A report on the potential reduction in uncertainty from traceable comparisons of platinum-iridium and stainless steel kilogram mass standards in vacuum

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ABSTRACT

Work has been undertaken to characterise the mass change of platinum-iridium and stainless steel weights on transfer between air and vacuum**.** Measurements were made on three 1-kilogram mass comparators; a Mettler HK1000MC in air and a similar instrument in vacuum (at 10^{-6} mbar), and on the NPLone mass comparator at ambient pressure, at vacuum (10^{-3} mbar) and at a partial pressure of 1 mbar. Specially designed sets of artefacts with different surface areas were used to calculate the mass change on exposure to vacuum and its repeatability. Results showed good repeatability and uncertainty evaluations indicate a potential reduction of the uncertainty for the calibration of stainless steel against platinum-iridium by comparison in vacuum, therefore eliminating the need for air buoyancy measurements. The work performed establishes traceability to mass in vacuum which will become increasingly important, not least because all the methods currently under investigation for the re-definition of the kilogram involve realising the unit of mass in vacuum.

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Approved on behalf of the Managing Director, NPL,
by Dr Roy Preston, authorised by Head of Materials Centre

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1. INTRODUCTION

This report summarises the work carried out for the NMS Mass Programme, 1999-2002 Project 1.2.9. The aim of the work was to investigate the advantages of calibrating stainless steel mass standards in vacuum.

2. BACKGROUND

2.1 The requirements for this work

The major source of uncertainty in the dissemination of the mass scale within the UK occurs in the calibration of NPL's primary stainless steel mass standards with the National Standard of Mass (kilogram 18) and the other platinum-iridium mass standards used to define the mass scale in the UK.

When comparing kilogram weights of platinum-iridium with those of stainless steel, from which the majority of laboratory and industrial standards are manufactured, there is a volume difference of approximately 80 cm^3. In air this means a buoyancy correction equal to approximately 0.1 grams must be applied. Air density can be measured to an uncertainty of about 1.6 parts in 10^4 (k=1) so this buoyancy correction introduces an uncertainty of about 16 micrograms (k=1) to the calibration of a stainless steel kilogram weight. Given that the balances on which kilogram mass standards are compared can have a repeatability approaching 1 microgram and that the uncertainty on kilogram 18 is 2.9 micrograms (k=1) the air buoyancy correction is significantly the largest uncertainty contribution.

Additionally, traceability to mass in vacuum becomes important with the increasing development of potential methods to replace the current definition of the kilogram. All the potential methods for redefinition, the two most significant of which are the Avogadro project [1,2] and the Watt balance [3,4], involve realising the kilogram in vacuum. Traceability to mass in vacuum therefore becomes essential for the practical dissemination of the unit of mass.

2.2 Potential improvement in uncertainties

The current uncertainty on NPL's primary stainless steel kilograms is about 20 micrograms (k=1). As discussed in Section 2.1 the main contribution to this is the uncertainty in the measurement of air density. By performing the comparison of stainless steel and platinum-iridium masses in vacuum, this source of uncertainty can be eliminated. Without this uncertainty contribution the overall uncertainty on the calibration comes down to less that 10 micrograms. An additional uncertainty contribution for the repeatability of transferring the weights into and out of vacuum needs to be added and part of the purpose of this study is to assess the magnitude of this uncertainty component.

2.3 Aims of the work

The aim of the work is to allow traceable comparisons of stainless steel and platinum-iridium weights to be made in vacuum, thus eliminating the uncertainty contribution due to the air buoyancy effect. To provide traceable measurements, two variables must be assessed. The first

is the change in mass experienced by weights, of both platinum-iridium and stainless steel, when transferred between air and vacuum. The second is the repeatability of this change.

3. EQUIPMENT USED FOR THE STUDY

3.1 Balances

The three balances used for the measurements described here were NPL's two HK1000MC mass comparators (one in air and one in vacuum) and NPLone the NPL's custom built vacuum mass comparator with six weighing stations.

3.1.1 HK1000MC mass comparator

The Mettler HK1000MC is an automatic mass comparator with a four-station carousel to allow intercomparison of either two or four weights. The capacity of the balance is 1 kilogram and the resolution is 0.1 micrograms. A typical standard deviation for ten comparisons at 1 kilogram is 0.4 micrograms. NPL has two HK1000MC comparators, one used in air and one in vacuum. Figure 1 shows the two balances. The vacuum balance consists of an HK1000MC comparator in an enclosure to allow evacuation of the balance. The apparatus incorporates a load-lock which allows the transfer of weights between ambient conditions and vacuum while maintaining the balance (and any weights on the carousel) at vacuum. Pump-down of the load-lock takes about 10 minutes. Two magnetically levitated turbo-molecular pumps provide the vacuum and the balance operates at an average pressure of 1×10^{-6} mbar.

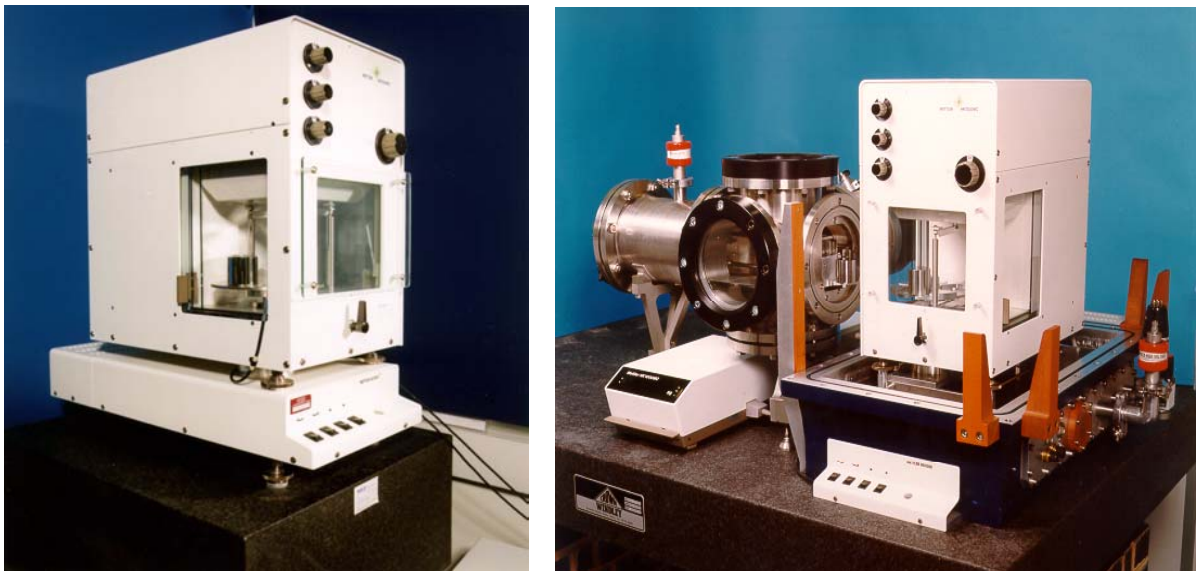

Figure 1: Air and Vacuum Mettler HK1000MC mass comparators

3.1.2 NPLone vacuum balance

The NPLone vacuum balance is the product of collaboration between NPL and Metrotec AG of Switzerland, part of the Mettler-Toledo group. The balance was designed to inter-compare up to six weights and can work both at vacuum and under ambient conditions. The balance has a capacity of 1 kilogram and its resolution is 0.01 micrograms. A typical standard deviation for a series of ten 1 kilogram comparison is 0.2 micrograms. The balance also incorporates a load-lock to allow the transfer of weights between air and vacuum without disturbing the balance environment. When under vacuum the balance operates at an average pressure of 1 x 10^{-3} mbar. Figure 2 shows the balance and the carousel mechanism.

Figure 2: NPLone vacuum balance

3.2 Mass Standards

Two sets of mass standards were manufactured, one of platinum-iridium and one of stainless steel, to investigate the effect of vacuum exposure on the two materials. Each set consists of three, nominally similar, integral cylindrical kilograms, one of two pieces and one of four pieces. Figure 3 shows the design of the platinum-iridium weight set.

