NPL Report MOT 2

November 1996

The Assignment of Values to NPL's 1 kg Standards Following the Third Periodic Verification of Prototype Kilograms

I Severn and N M Raymond
Centre for Mechanical and Optical Technology
National Physical Laboratory
Teddington
Middlesex
United Kingdom
TW11 0LW

ABSTRACT

The United Kingdom's national standard of mass, Kilogram 18, was assigned a value by BIPM in 1991 as part of the Third Periodic Verification of National Prototypes of the Kilogram. The assignment of values to other kilogram standards belonging to NPL, based on this value of Kilogram 18, is the first stage in disseminating the UK mass scale. The standards involved in this process and the measurements made on them are described in this report.

ISSN 0309-3069

National Physical Laboratory
Teddington, Middlesex, United Kingdom, TW11 0LW

Approved on behalf of the Managing Director, NPL,
by Dr A R Colclough, Director,
Centre for Mechanical and Optical Technology

1 INTRODUCTION

Mass is unique amongst the SI units in that it is defined in terms of an artefact, a kilogram of platinum-iridium known as 'The International Prototype Kilogram', kept at the Bureau International des Poids et Mesures (BIPM). The United Kingdom's mass scale is based on Kilogram 18, its official copy of the International Prototype Kilogram, which is held by the National Physical Laboratory (NPL).

This report describes the work that was carried out to give mass values to NPL's working standard kilograms, as well as its best research weights, from the value assigned to Kilogram 18 in October 1991 following the Third Periodic Verification of National Prototypes of the Kilogram at BIPM.

2 NPL'S KILOGRAMS

2.1 THE PLATINUM-IRIDIUM AND PLATINUM KILOGRAMS

Kilogram 18

Kilogram 18 is the United Kingdom's official copy of the International Prototype Kilogram. As with all the platinum (Pt) and platinum-iridium (Pt-Ir) kilogram artefacts held by NPL it is cylindrical in form and has a diameter nominally equal to its height. Its volume at 0 °C is quoted as 46.4149 cm^3 in recent BIPM certificates and the same source gives a cubic coefficient of thermal expansion of $(25.869 + 0.00565t) \times 10^{-6}$ °C^{-1}.

Prior to the work under discussion here it was calibrated by BIPM and assigned a mass value of 1 kg + 53 μg. This value is referenced to 22 October 1991 which is the date when it was cleaned using the standard BIPM method [1].

Kilogram E

This weight was purchased in 1844 by Professor W H Miller of the University of Cambridge and is manufactured from platinum. Its volume was determined by Miller using hydrostatic methods to give a value at 0 °C of 47.3096 cm^3 in present day units. The importance of this weight to NPL is that it is extremely stable, principally because it has not been vigorously cleaned since the 1920s. In practice the stability of this weight makes it at least as important to NPL as Kilogram 18. The cubic coefficient of thermal expansion is taken to be 27.00×10^{-6} °C^{-1}. However, from approximately 1883 until the start of this exercise this coefficient had been assumed to be 25.89×10^{-6} °C^{-1}, as if the weight was manufactured from Pt-Ir [2]. It should be noted that this error leads to an offset in the mass value of the weight of 1.2 μg for the period up to 1993. The historical values have been corrected whenever they appear in this document to take this into account.

Kilograms A and B

The manufacture of these Pt-Ir kilograms was completed at BIPM in 1982. They have the best surface finish of the weights described here, having been diamond turned. Their densities were determined at NPL by hydrostatic weighing prior to the final finishing at BIPM. The volumes at 0 °C of A and B respectively are 46.4354 cm^3 and 46.4399 cm^3. Their cubic coefficient of thermal expansion is assumed to be the same as that of Kilogram 18.

