessment of the dependence of the sorption effect on the balance used

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1 Introduction

Within the scope of the redefinition of the kilogram, which will be realised under vacuum via watt balance experiments or the Avogadro project, the sorption behaviour of mass standards when transferred from vacuum to air is one of the main aspects to be controlled. This sorption effect can be affected by several parameters and the environment in which the standards are placed must be carefully monitored to limit as much surface contamination as possible.

The aim of this task is to assess the influence of the balance (and vacuum chamber construction) used by the JRP-partners on the measured sorption behaviour of mass standards.

Measurements of the sorption coefficients of selected mass standards have been performed under similar conditions (temperature, pressure and humidity of air, vacuum pressure) in different vacuum mass comparators (enclosures made of different materials and with different surface properties). Comparison measurements have been undertaken in order to validate the results and to obtain an estimate of the reproducibility.

Table 1 lists the participating laboratories.

Table 1: List of Participating Laboratories

Laboratory		**Country**
Physikalisch-Technische Bundesanstalt	PTB	Germany
National Physical Laboratory	NPL	United Kingdom

At least, two mass comparators have been used by each JRP-partner, except LNE whose second vacuum comparator was under maintenance during the loop of the comparison. Therefore, only PTB and NPL results are presented in this report. LNE, measurements realized with the M-one vacuum mass comparator are presented in the report of Task 2.2.2, as well as INRIM and NRC results.

2 Description of mass comparators

In this task, three different types of comparators have been used. All JRP-partners involved in this task are equipped with an M-one comparator from Mettler Toledo. NPL also uses an HK1000 from Mettler Toledo, whereas PTB uses a CCL1007 from Sartorius weighing technology GmbH. LNE is also equipped with a CCL1007 mass comparator, but unfortunately, this one was under maintenance during the loop of the comparison.

The vacuum chambers of these mass comparators have different shapes (Figure 1 to 3) and are realised in different materials. M-one enclosure consists of a round bell jar, whereas the HK1000 and CCL1007 chambers have a cubic shape. As well, materials used for the vacuum chambers are different. M-one enclosure is made in stainless steel when the two other enclosures are realised in aluminium, material which presents a very low magnetic susceptibility to limit as much as possible the magnetic interaction between the enclosure and the weighing cell.

All these mass comparators are automatic and are equipped with a carousel to allow comparison of between two and eight weights. The capacity of all these mass comparators is 1 kilogram and their resolution is 0.1 microgram. The typical standard deviation for comparisons at 1 kg lies in the range 0.2 – 0.4 microgram.

Figure 1 : PTB M-one vacuum comparator

Figure 2 : NPL HK1000 vacuum comparator

Figure 3 : PTB CCL1007 vacuum comparator

3 Description of sorption artefacts

To investigate the sorption behaviour of materials by using different vacuum mass comparators, sorption artefacts consisting of a pair of kilograms realised in the same material with different shapes in order to have a large surface area difference but with a small volume difference. Three pairs of artefacts have been used in this study.

The first set of artefacts that circulated between the JRP-partners was provided by NPL and realised in platinum iridium (PtIr). It consisted of an integral cylindrical kilogram and one kilogram constituted by four discs. The four discs are separated by a set of 9 spacers to expose all the surface of the stack. The surface area ratio between the two artefacts was approximately 1:2.

In this study, NPL and PTB also used other pairs of sorption artefacts. As for the platinum iridium set, they consisted of an integral cylinder and a stack of discs separated by spacers. They were made from silicon for the NPL artefacts and stainless steel (SS) for the PTB artefacts and their nominal value was 500 g and 1 kg, respectively. The surface area ratios between the artefacts were approximately 1:2 for silicon and 1:4 for stainless steel. The characteristics of the sets of artefacts are given in Table 2.

Table 2: Artefacts information

Artefact Identification	Material	Volume (@ 20 °C)	Volume Uncertainty	Coefficient of Thermal Expansion	Surface Area
		cm^3	cm^3	°C^{-1} (x10^{-6})	cm^2
Integral	Pt/Ir	46.416	0.0002	25.869+0.00565t	71.501 7
Stack	Pt/Ir	46.415 2	0.0032	25.869+0.00565t	149.652
Integral	SS	124.834	0.001	45.6	138.3
Stack	SS	124.834	0.004	45.6	573.8
Integral	silicon	213.795 7	0.0024	7.8	195.191
Stack	silicon	213.734 3	0.0013	7.8	383.278 5

4 Air-vacuum measurements

To quantify the effect of transfer between air and vacuum, and to assess the reproducibility of the mass change according to the comparator used, the pairs of artefacts were repeatedly transferred between air and vacuum with respect to the scheme below, as defined in the protocol.