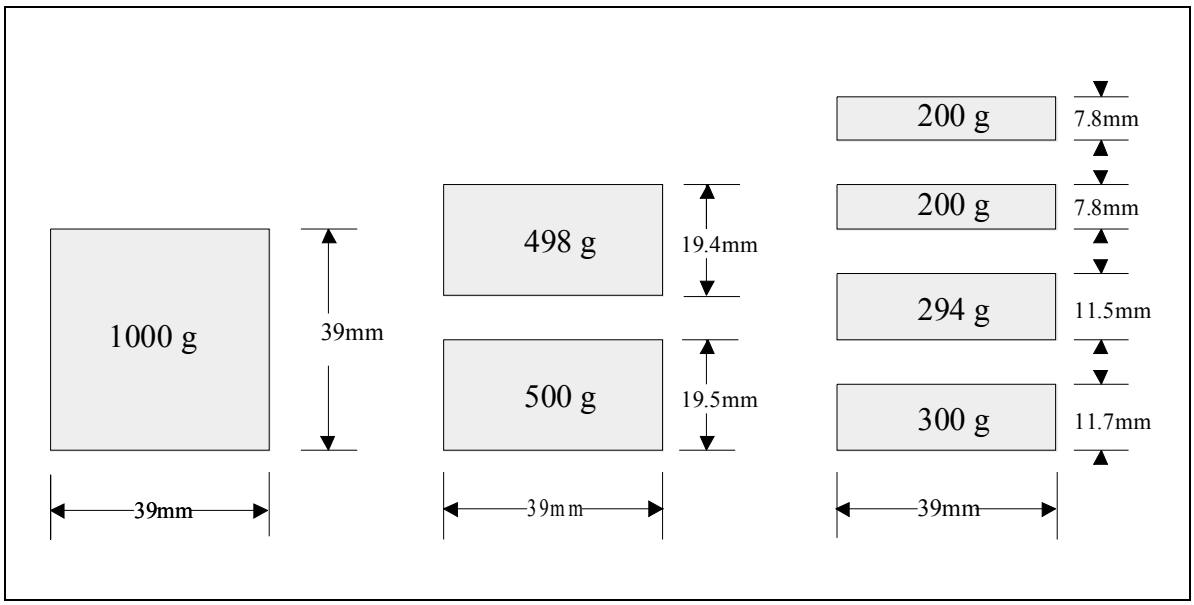

Figure 3: Design for platinum-iridium weight set

The design of the sets of weights (the stainless steel set was of similar construction to that of platinum-iridium) was such that surface area ratios of approximately 1:1.33:2.0 were achieved. By transferring these weights between ambient and vacuum conditions the effect of vacuum exposure, in terms of unit surface area, could be calculated from the differential changes within the set of weights. The two additional cylindrical standards were also manufactured, and used to provide monitoring standards; one remaining permanently in air and the other in vacuum.

The weight sets were assembled using 1 cm long spacers of 2 mm diameter wire (of the appropriate material). Three spacers were used for each gap to expose all the surfaces of the composite weights to vacuum. The volumes, masses and surface areas of the spacers were added to the overall values for the weight stack. The surfaces of the spacers were assumed to behave in the same way as the surfaces of the weights. Since the maximum surface area contribution of the spaces was 2.6% (for the 2/300s stack) any difference between the behaviour of the surfaces of the weights and spacers would have minimal effect on the overall result (given the small weight changes being measured), Figure 4 shows an assembled set of weights. Full designations ascribed to the weights are given in Table 1 together with their surface areas.

Figure 4: An assembled set of 1 kilogram weights of different surface areas designated 500s, 2/300s and 1000(2)

Material	Designation	Description	Surface Area	Function
Stainless Steel	1000(1)	Integral cylinder	139.7 cm^2	'In vacuum' standard
	1000(2)	Integral cylinder	139.7 cm^2	Transfer standards
	500s	Stack of 2 pieces (2x500g)	188.1 cm^2	
	2/300s	Stack of 4 pieces (2x300g & 2x200g)	284.5 cm^2	
	1000(3)	Integral cylinder	139.7 cm^2	'In air' standard
Platinum-iridium	81	Integral cylinder (official copy of K)	71.50 cm^2	'In vacuum' standard
	82	Integral cylinder (official copy of K)	71.50 cm^2	Transfer standards
	500p	Stack of 2 pieces (2x500g)	96.71 cm^2	
	2/300p	Stack of 4 pieces (2x300g & 2x200g)	149.15 cm^2	
	A	Integral cylinder (copy of K)	71.54 cm^2	'In air' standard

Table 1: Designation of stainless steel and platinum-iridium weights used for this work

The stainless steel weights were manufactured by Häfner in Germany to OIML Class E_1 specifications [5]. The platinum-iridium weights were manufactured from raw material provided by Johnson Matthey. The rough machining was done at NPL and the weights were finished at the BIPM to the same surface finish as official copies of the International Prototype Kilogram.

4. EXPERIMENTAL PROCEDURE

The aim of the experiment was to assess the change in the mass values of stainless steel and platinum-iridium weights transferred between air and vacuum and the repeatability of this change. The majority of the measurements were made on NPL's two HK1000MC mass comparators, as described in Section 3.1.1 at a time before the installation of the NPLone vacuum balance. Consequently, additional measurements were made on NPLone to check the mass change figures calculated from the initial measurements and to assess the effect of the level of vacuum on the measured change (NPLone runs at a vacuum of 10^{-3} mbar whereas the HK1000MC vacuum balance runs at 10^{-6} mbar). The measurements on NPLone were also used to assess the practical use of the balance for traceable in-vacuum calibrations.

4.1 Preparatory measurements

Preparatory measurements made on the standards used in this study included measurements of surface roughness, density and mass stability. Table 2 summarises the range of results from the measurements on all the weights used.

Weight material	Surface roughness range (R_z) (nm)	Density range (kg/m^3)	Mass stability in air (µg)
Platinum-iridium	3.9 to 4.8	21 542.70 to 21 545.33	Better than ± 3 µg
Stainless steel	34 to 42	7 887.95 to 7 888.32	Better than ± 5 µg

Table 2: Preliminary measurements on platinum-iridium and stainless steel weights

The surface roughness of the stainless steel weights is well below that required by the OIML recommendation [5], which is 0.1 µm. The roughness of the platinum-iridium surfaces is typical of the diamond turning process used at the BIPM to produce copies of the International Prototype Kilogram. The density ranges for both materials indicate good homogeneity. Mass stabilities, measured over a few months prior to the start of the vacuum work are typical of those achievable for weights of this type.

4.2 Vacuum/air transfer measurements

To quantify the effect of transfer between air and vacuum on the mass of the weights transferred, and to assess the repeatability of this mass change the weight sets described in 3.2 were repeatedly transferred between air and vacuum. The stainless steel weight set consisted of an integral kilogram (1000(2)) a two-piece composite kilogram (500s) and a four piece composite kilogram (2/300s). Similarly, the platinum-iridium weight set comprised integral kilogram 82 and composite kilograms 500p and 2/300p. Measurements were performed using the two HK1000MC comparators (one in air and one in vacuum), transferring the weights between the two balances and using NPLone, which was cycled between ambient and vacuum conditions with the weights remaining on the balance.

4.3 Vacuum/air stability measurements

In addition to the transfer standard set described in 3.2, integral cylindrical weights were held permanently in air and in vacuum to allow stability checks to be performed on the transfer

standards. The ‘in vacuum’ standard, having been held in vacuum for several months prior the start of the weight transfer, was assumed to be stable. Against this standard the behaviour of the weights after initial exposure to vacuum could be assessed. Additionally, the ‘in air’ and ‘in vacuum’ standards were used to measure any longer term changes in the values of the transfer standards. These measurements were performed using the HK1000MC comparators. Table 1 summarises the designations of all the weights used.

5. RESULTS

5.1 Stainless steel weights

5.1.1 Stability in vacuum

Initially, 1 kilogram integral stainless steel weight (1000(1)) was introduced into vacuum and its mass monitored against a weight which had been in vacuum for several months (55d), which was assumed to be stable. Figures 5 and 6 show the short and longer-term stability of the weight, respectively.