Kilogram PI

Kilogram PI, sometimes known as ΣPI, is a composite standard consisting of a 500 g, two 200 g and one 100 g weights from the set PI Grams. The set covers the range 500 g to 1 mg and is manufactured from platinum-iridium down to 0.02 g and aluminium wire below that level. It is housed in a felt lined wooden box. The set was manufactured in 1884 by Oertling and has a mean density value derived by the Board of Trade which is equivalent to 21 354.4 kg m^{-3} at 0 °C.

During this exercise the cubic coefficient of thermal expansion was assumed to be the same as that for Kilogram 18 rather than the previously used value of 25.7×10^{-6} °C^{-1} which is taken from an uncertain source at the Board of Trade. The use of a different cubic coefficient of thermal expansion leads to an offset of 0.2 μg in the mass value of Kilogram PI. Such a small change is insignificant in terms of the overall uncertainty on the weights.

2.2 STAINLESS STEEL KILOGRAMS

For the first time in many years NPL introduced some new stainless steel weights into the traceability chain at the 1 kg level. These were used in conjunction with sets 36 and OC that have been in use at NPL for some time.

Set NPLW 36

Set NPLW 36 consists of a pair of integral knobbed 1 kg weights that were manufactured in 1955 by Stanton Instruments from a material believed to be similar to Immaculate V [1]. Their densities have been measured to be 7 832.0 kg m^{-3} by hydrostatic weighing at NPL. They are assumed to have a cubic coefficient of thermal expansion of 45×10^{-6} $°C^{-1}$ and are generally stored in a felt lined wooden box. The centre of gravity of these weights is estimated to be 30 mm above their base. This figure, as with the centre of gravity of all the other stainless steel weights, is based on measurements of their dimensions. Unfortunately these weights have suffered surface scratching since their previous calibration against platinum-iridium weights.

Set OC

This weight set consists of a pair of integral 1 kg weights which are stored in a felt lined wooden box. These weights were manufactured by Oertling in 1980 as part of a set of five weights, the other three of which were used in an international comparison. They are cylindrical in shape with a recessed base and are manufactured from Immaculate V. The density of set OC, so called because its top surfaces are marked with Off Centre circles to distinguish each weight in the set, has been hydrostatically measured at NPL to give a figure of 7 889.4 kg m^{-3}. These weights have, until now, been calibrated against set NPLW36 and have therefore been below them in the traceability chain. However, it was anticipated that they would have equal stature with NPLW 36 after this exercise. The centre of gravity of these weights has been calculated to be approximately 28.5 mm above their base. These weights are assumed to have a cubic coefficient of thermal expansion of 45×10^{-6} $°C^{-1}$.

---

[1] Composition of Immaculate V: 0.1% carbon, 23% chromium, 21% nickel, remainder iron

2.2.3 Set NPLW 55

Set NPLW 55 was purchased from Mettler in 1988 and consists of four integral, knobbed stainless steel kilogram weights. These weights have been marked with different numbers of dots on their top surfaces in order to distinguish them from each other. Individually the weights are called 55 plain (55), 55 dot (55d), 55 double dot (55dd) and 55 triple dot (55td). Since their purchase three of these weights have had their density determined by hydrostatic methods. The other weight, 55dd, has been allocated an assumed density based on the values of the others. These values are shown in Table 2.2.1. The density of 55 was measured over a range of temperatures from 19.6 °C to 20.6 °C to allow the cubic coefficient of thermal expansion to be calculated.

TABLE 2.2.1: DENSITY VALUES OF SET NPLW 55

Identification	Density (kg m^{-3})	Density Uncertainty (kg m^{-3}) k=1
55	7 961.04	0.07
55d	7 960.81	0.07
55dd	7 961	2
55td	7 961.14	0.07
Centre of gravity height above base (mm)		36.2
Cubic coefficient of thermal expansion (°C^{-1})		48×10^{-6}

Following the assignment of mass values to this set of weights 55dd and 55td have become NPL's standards for use in its Class E_1 calibration service. Weight 55d has been housed almost permanently in vacuum to assist in the calibration of weights under such conditions while 55 has been used to monitor the mass gain characteristics of weights which have been subjected to vacuum.