The first set of measurements (1) is done at 1 × 10^5 Pa (atmospheric pressure) at a humidity of about 50% RH with the first comparator. The artefacts should be left inside the enclosure of the comparator for a period of at least 24 hours to allow them to stabilise before the first set of measurements. The second set of measurements (2) are performed at a vacuum pressure of 0.01 Pa and the artefacts should be left at this pressure level for at least 24 hours before starting the measurements. The desired pressure can be reached using a gas needle valve to leak filtered dry air. The third (3) set of measurements with the first comparator is completed by switching off the vacuum pumps and taking the chamber back up to 1 × 10^5 Pa (atmospheric pressure). The humidity within the chamber should be increased to about 50% RH and the sorption artefacts should be allowed to stabilise for 48 hours before the start of the measurements.
Then, the sorption artefacts are transferred to the second comparator and steps (1) to (3) are repeated in the same way.
The measurement cycle is shown graphically in figure 2 and a cycle will take about 2 weeks to complete. At least two repeated cycles were performed to evaluate the reproducibility of the balance dependence.

As travelling sorption artefacts were cleaned just before T.2.2, no further cleaning was performed on the artefacts. Only visible dust on the artefacts was removed using a soft brush.

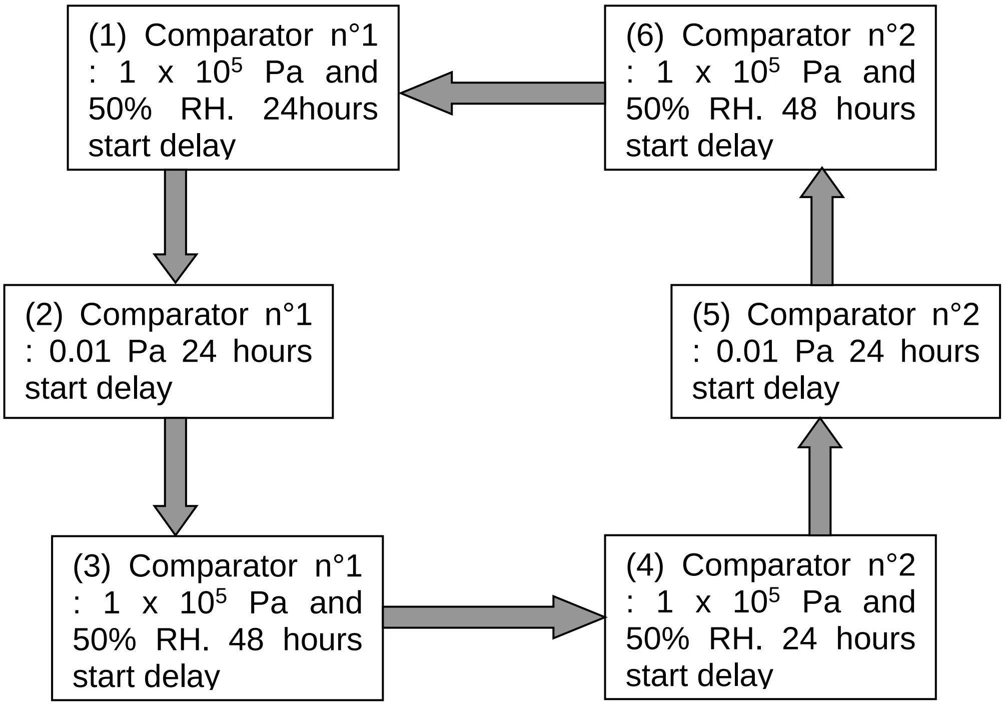

Figure 4. Measurement cycle between atmospheric pressure and vacuum using two types of mass comparators

5 Results of air-vacuum transfers

Measurements of the successive air-vacuum transfers have been realised between July and December 2013. In this study, the mass differences obtained in air were not corrected for sorption effects. They were only corrected for air buoyancy effects. To apply this correction, participants used either the CIPM formula by recording temperature, pressure and relative humidity to determine the air density or using buoyancy artefacts.