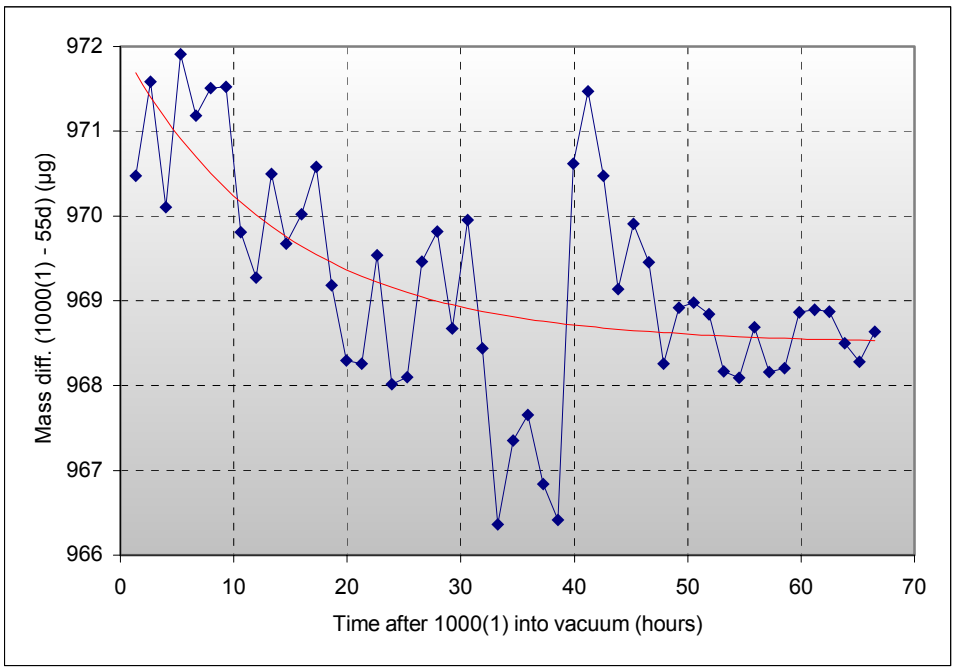

Figure 5: Short term stability of stainless steel cylindrical weight in vacuum

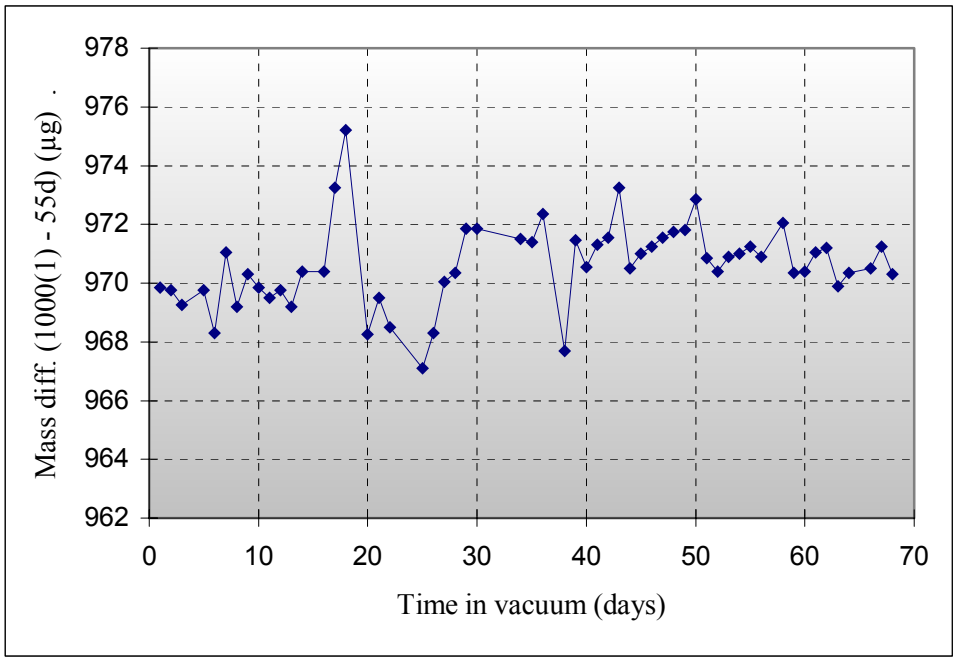

Figure 6: Longer term stability of stainless steel cylindrical weight in vacuum

The graphs show that the weight experiences a small initial weight loss, of the order of 3 micrograms, on exposure to vacuum. This is followed by a gradual long-term gain of about 1 microgram over 2 months. The stability of the weight suggests that mass standards should be left in vacuum for a period of at least 48 hours to ensure that the weights are stable. It should be noted that the initial loss of 3 micrograms does not represent the total loss of mass on transfer between air and vacuum. Due to the finite time it takes to introduce the weights through the load-lock to the main vacuum chamber and commence the weighings (about 10 minutes) the total mass loss cannot be calculated from these weighings. The short-term stability graph (Figure 5) shows a variation in the apparent weight of 1000d of ± 2.5 micrograms between 30 and 40 hours vacuum exposure. There is no physical reason for this behaviour and it can probably be attributed to a function of the balance performance. The standard deviations of the individual series of comparisons for this period (each point on the graph represents the average of 10 comparisons) are significantly larger than the average (7 or 8 micrograms compared with the normal 2 micrograms). It is likely that “stiction” (the micro-welding of clean surfaces brought into contact in vacuum) has occurred between the pan break and the pan and that a slight error in the weighing result has resulted due to increased swinging of the pan.

5.1.2 Effect of transfer between air and vacuum

Using the set of weights with different surface areas (S.A.), a total of eight transfers between air and vacuum were made. After each transfer the weights spent at least 7 days in the medium into which it had been transferred and at least four series of comparisons were performed, the weights being left for at least 48 hours before taking the first measurements. The relative mass values for the weights within the set allowed the calculation of the mass change per unit surface area for stainless steel weights. Figures 7 and 8 show the mass values of the two (500s) and four (2/300s) piece composite weights relative to the integral kilogram weight

(1000(2)) in air and vacuum. Values in air have been corrected to a relative humidity value of 50% from ambient humidity (in the range 40 to 60%) using a mass correction of 1.1 ng/cm^2/%RH calculated by Gläser [14].

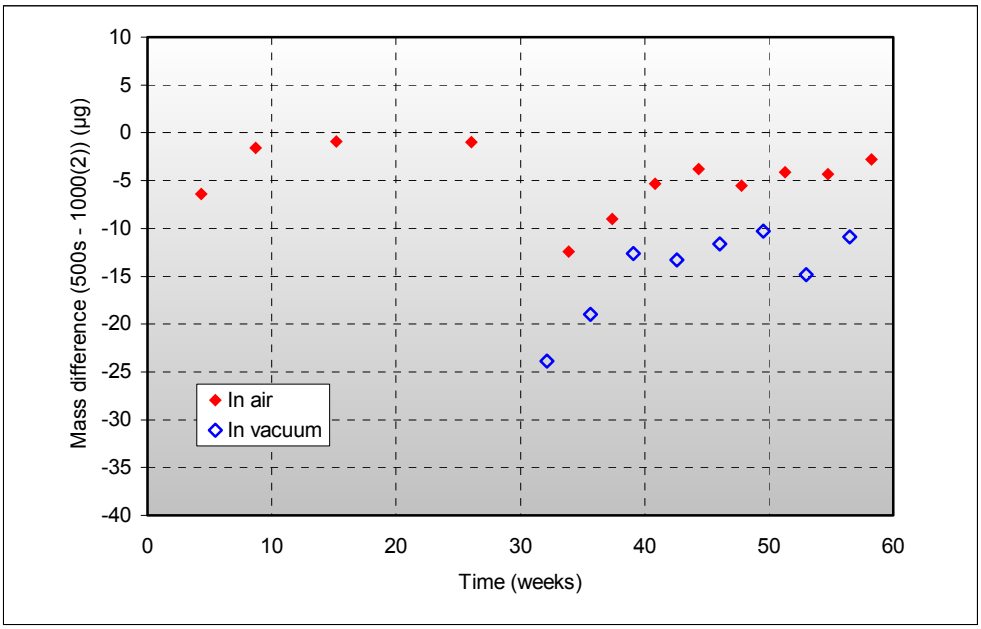

Figure 7: Value of 500s relative to 1000(2) in air and in vacuum

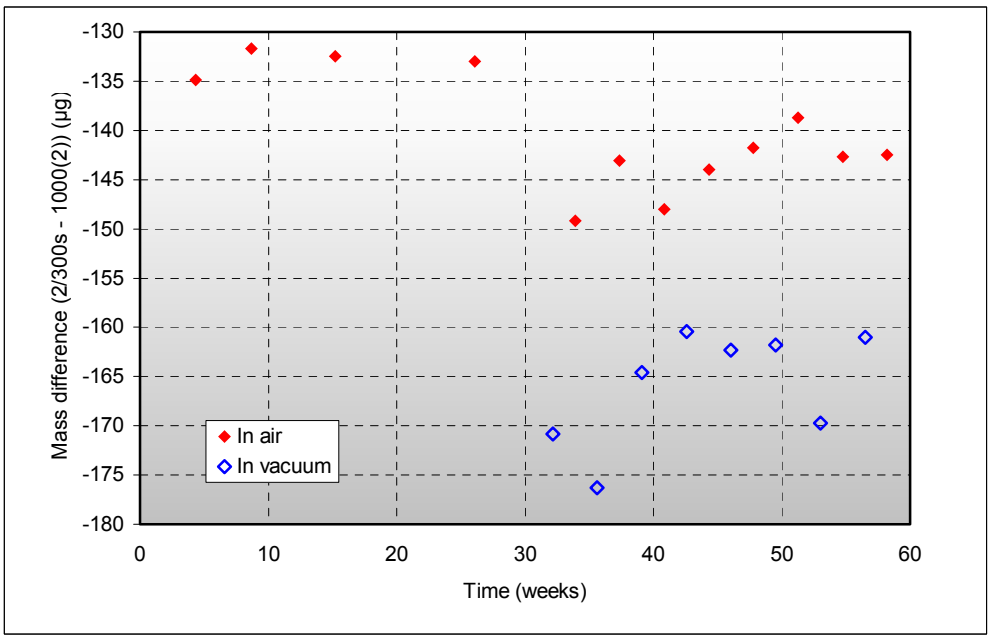

Figure 8: Value of 2/300s relative to 1000(2) in air and in vacuum

The graphs show that the value of the two composite weights were relatively stable prior to the initial transfer into vacuum (32 weeks). As expected, the composite weights show a relative mass loss on exposure to vacuum, with the weight with the larger surface area (2/300s) showing a bigger loss. When the weights are subsequently returned to air, a residual (non-recoverable) mass loss can be seen. After this initial air-vacuum-air cycle, which gives a net mass loss, the mass change between air and vacuum is relatively repeatable. Table 3 summarises the data displayed on the graphs. Standard deviations represent values calculated for the population rather than for the mean. These values have been used since the average changes calculated will be applied for each (singular) occasion that a weight is transferred between vacuum and air and the best estimate of the error of this applied correction is the SD of a population of measured changes.