2.2.4 NPLW Set 56

Set NPLW 56 was purchased from Precisa Balances Limited at about the same time as set NPLW 55 was obtained. The weights were manufactured as Class E_1 weights by Häfner of Germany and are similar in appearance to set 55, both sets being made to the design recommended in OIML Recommendation number 111. Once more the densities of three of the weights have been determined by hydrostatic means with 56 plain being assigned an assumed value. The cubic coefficient of thermal expansion was measured over a range of temperatures from 19.8 °C to 22.2 °C. The densities of these weights are shown in Table 2.2.2.

TABLE 2.2.2: DENSITY VALUES OF SET NPLW 56

Identification	Density (kg m^{-3})	Density Uncertainty (kg m^{-3}) k=1
56	8 050	2
56d	8 049.73	0.07
56dd	8 049.50	0.06
56td	8 049.85	0.06
Centre of gravity height above base (mm)		36.2
Cubic coefficient of thermal expansion (°C^{-1})		45×10^{-6}

This set of weights is now regarded as NPL's best stainless steel kilogram standards and is used in activities such as international inter-comparisons and the monitoring of other NPL standards. Their use is kept to a minimum and their values are checked against Pt-Ir standards on a regular basis.

3 EQUIPMENT USED IN THE MEASUREMENTS

For the measurements described here three 1 kilogram mass comparators were used to compare NPL's 1 kilogram standards. These balances, together with their ancillary equipment are described below.

3.1 THE NPL PRECISION BALANCE

The NPL Precision Balance was built during the 1930s and has been used since the 1940s for top level mass metrology in the range 200 g to 1 kg. Its construction and operation are described in detail by Havard and Lewis [3]. Here, it is only intended to give a brief description of its operation and to outline the changes that have been made since that work.

The balance is a conventional three knife, two-pan undamped balance which has been modified to allow for computer control of its operation. In use the two weights to be compared are placed on each of the scale pans. Once the balance has been loaded the arrestment mechanism is released to bring the knives and planes into contact. This contact is maintained throughout the remainder of the measurement run as recommended by Poynting [4]. A strip of metal, known as the steady, allows the beam to be held stationary without separating the knives and planes while the weights and their associated pan plates are being exchanged. The pans are prevented from swinging during the weight exchange by a three point support that is brought into contact with each of them. This mechanism is known as the pan-stop.

A measurement run using the Precision Balance consists of exchanging the pan-plates and their contents fifteen times. After each exchange the pan-stops and steady are removed to permit the beam to swing freely, and the theoretical rest-point is calculated from seven turning points. Immediately after the fifteenth measurement a small sensitivity weight is applied to the left hand end of the beam. A set of seven turning points is taken with this weight applied before its removal and a further set of turning points being taken. This process is repeated twice more. A similar procedure is then carried out with a sensitivity weight on the right hand end of the beam.

When the balance was first built it was entirely manually operated, but during the early 1980s its operation was automated using an early microcomputer. This computer was used to automatically log data and control all of the balance operations, except the arrestment mechanism, by means of a set of synchronous and stepper motors. The report of Havard and Lewis [3] is based on work carried out with such a control system. However, in 1990 the balance control system was updated to create an architecture based around an IBM compatible personal computer. This change necessitated the purchase of a new computer and also some new ancillary equipment. All of this equipment is described below and a schematic of the control and measurement system is shown in Figure 3.1.1.

3.1.1 Control Computer

An Olivetti M290 IBM-compatible personal computer (PC) was selected to control the balance. This computer has a 80286 microprocessor with a 80287 mathematical co-processor.