The average mass differences and uncertainties are given in Table 3. The successive air to vacuum mass differences are plotted in Figures 5 to 7 for PtIr, silicon and stainless steel artefacts respectively.

The mass changes have been calculated individually for each air-vacuum-air transfer according to equation (1), as already done in a previous study [1] :

$$\Delta m = \frac{Mair_n + Mair_{n+1}}{2} - Mvac_n \qquad (1)$$

where Δm is the mass change between air and vacuum, $Mair_n$ is the mass determined in air before the vacuum transfer, $Mair_{n+1}$ is the mass determined in air after the vacuum transfer and $Mvac_n$ is the mass determined in vacuum between the two air measurements.

The relative mass changes within the set of transfer standards and their different surface areas allowed the calculation of the mass change per unit surface area for all

pairs of artefacts, i.e. their sorption coefficient. These data are given in Tables 4 and 5.
Results obtained by participants on PtIr artefacts show excellent agreement in terms of absolute mass change for both M-one and CCL1007 mass comparators and for both NMIs. Results on HK1000 mass comparator at NPL are slightly discrepant with the others, but mass differences in air do not show any difference within the claimed uncertainties (Figure 5). For the silicon artefacts measured at NPL, a small gap of some micrograms is observed between mass differences from one comparator to the other, but mass changes between air and vacuum remain identical for both mass comparators (Figure 6). Finally, for stainless steel artefacts measured at PTB, no significant variation was observed between mass differences in air or under vacuum for both CCL1007 and M-one mass comparators.

According to the data given by the participants, a remark can be done on the humidity level. The relative humidity at PTB was relatively low in the interval 30-40 %RH, whereas NPL investigated a larger range between 40 and 70 %RH. However, this did not affect the sorption behaviour of the artefacts. And all these results are in quite good agreement with other studies, except for the PtIr set of artefacts where the sorption values were lower than previous measurements [1-3]. An explanation could be that the artefacts were cleaned at the beginning of the study, leading on a difference of surface cleanliness as already mentioned in the report of Task 2.2.

6 Conclusions

In this study, three sets of artefacts realised in different materials have been used on three different types of vacuum mass comparators. The aim was to investigate the influence of the balances and enclosures, realised in different materials and designed with different shapes, on the sorption behaviour of artefacts. Two JRP-partners having the capability to perform measurements using two types of vacuum mass comparators participated in this task.

It has been demonstrated that the reversible sorption behaviour of the three sets of artefacts, within the given uncertainties, is not dependent of the weighing environment, i.e. the mass comparator itself and its vacuum enclosure.

7 References

[1] Davidson S., 2010, Determination of the effect of transfer between vacuum and air on mass standards of platinum-iridium and stainless steel, Metrologia 47, pp 487-497

[2] Picard A and Fang H 2004 Methods to determine water vapour sorption on mass standards Metrologia 41 333-339

[3] Schwartz R 1994 Precision Determination of Adsorption Layers on Stainless Steel Mass Standards by Mass Comparison and Ellipsometry. Part II: Sorption Phenomena in Vacuum Metrologia 31 129-136