	Surface area difference vs. 1000(2) (cm^2)	Non-recoverable change due to first vacuum exposure		Reversible change between air and vacuum (subsequent to first exposure)		
		Absolute change (µg)	Change per unit S.A. (µg/cm^2)	Absolute change (µg)	Change per unit S.A. (µg/cm^2)	Standard Deviation (µg/cm^2)
500s	48.4	-3.6	-0.074	-7.5	-0.155	0.022
2/300s	144.8	-10.8	-0.075	-22.1	-0.153	0.018
Av.			-0.074		-0.154	0.016[1]

[1]This represents the standard deviations for the calculated changes per unit surface area for both artefacts

Table 3: Mass loss per unit surface area for 500s and 2/300s relative to 1000(2) (HK1000MC at 10^{-6} mbar)

In terms of the change per unit surface area the results for the two composite kilograms show excellent agreement. Based on these results it can be concluded that a typical OIML Class E_1 (stainless steel) weight will change by 0.154 µg/cm^2 when moved between air and vacuum. On initial exposure to vacuum the weight will experience an additional, permanent mass loss of 0.074 µg/cm^2. On a stainless steel kilogram weight of OIML recommended construction (surface area approximately 150 cm^2), these figures equate to an initial permanent mass loss of 11.1 µg on initial exposure to vacuum and a (subsequent) reversible mass change of 23.1 µg on transfer between air and vacuum. The standard deviation on this measured mass change is equivalent to 2.4 µg.

5.1.3 Repeatability of mass in vacuum

During this study, cylindrical stainless steel kilograms 1000(1) and 1000(3) were stored permanently in vacuum and air respectively. Using these weights as standards, the repeatability of the cylindrical transfer standard (1000(2)) in air and vacuum could be assessed. Figure 9 shows the stability of this transfer standard over the period of the study.

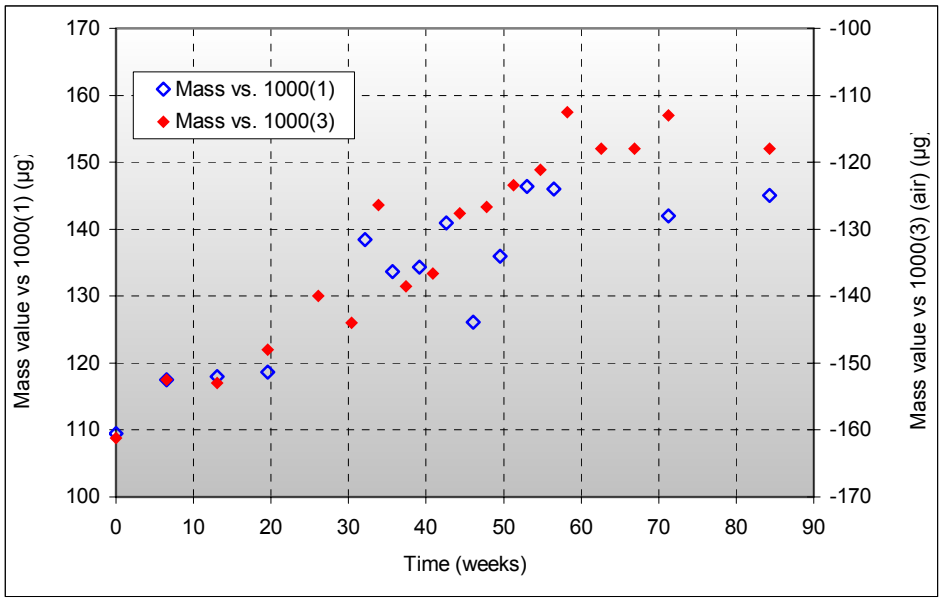

Figure 9: Stability of 1000(2) transfer standard in air and vacuum

The graph shows that the transfer standard appears to gain weight relative to both the 'in air' and 'in vacuum' standards. However, the repeatability of the values in the two media is good with an average change of about 2 micrograms between consecutive values and a maximum change of 12 micrograms. Note that for the first 20 weeks of this test all weights were compared in air. After 30 weeks comparisons with 1000(1) are made in vacuum and those with 1000(3) are in air. The mass gain of 1000(2) relative to the other two weights occurs both when the weights are being compared in air (up to 20 weeks) and when 1000(2) is being moved between air and vacuum (30 – 90 weeks) so appears independent of the exposure of 1000(2) to vacuum and may be a function of the intrinsic stability of the weight rather than its exposure to vacuum. The mass gain seen between the in-air values at 30 and 34 weeks is due to the non-reversible change on initial exposure to vacuum discussed earlier.

5.2 Platinum-iridium weights

The tests described in 4.1 on stainless steel weights were repeated for platinum-iridium mass standards.

5.2.1 Stability in vacuum

An integral platinum-iridium cylindrical weight (copy no 81 of the International Prototype Kilogram) was introduced into vacuum and its stability monitored. Figures 10 and 11 show the short and longer-term stability of the weight in vacuum. The stability of 81 was monitored against stainless steel weight 1000(1) which had been in vacuum for several months and was assumed to be stable.