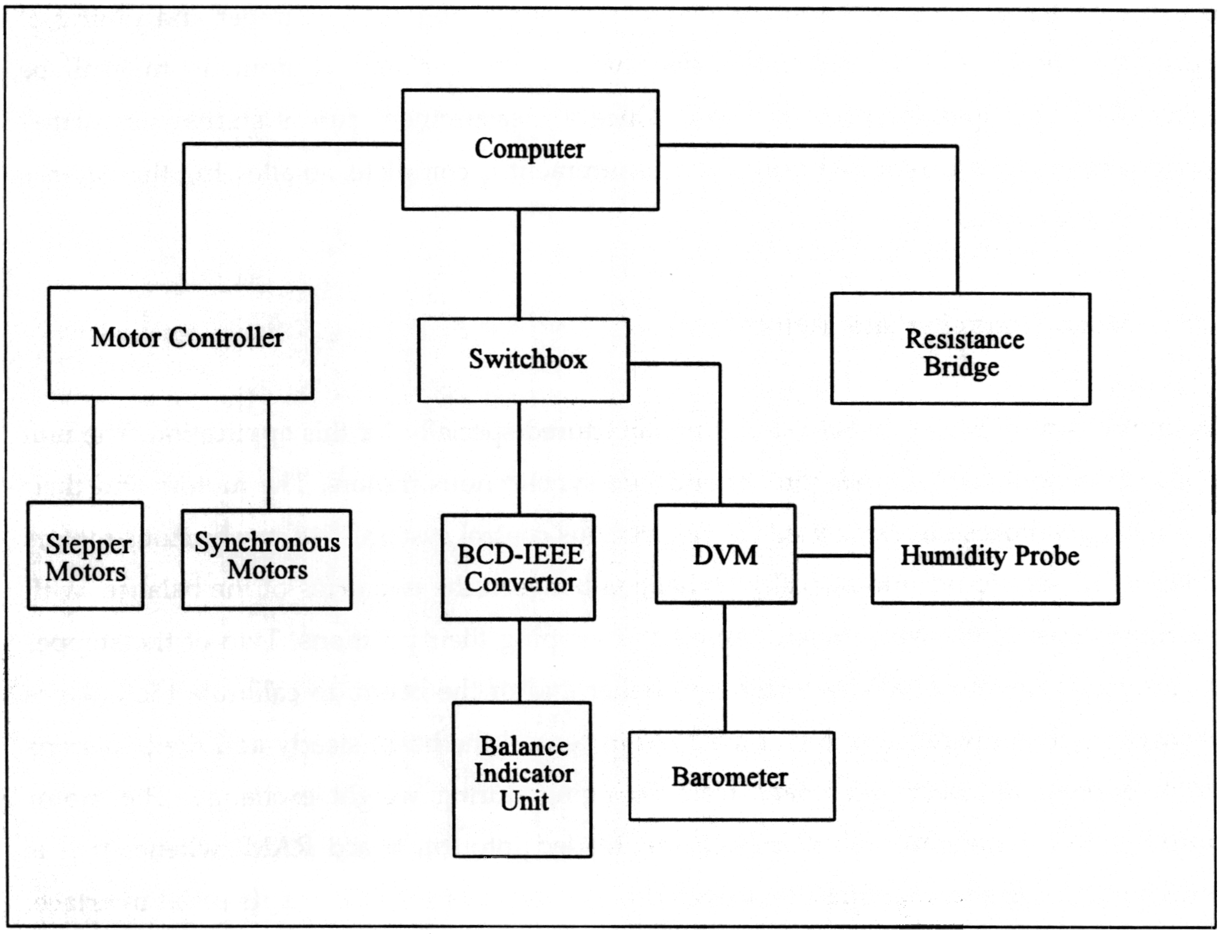

Figure 3.1.1: Schematic of Precision Balance Control and Measurement System

A CEC IEEE-488 interface has been added to the computer to enable it to communicate with most of the ancillary devices.