8 Figures

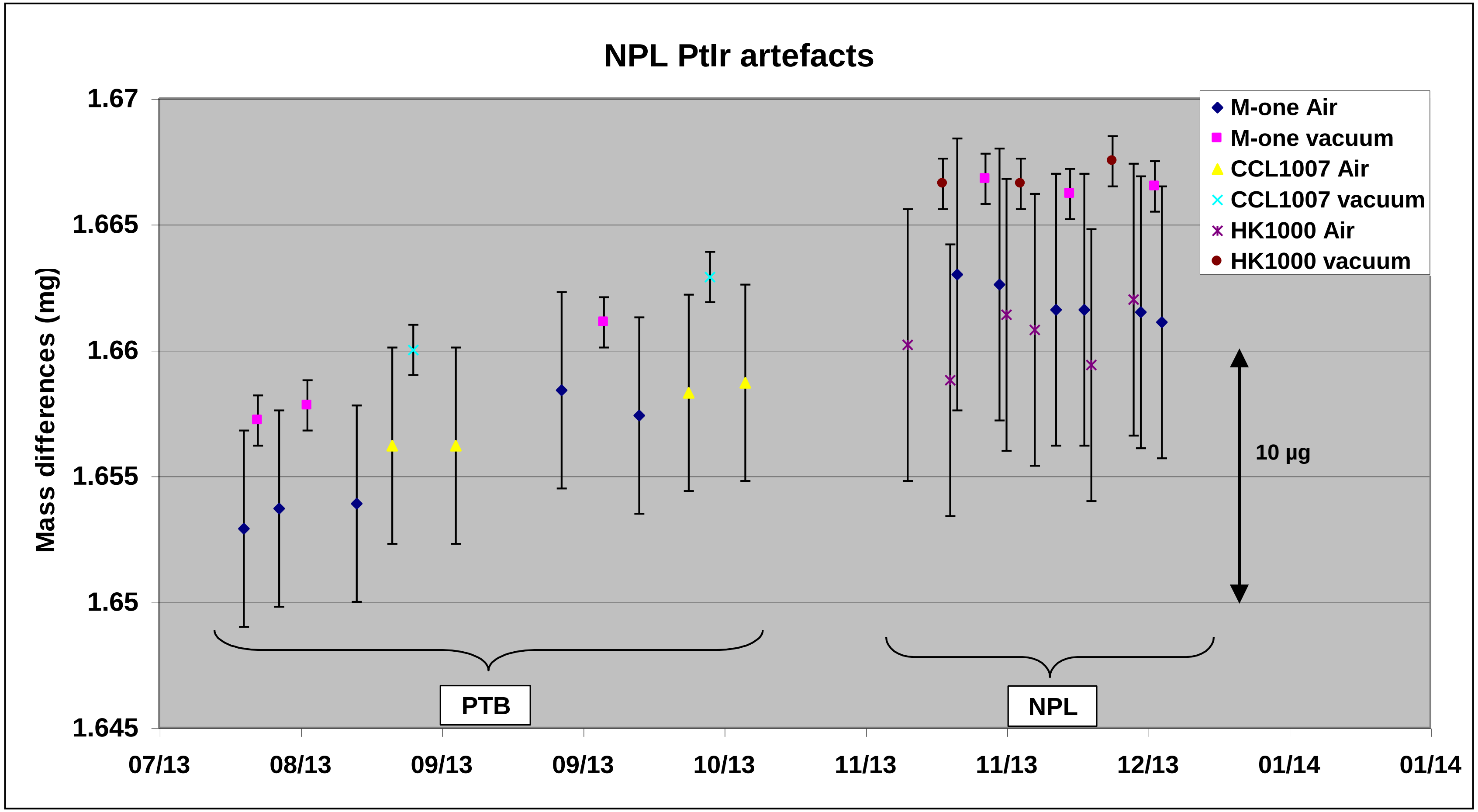

Figure 5. Mass differences of NPL-PtIr artefacts measured at PTB and NPL. Error bars represent the standard uncertainty (*k* = 1)