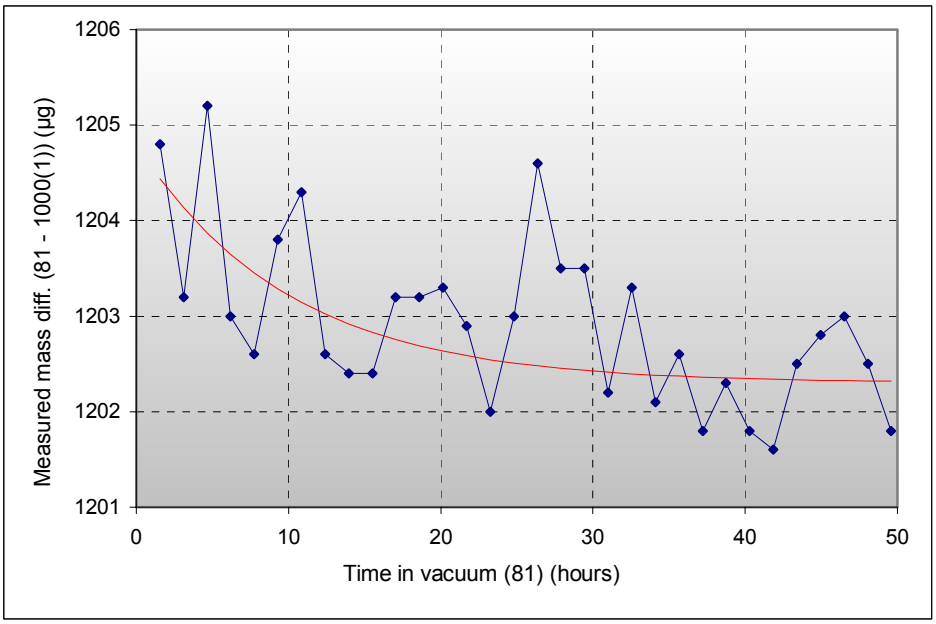

Figure 10: Stability of kilogram 81 following initial introduction into vacuum

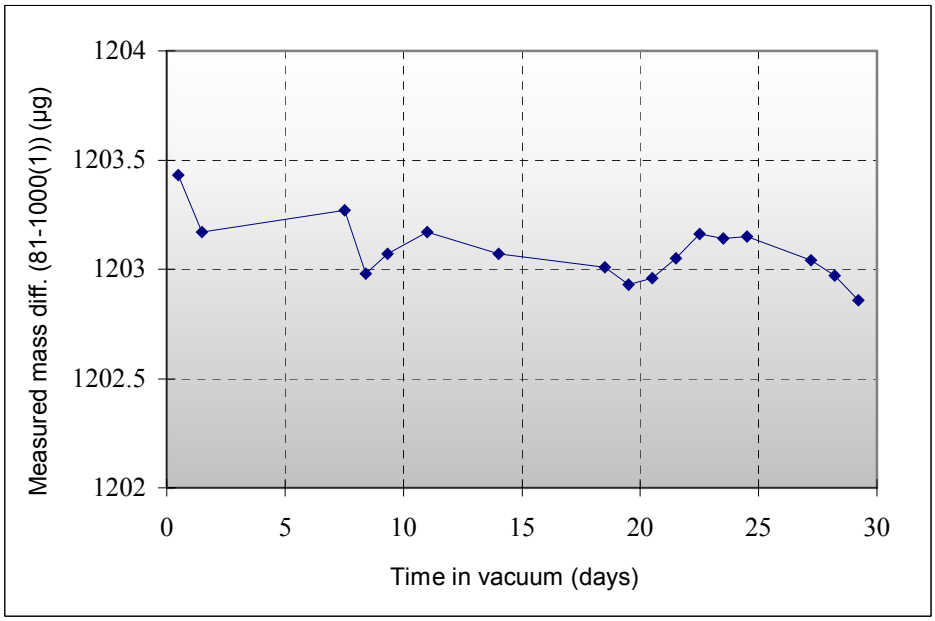

Figure 11: Longer term stability of kilogram 81 in vacuum

The graphs shows that the platinum-iridium kilogram exhibits similar behaviour to the stainless steel weight on exposure to vacuum. There is an initial loss of about 2 micrograms over a period of about 30 hours, after which the weight is stable. Both the mass loss and the time it takes are slightly less than for the stainless steel kilogram, probably due to the smaller surface area of the platinum-iridium weight (71.5 cm^2 for a platinum-iridium cylinder against 139.47 cm^2 for a cylinder of stainless steel). As with the stainless steel kilogram, the mass loss measured does not represent the total mass loss experienced by the weight on exposure to vacuum.

5.2.2 Effect of transfer between air and vacuum

Using the set of weights with different surface areas, the effect of vacuum exposure on the platinum-iridium weights was measured. A total of ten transfers between air and vacuum were made. After each transfer the weights spent at least 5 days in the medium into which it had been transferred and at least four series of comparisons were performed. The relative values of the weights within the set allowed the calculation of the mass change per unit surface area for stainless steel weights. Figures 12 and 13 show the values of the two (500p) and four (2/300p) piece composite weights relative to the integral kilogram weight (82) in air and vacuum.

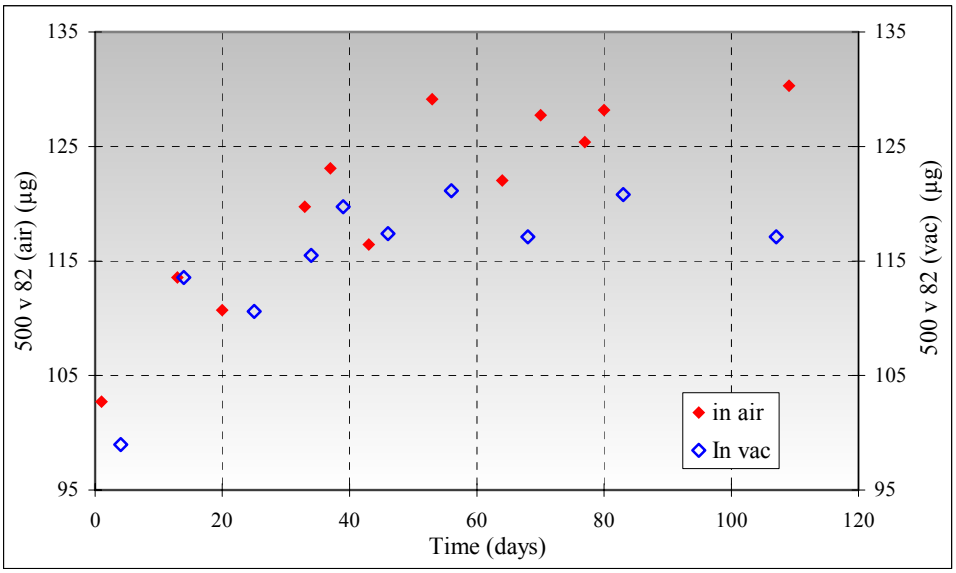

Figure 12: Value of 500p relative to 82 in air and vacuum

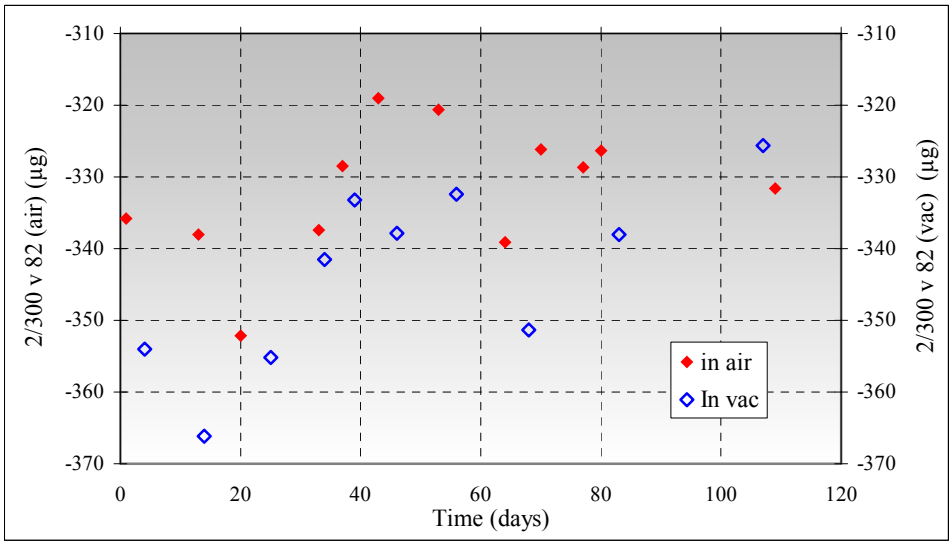

Figure 13: Value of 2/300p relative to 82 in air and vacuum

Again the platinum-iridium can be seen to behave in a similar way to the stainless steel. The weights show a relative mass loss on exposure to vacuum with the weight with the larger surface area showing a bigger loss. Unlike the stainless steel, no non-recoverable mass loss is

experienced by the weights when initially exposed to vacuum, this may be because the platinum-iridium weights have less residual contamination, having been through the BIPM nettoyage-lavage cleaning process [6]. Table 4 summarises the data from the two graphs. As with the results for the stainless steel measurements the standard deviation of the population has been used as this is the best estimate of the uncertainty on the calculated mass change which will be applied when a weight is transferred between air and vacuum.

Stack	Surface area difference from cylinder (82) (cm^2)	Mass change (vacuum – air) Relative to 82 (µg)	Standard deviation of measured mass change (µg)	Mass change per unit surface area (µg/cm^2)	Standard deviation of unit change (µg/cm^2)
500p	25.2	-4.0	2.4	-0.16	0.10
2/300p	77.6	-12.7	5.2	-0.16	0.07
Av.				-0.16_2	0.06[1]

[1] This represents the standard deviation of the calculated unit changes for both weight stacks

Table 4: Mass loss per unit surface area for 500p and 2/300p relative to 82 (HK1000MC at 10^{-6} mbar)

The mass change on transfer between air and vacuum is very similar to the repeatable mass change calculated for the stainless steel weights (see Table 3). The standard deviations of the mass change readings are relatively large compared with the performance of the balance. This is due to the relatively small change being measured and to the difficulty of handling and aligning the composite (stack) weights on the balance – particularly when transferring the weights into vacuum. The calculated mass change between air and vacuum is equivalent to a change of 12.6 µg on a cylindrical platinum-iridium mass standard, the standard deviation on the calculated change being the equivalent of 4.6 µg.

5.2.3 Repeatability of mass in vacuum

Kilogram 82, the integral platinum-iridium cylindrical mass standard was transferred between air and vacuum as part of this study. Figure 14 shows the comparison of 82 with platinum-iridium kilograms A (in air) and 81 (in vacuum).