The Control Program

The control program for the system is written in Microsoft QuickBasic and is modelled on that of its predecessor. The user is able to manually control any aspect of the balance operation in order to aid the setting up of a measurement run. The parameters of each measurement run, such as the number of weight interchanges, the number and timing of sensitivity checks and the calibration constants of the ancillary equipment, may all be changed by the operator prior to a run. Once a measurement run is started no further operator interaction is required until the measurement is complete, so allowing the balance to be run overnight.

3.1.3 Motor Controller and Motors

The motor controller is a dedicated unit manufactured specially for this application. The unit is able to control four stepper motors and two synchronous motors. The motors and their associated gearboxes are those used by the previous control system. The synchronous motors allow the masses to be automatically exchanged between the two arms of the balance, with one motor raising the weights and the other swapping their positions. Two of the stepper motors apply small sensitivity weights to either end of the beam, to calibrate the balance sensitivity, while the remaining pair are used to control the beam steady and the pan-stops which prevent the beam and pans from swinging during weight exchange. The motor controller has a standard set of instructions loaded into 'on board RAM' whenever it is switched on. These instructions are activated on request from the PC via its serial interface.

Balance Indicator Unit

The angular displacement of the beam is measured by an NPL Balance Indicator Unit. A schematic of this is shown in Figure 3.1.2. Light from the bulb is reflected down onto a concave mirror mounted on top of the beam. The mirror then reflects and focuses the light to produce a spot on the photo-diode array. The position of this spot corresponds to the angular displacement of the beam and is continuously monitored by the Balance Indicator

Unit. The Balance Indicator Unit may be programmed to output the position of the light spot when the balance beam's motion changes direction, the turning point. This output is in the form of a binary coded decimal (BCD) number which is fed into a commercial unit that converts it into an IEEE signal for transfer to the computer.

Air Density Monitoring Equipment

The air density inside the Precision Balance enclosure is monitored using the equipment indicated in Table 3.1.1. The platinum resistance thermometer (prt) is located inside the Precision Balance enclosure, mid way between the two pans, at approximately the height of the centre of gravity of a platinum or platinum-iridium kilogram when placed on the balance pans. A plastic tube is used to connect the balance chamber to the barometer which is at the same height as the pans but in an outer room. The Testoterm dew-point meter is clamped to the inside of the balance chamber, with a Michell cooled mirror dew-point instrument being linked to the chamber by two short stainless steel pipes and a small electric pump which is run before and after each measurement run in order to calibrate the Testoterm device.

TABLE 3.1.1: AIR DENSITY MONITORING EQUIPMENT FOR PRECISION BALANCE

Parameter	Instrument	Uncertainty	Notes
Temperature	25 Ω prt (A1)	0.02 °C	Used in conjunction with a Tinsley Ambassador resistance bridge
Pressure	Ruska DDR-6000	0.05 mbar	Read via Datron DVM. Calibrated before and after each run using a Mechanism Precision Aneroid Barometer
Dew-point	Testoterm 601	0.25 °C	Measures relative humidity with dew-point being calculated using PRT reading. Calibrated before and after each run with a Michell 3000 hygrometer.