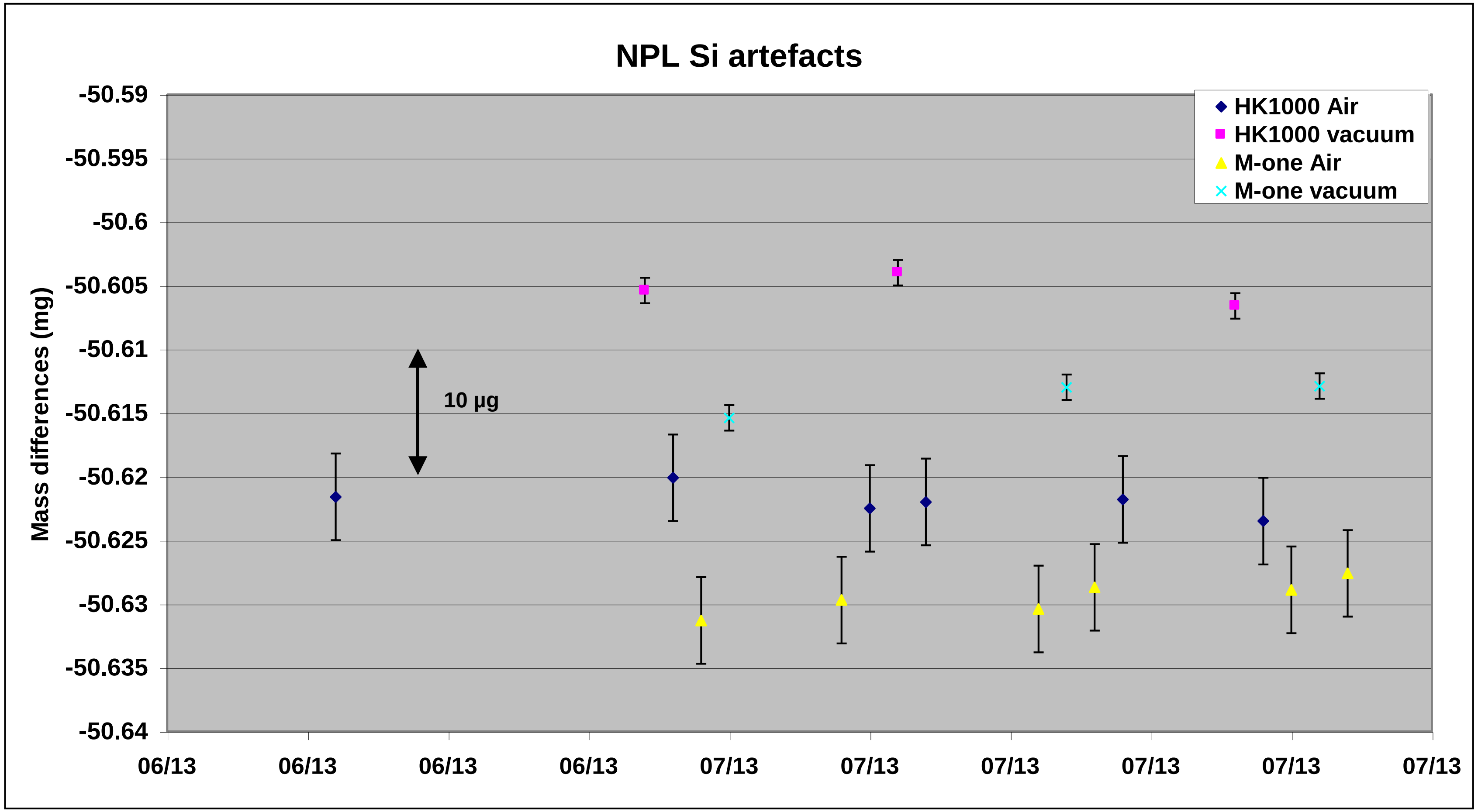

Figure 6. Mass differences of NPL-Si artefacts measured at NPL. Error bars represent the standard uncertainty (*k* = 1)