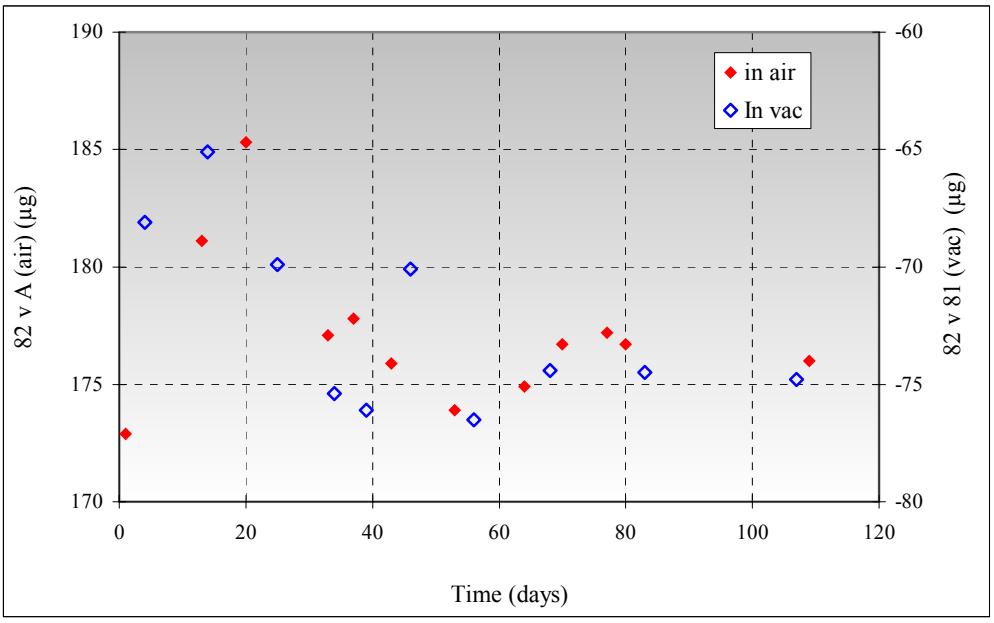

Figure 14: Mass of platinum-iridium transfer standard 82 against kilograms A (in air) and 81 (in vacuum)

The graph shows that 82 appears to have gained weight following the initial transfer into vacuum (first blue to first red point) but loses roughly the same amount over the next 4 to 5 transfers between air and vacuum. The last seven sets of reading show good repeatability with a standard deviation of 2.1 micrograms for the in-air measurements and 3.5 micrograms for the in-vacuum measurements, the maximum difference between consecutive readings is 6.2 micrograms in vacuum and 1.8 micrograms in air. The repeatability of these values is partly due to the repeatability of the measurements (rather than due to any change in the mass of the artefacts). The difficulty of assembling the composite artefacts (see section 3.2), particularly in vacuum limited the repeatability of the comparison to 2-3 micrograms.

5.3 Measurements on NPLone vacuum balance

The mass change measurements for stainless steel and platinum-iridium weights, as assessed on the two HK1000MC balances (see results in Sections 5.1.2 and 5.2.2), were repeated on the NPLone vacuum balance using the same weight sets. Several series of measurements at ambient and vacuum (10^{-3} mbar) pressures were made using the comparator. In addition, a series of intermediate measurements at approximately 1 mbar were made to examine any hysteresis. These measurements could then be compared with the results for the HK1000MC vacuum balance running at a lower vacuum (10^{-6} mbar).

NPLone was also used to assess the repeatability of mass change on transfer to and from vacuum for mass standards of OIML shape. Weights from NPL standard set NPLW 55 were selected, with one weight remaining in air (55), one in vacuum (55td) and one acting as a transfer standard (55d).

5.3.1 Mass stability on exposure to vacuum

Figure 15 shows the behaviour of 55d, calibrated against 55td, after being transferred into vacuum, 55td having been in vacuum for a period of some weeks.

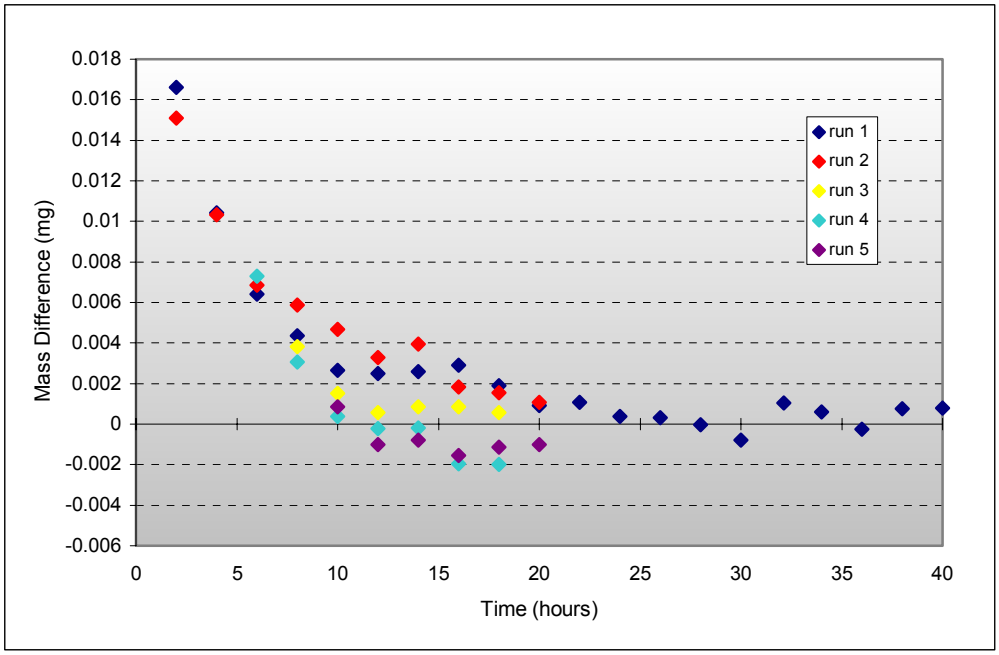

Figure 15: Transfer standard 55d compared with "in-vacuum" standard 55td

The behaviour of the weight on introduction to vacuum follows the trends seen previously for both stainless steel and platinum-iridium weights (see Figures 5 and 10) in taking between 10 and 20 hours to become stable in vacuum. It is interesting to note that, although the overall weight loss was shown to be approximately the same on the HK1000MC and NPLone (see Sections 5.1.2 and 5.3.3), the majority of the weight loss occurs almost immediately on the HK1000MC at 10^{-6} mbar and was therefore not seen on the weighings shown in Figures 5 and 10. Figure 5, which show a weight loss of about 3 micrograms over the weighing period (starting about 10 minutes after exposure to vacuum), the majority of the loss having taken place before the start of the first weighing. The overall weight loss for a cylindrical stainless steel weight was calculated as about 23 micrograms. The work on NPLone at 10^{-3} mbar showed a mass change of 19.5 micrograms for a similar weight but, from the mass loss curves for 55d, it can be seen that this comes off gradually over a period of 10 to 20 hours after exposure to vacuum rather than almost immediately as seen on the HK1000MC operating at 10^{-6} mbar.

5.3.2 Repeatability of values in air and vacuum

The repeatability of the value of 55d in air (against 55) and in vacuum (against 55td) was assessed by performing six transfers of the weight between air and vacuum conditions. The results of these weighings are summarised in Table 5 with SD being the standard deviation of the population.

Time (days)	Weight in air (55-55d) (µg)	Weight in vacuum (55td-55d) (µg)
1	-22.5	0.56
3	-19.6	
6		-2.20
8	-19.3	
9		1.36
12	-14.6	1.19
13	-18.6	
15		1.07
16	-22.7	
17		-2.72
Average	-19.6	-0.1
SD	3.0	1.8

Table 5: Stability of 55d in air and vacuum

The results show a repeatability of 3.0 micrograms for the in-air weighings and 1.8 micrograms for the in-vacuum weighings. These figures are only slightly greater than the changes which could be expected by simply removing and replacing the weights on the carousel of the mass comparator.

5.3.3 Cyclic measurements at ambient, intermediate and full vacuum

Measurements were taken under ambient conditions, at partial vacuum (approximately 1 mbar) and at full vacuum (approximately 2 x 10^{-3} mbar). The measurements were taken in a complete cycle from ambient to vacuum and back to ambient in order to examine the hysteresis effect on the comparative mass values of the weights. Tables 6 and 7 summarise the results for this cycle for the weights of the two materials under test.

Measurement Run	Pressure (mbar)	Relative mass change (µg)		
		1000 vs 500s	1000 vs 2/300s	500s vs 2/300s
1	1019.5			
2	1.2	-7.25	-14.06	-9.94
3	0.0024	-11.52	-26.01	-17.40
4	1.0	-9.30	-21.31	-15.35
5	1012.5	1.57	-1.17	-0.23

Table 6: Results from NPLone for transfer of stainless steel between air and vacuum

Measurement Run	Pressure (mbar)	Relative mass change (µg)		
		1000 vs 500s	1000 vs 2/300s	500s vs 2/300s
1	1019.5			
2	1.2	-3.05	-5.96	-4.39
3	0.0024	-4.35	-9.16	-5.69
4	1.0	-4.16	-7.93	-5.49
5	1012.5	0.70	-1.27	-0.44

Table 7: Results from NPLone for transfer of platinum-iridium between air & vacuum

The results for the transfer of the two weight sets are plotted in the graphs shown in Figures 16 and 17.