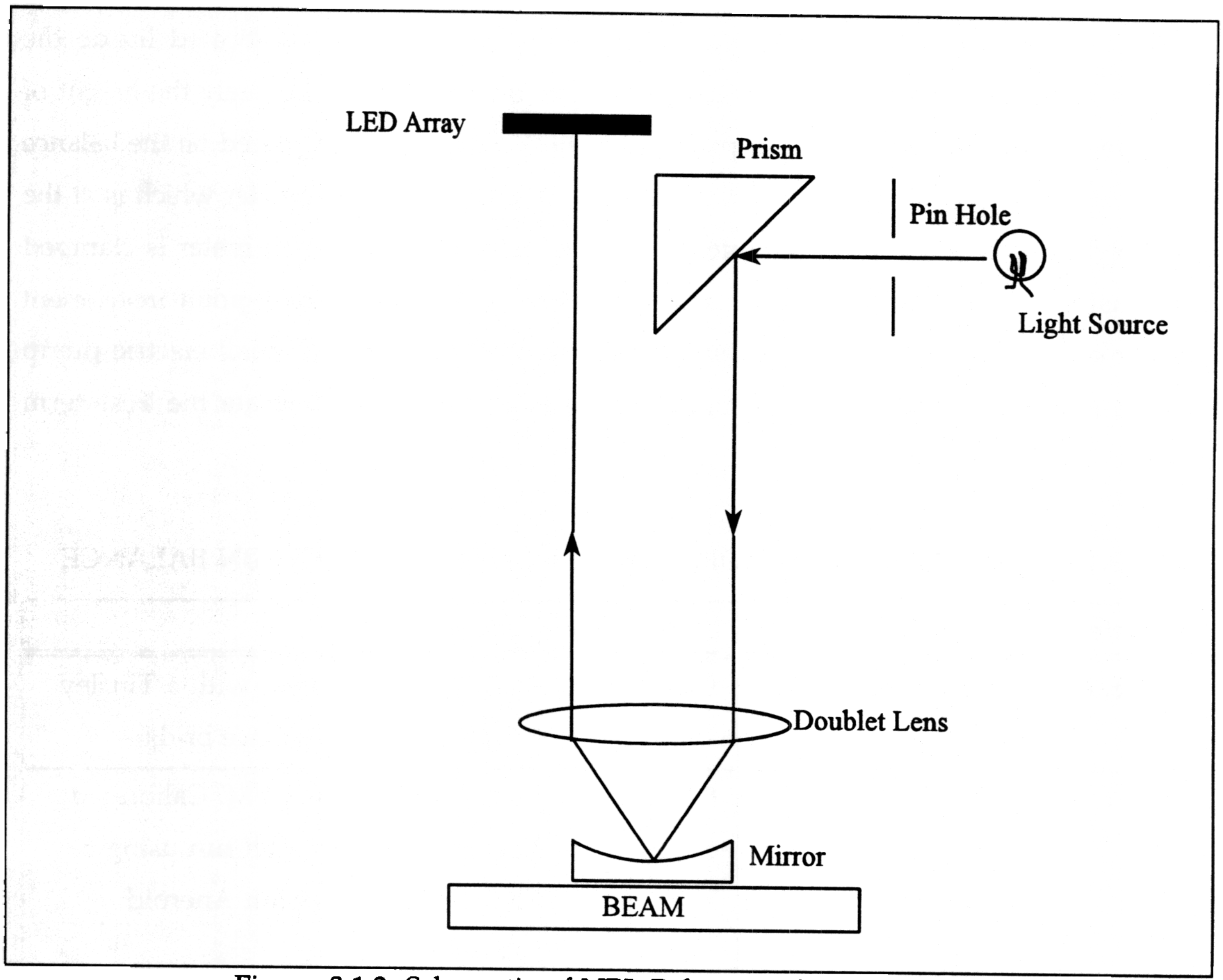

Figure 3.1.2: Schematic of NPL Balance Indicator System

3.2 METTLER HK1000MC (AMBIENT CONDITIONS)

3.2.1 General Description

The Mettler HK1000MC is a commercial 1 kg mass comparator which is capable of comparing up to four mass standards. It has a scale readability of 1 μg, but when used under computer control, measurement results are averaged to give a 0.1 μg resolution in the output with a reproducibility of approximately 2 μg. Figure 3.2.1 shows a photograph of the balance. NPL has owned this balance since 1988 but it has only recently, with the installation of a new weight handler, been found to be suitable for the highest level of standards work. Hence the work described here is the first time that NPL has used such a commercial balance in the assignment of values to its best mass standards.