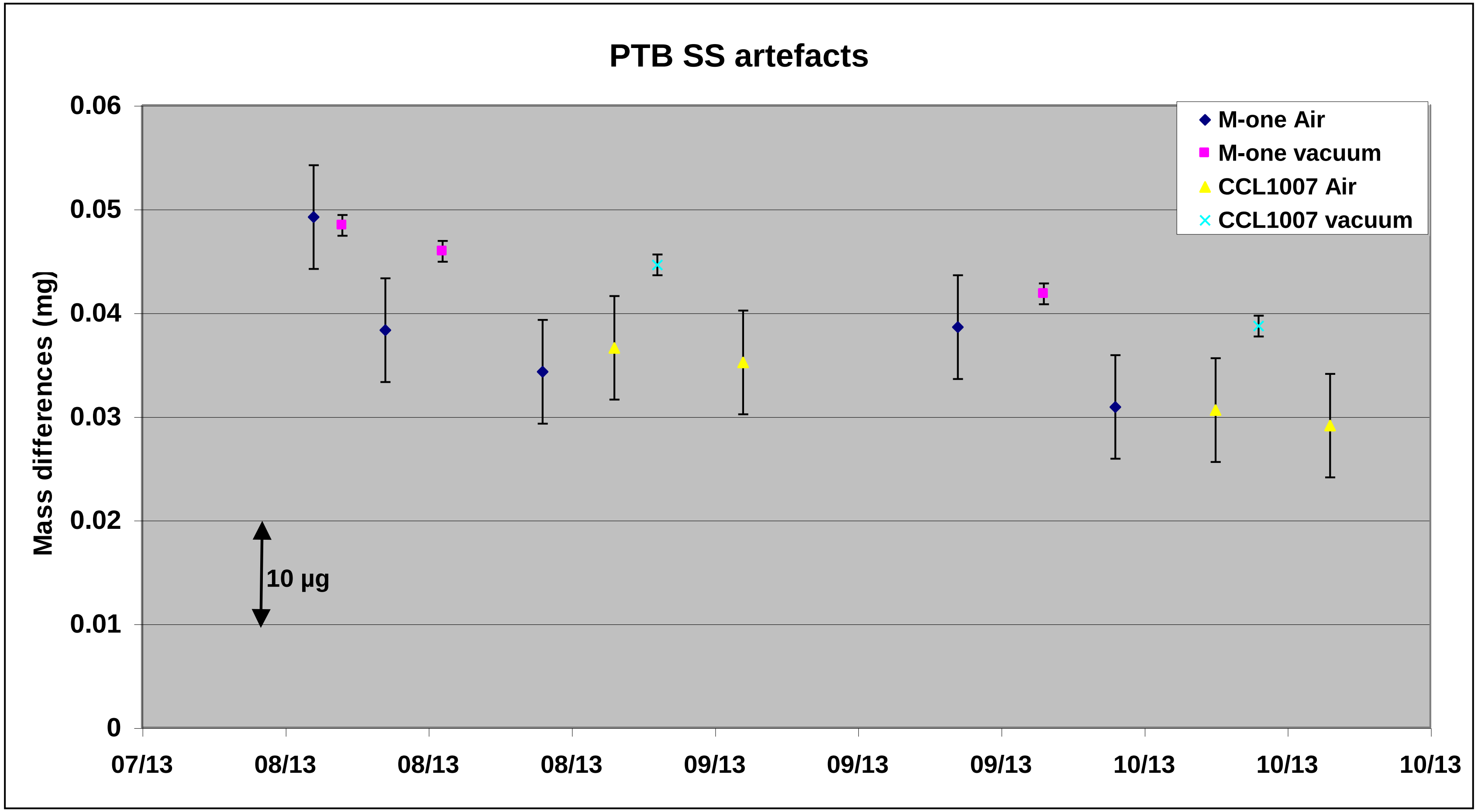

Figure 7. Mass differences of PTB-SS artefacts measured at PTB. Error bars represent the standard uncertainty (*k* = 1)

9 Table of results

Table 3. Average mass differences reported for the artefacts with standard uncertainties (*k*=1)

		Δm (integral – stack) / mg					
		M-one		**HK1000**		**CCL1007**	
Participant	Artefact material	Air	Vacuum	Air	Vacuum	Air	Vacuum
NPL	PtIr-NPL	1.661 9	1.666 5	1.660 4	1.666 9		
PTB	PtIr-NPL	1.655 3	1.658 7			1.657 4	1.661 5
NPL	Si-NPL	-50.629 4	-50.613 8	-50.621 9	-50.605 3		
PTB	SS-PTB	0.038 3	0.045 4			0.032 9	0.041 7
		u (integral-stack) / mg					
		M-one		**HK1000**		**CCL1007**	
		Air	Vacuum	Air	Vacuum	Air	Vacuum
NPL	PtIr-NPL	0.005 4	0.001 0	0.005 4	0.001 0		
PTB	PtIr-NPL	0.003 9	0.001 0			0.003 9	0.001 0
NPL	Si-NPL	0.003 4	0.001 0	0.003 4	0.001 0		
PTB	SS-PTB	0.005 0	0.001 0			0.005 0	0.001 0

Table 4 : Mass change between integral kilogram vs stack from air to vacuum of PtIr artefacts

Institute	Mass comparator	Absolute mass change (µg)	Change per unit SA (µg.cm^{-2})
PTB	M-one	-3.9	-0.050
		-4	-0.051
	CCL1007	-3.8	-0.049
	M-one	-3.2	-0.041
	CCL1007	-4.4	-0.056
NPL	HK1000	-7.1	-0.091
	M-one	-4	-0.051
	HK1000	-5.5	-0.070
	M-one	-4.6	-0.059
	HK1000	-6.8	-0.087
	M-one	-5.2	-0.067

Table 5 : Mass change between integral cylinder vs stack from air to vacuum of SS-PTB and Si-NPL artefacts

Artefact	Mass comparator	Absolute mass change (µg)	Change per unit SA (µg.cm^{-2})
SS-PTB	M-one	-4.7	-0.011
		-10	-0.022
	CCL1007	-8.7	-0.020
	M-one	-7.1	-0.016
	CCL1007	-8.9	-0.020
Si-NPL	HK1000	-15.5	-0.082
	M-one	-15.1	-0.080
	HK1000	-18.3	-0.097
	M-one	-16.6	-0.088
	HK1000	-16	-0.085
	M-one	-15.4	-0.082