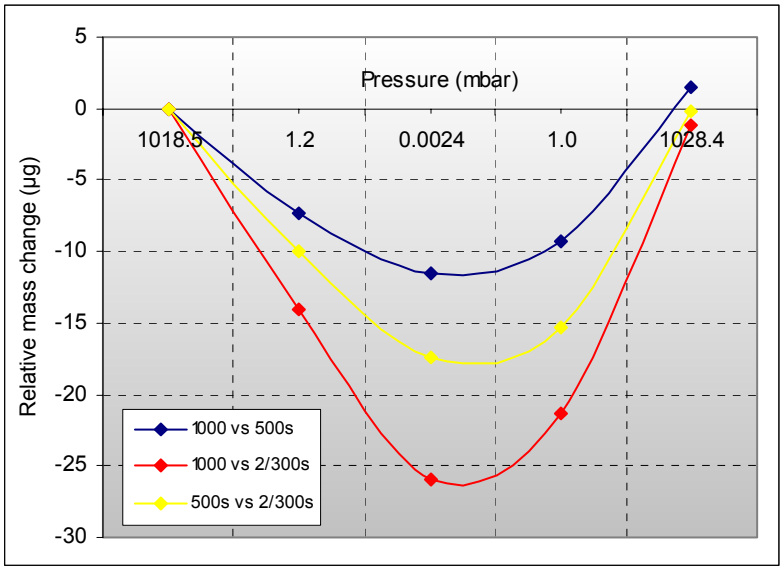

Figure 16: Mass change for stainless steel weight set on NPLone balance

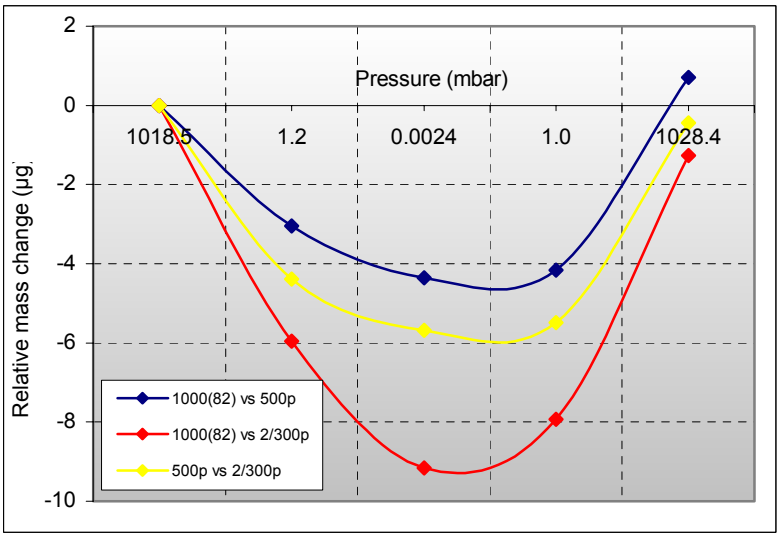

Figure 17: Mass change for platinum-iridium weight set on NPLone balance

The results show that at the partial vacuum the mass loss (for the weights of larger surface area) is less than at full vacuum. Some hysteresis can also be seen as the weights at partial vacuum show a larger weight loss if they had previously been at full vacuum suggesting that not all the accreted layer have returned to the surfaces of the weights. This is similar to the behaviour seen when comparing weights of different surface areas under conditions of changing humidity [7-20]. The final values at ambient conditions, however, agree well with the initial values. The hysteresis of the weight gain/loss curve, for transfer between air and partial and full vacuum, is illustrated in Figure 18.

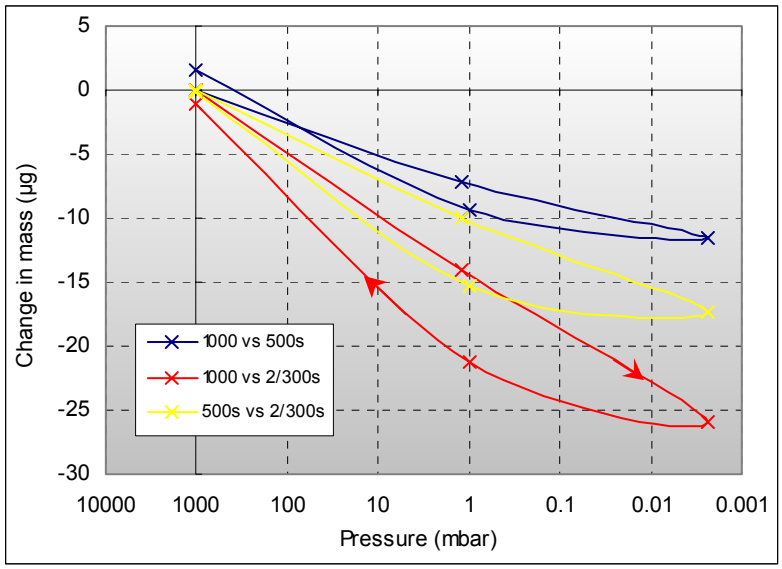

Figure 18: Mass change curve for (stainless steel) weight

5.3.4 Effect of transfer between air and vacuum

In addition to the measurements described in 5.3.3, several transfers between ambient and full vacuum (10^{-3} mbar) were performed with the platinum-iridium and stainless steel weights on NPLone. Together with the results at partial vacuum (1 mbar), the results for the effect of the transfer, expressed in terms of unit surface area, are summarised in Table 7.

Material	Comparison	Surface area diff. (cm^2)	Air to partial vac. (1mbar)		Air to full vac. (10^{-3} mbar)	
			Mass change[1] (µg)	Change per unit SA (µg/cm^2)	Mass change (µg)	Change per unit SA (µg/cm^2)
Stainless steel	1000(2) v 500s	48.2	3.55	0.07	7.52	0.16
	1000(2) v 2/300s	145.4	7.06	0.05	16.01	0.11
	500s v 2/300s	97.1	4.94	0.05	11.40	0.12
	Av.			0.06		0.13
Platinum-iridium	1000(82) v 500p	26.1	2.05	0.08	2.35	0.09
	1000(82) v 2/300p	78.2	3.96	0.05	7.16	0.09
	500p v 2/300p	52.1	2.39	0.05	4.69	0.09
	Av.			0.06		0.09

[1]Mass changes are only for transfer from air to partial vacuum without interim exposure to full vacuum

Table 7: NPLone results for the effect of transfer from air to partial and full vacuum

The results for the exposure to full vacuum on the NPLone vacuum balance (10^{-3} mbar) are lower than those previously calculated (see Tables 3 and 4) using the HK1000MC at vacuum of about 10^{-6} mbar. The results at partial vacuum (approximately 1 mbar) show a significantly smaller loss in mass per unit surface area, the effect on both materials being approximately linear with logarithmic pressure. Figure 19 illustrates this phenomenon.

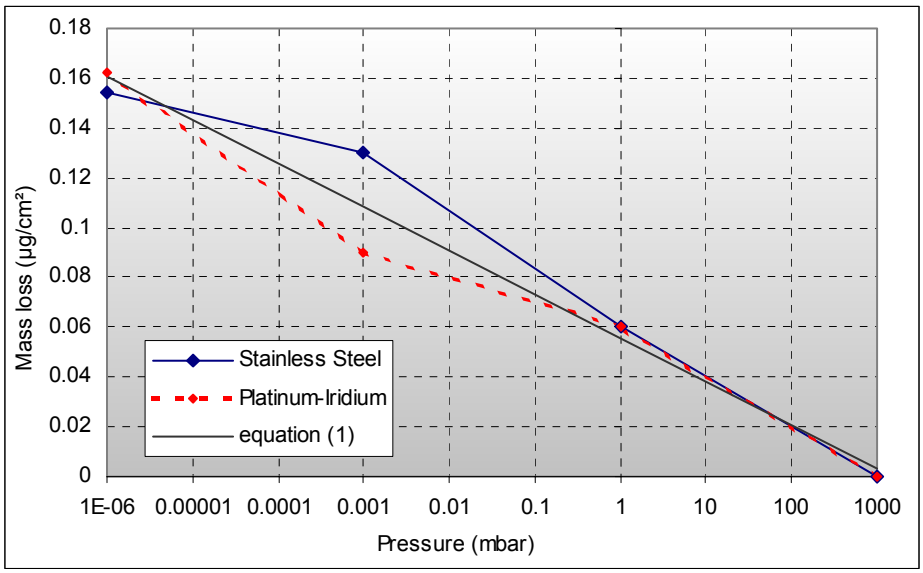

Figure 19: Pressure dependence of the mass change due to transfer from air to vacuum for stainless steel and platinum-iridium

Figure 19 shows the pressure dependence of the mass loss for transfer from air to different levels of vacuum. The behaviour of the two materials appears to be slightly different at 10^{-3} mbar but within the uncertainty of the measurements (approximately 25% of the overall change in each case) it is safe to assume a linear dependence of mass loss with logarithmic pressure. Taking all the data into consideration the relationship between mass loss and pressure can be derived from the following equation:

$$\Delta m = 0.0558 - 0.00759 \ln p \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where Δm is the mass loss per unit surface area in micrograms per square centimetre and p is the pressure in mbar.

6. UNCERTAINTY COMPARISONS

Tables 9 and 10 give typical uncertainty budgets for stainless steel kilogram weights calibrated against platinum-iridium mass standards in air and in vacuum. Note that usually components for the goodness of fit of a series of weighings (repeatability) and for the mass change in the standard from the last calibration would be included. It has been assumed that these would be the same for the two calibration methods and they have therefore been ignored. All uncertainties have been quoted at k=1.

Source of uncertainty	Uncertainty	Uncertainty contribution
Uncertainty of standard	2.9 µg	2.9 µg
Density of standard	2 kg/m^3	0.3 µg
Density of testweight	0.15 kg/m^3	0.2 µg
Air density (temperature)	0.01 ^{O}C	3.5 µg
Air density (pressure)	0.05 mbar	4.8 µg
Air density (dew point)	0.25 ^{O}C	5.6 µg
Air density (CO_2 content)	100 ppm	4.0 µg
Air density (equation)	1 in 10^4	9.7 µg
Balance repeatability	1.0 µg	1.0 µg
Total Uncertainty (k=1)		13.6 µg

Table 9: Typical uncertainty budget for stainless steel kilogram calibrated in air against a platinum-iridium standard

Source of uncertainty	Uncertainty	Uncertainty Contribution	Note
Uncertainty of standard	2.9 µg	2.9 µg	As before
Transfer of standard to vacuum	4.3 µg	4.3 µg	4.3 µg sd on calculated change for Pt-Ir on going into vacuum (see 5.2.2)
Transfer of testweight to vacuum	2.4 µg	2.4 µg	2.4 µg sd on calculated change for SS on going into of vacuum (see 5.1.2)
Repeatability of testweight in vacuum	1.8 µg	1.8 µg	1.8 µg sd on repeated weighing in vacuum (see 5.3.2)
Repeatability of testweight in air	3.0 µg	3.0 µg	3.0 µg sd on repeated weighing in air (see 5.3.2)
Total Uncertainty (k=1)		6.7 µg	

Table 10: Typical uncertainty budget for stainless steel kilogram calibrated in vacuum against a platinum-iridium standard

Except for the uncertainty in the value of the (platinum-iridium) standard mass, all the uncertainty contributions for the in-vacuum comparison come from the repeatability of the transfer to and use of the two weights in vacuum. The standard deviations used are those of the population rather than of the mean. The elimination of the uncertainty components for the measurement of air density can be seen to have a significant effect on the overall uncertainty on the stainless steel kilogram. Even taking into account the need to make a correction for the surface effects of the two weights going into vacuum and the repeatability of the value of the stainless steel weight in vacuum and air the uncertainty is much lower for the calibration in vacuum.

7. PRACTICAL TRACEABILITY

Studies at NPL [21] have shown that continual transfer between air and vacuum accelerates the rate of accretion of contaminants onto the surface of mass standards. This is due to the removal of the protective water film on exposure to vacuum and the finite time the weight takes to recover this film on re-exposure to air. During this time the weight surface is particularly sensitive to the accretion of contaminants. The repeated transfer of primary mass standards between air and vacuum is therefore not desirable. Figure 20 illustrates the proposed route to ensure traceability of the comparison of platinum-iridium and stainless steel kilograms in vacuum.

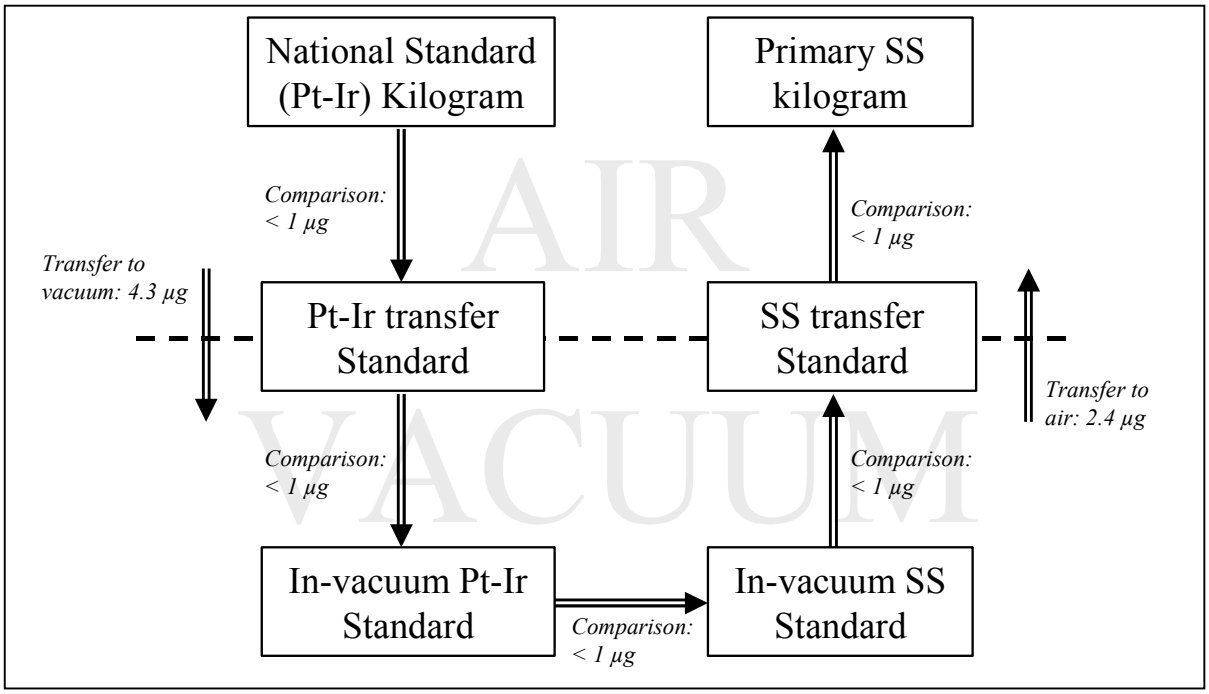

Figure 20: Proposed traceability route for calibration in vacuum

The proposed calibration scheme involves a number of comparisons but most of these are will be necessary for the routine maintenance of traceability for weights in vacuum and not preformed specially for this calibration. The major sources of uncertainty in the calibration are the uncertainties associated with the estimated change in the value of the standards on transfer and from vacuum.

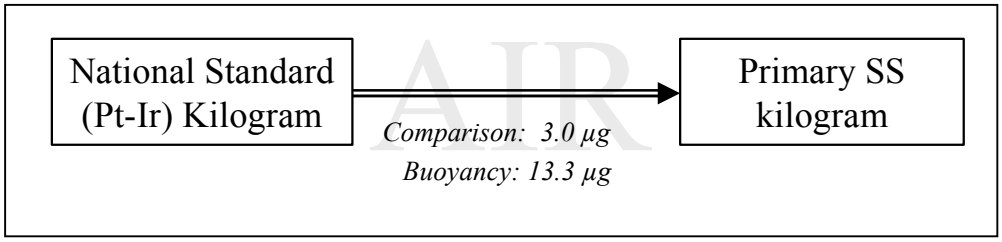

Figure 21: Calibration of Pt-Ir against stainless steel in air

Figure 21 illustrates the same calibration performed in air. The uncertainty due to the comparison is higher than those in figure 20 due to the difficulty of comparing weights of different sizes/shapes in air (mainly due to thermal effects). All comparisons in figure 20 involve weights of similar materials or are performed in vacuum where thermal effects are negligible. Summing the typical uncertainties associated with the two methods of comparison gives 5.4 µg for the vacuum method and 13.6 µg for the in-air comparison. Adding in the typical uncertainty for the National Standard Kilogram (2.9 µg) gives uncertainties of 6.1 µg and 13.9 µg on a stainless steel kilogram calibrated in via vacuum comparison and in air respectively. These uncertainties will depend on the standard deviations of the comparisons at the time of the calibration but the values calculated give an indication of typical measurement uncertainties and agree broadly with those calculated in Section 6.

8. CONCLUSIONS

It has been demonstrated that a significant improvement in the uncertainty on the calibration of a stainless steel kilogram mass standard against platinum-iridium can be achieved by performing the calibration in vacuum. The uncertainty on the corrections for surface effects and the repeatability of the value of the stainless steel weight in air and vacuum result in an overall uncertainty of 6.7 µg (k=1) compared with an uncertainty of 13.6 µg for the same calibration performed in air. The level of vacuum at which the calibration is performed has been shown to effect the mass change due to surface effects and the time the weight takes to stabilise.

An algorithm has been developed to predict the mass loss per unit surface area of stainless steel and platinum-iridium weights on exposure to various levels of vacuum. While the mass change from air to vacuum will certainly depend to some extent on the cleanliness and surface finish of the artefacts in question, the data gathered as part of this study and the algorithm developed will provide a useful basis for calculating this mass change. With the increased used of weights in vacuum, due in part to the work being undertaken to re-define the kilogram, this data will become increasingly important.

9. ACKNOWLEDGEMENT

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