The balance is mounted on a granite plinth, supported on brick pillars, and is located inside a glass, wood and aluminium enclosure of approximate dimensions 3 m × 3 m × 3 m. The enclosure is in the centre of the NPL mass balance room. The temperature and relative humidity of the balance room are kept within the ranges 20 °C ± 2 °C and 50 % ± 20 % respectively.

The balance has been used in its four weight comparison mode for all of the measurements described here. When used in this mode, each of the weights is compared directly with all of the others. The operator is able to select the number of times a pair of weights are compared to give a single measurement result. In the case of the measurements made here this has generally been set to four comparisons. Such a measurement run is made in turn on each pair of weights and the whole process is repeated a number of times that is set by the user. Normally six measurement runs were carried out for each comparison made during this work. This measurement scheme takes approximately twelve hours and has been selected to allow the balance to run overnight when the local environment is at its most stable.

Every time that a weight is lowered onto the scale pan for a measurement to be made, the PC used to control the balance receives air density data from a PC that controls an air density monitoring kit. This information is recorded to allow air buoyancy corrections to be made to the raw data. The equipment used to gather the air density data is described below.

F   ure 3.2   NPL's HK1000MC Fo U   In Ambient C   diti

Air Density Equipment (Ambient HK1000MC)

The air density in the vicinity of this balance is monitored using the equipment in Table 3.2.1. The platinum resistance thermometers are housed inside the balance case, the Druck DPI-140 is located at the same height as the balance scale pan, but approximately 2 metres distant, and the dew-point hygrometer is approximately 1 metre from the balance. All of this equipment, as with air density monitoring equipment associated with the other balances, is calibrated at NPL.

TABLE 3.2.1: AIR DENSITY MONITORING EQUIPMENT FOR HK1000MC (AMBIENT)

Parameter	Instrument	Uncertainty	Notes
Temperature	2 × 25 Ω prt	0.01 °C	Used with a Tinsley Consort resistance bridge
Pressure	Druck DPI-140	0.05 mbar	
Dew-point	Michell 3020	0.2 °C	Read via Datron DVM

3.3 METTLER HK1000MC (VACUUM CHAMBER)

General Description

At the time when this exercise was started it was possible to use an HK1000MC that is housed in a vacuum chamber for some of the measurements. The balance, shown in Figure 3.3.1, is identical to that used in ambient conditions but is housed in a rectangular vacuum chamber. Throughout the measurements reported here the balance was operated inside the vacuum chamber but the pressure was not reduced below ambient. In effect the chamber was simply used to provide an environment of constant air density. The balance was used in exactly the same manner as the other HK1000MC.

Air Density Monitoring Equipment

The equipment in use with this balance is positioned so that it measures the conditions within the vacuum chamber. Where necessary the wiring is fed through the chamber via vacuum connectors.

There is a prt on each side of the weight carousel, the resistances of which are measured by a resistance bridge. The pressure in the chamber is transmitted to the barometer via a pipe and the humidity is measured by a capacitive sensor placed near to the scale pan. Before and after each measurement run the humidity sensor is calibrated against a Protimeter DP-989 hygrometer which is introduced into the chamber alongside it.

Table 3.3.1 lists the instruments used for monitoring the air density.

TABLE 3.3.1: AIR DENSITY MONITORING EQUIPMENT FOR HK1000MC (VACUUM)

Parameter	Instrument	Uncertainty	Notes
Temperature	2 × 25 Ω prt	0.01 °C	Used with a Tinsley Consort resistance bridge
Pressure	Druck DPI-140	0.05 mbar	
Dew-point	Testoterm 601	0.25 °C	Measures relative humidity with dew-point being calculated using PRT reading. Calibrated before and after each run with a Protimeter DP-989 hygrometer.

Figure 3.3.1: HK1000MC and Base of Vacuum Chamber

4 THE MEASUREMENTS

This section describes the measurements that were carried out and the results obtained. In order to obtain these results it is necessary to make several adjustments to the raw data to calculate a true mass value. These adjustments are described in Section 4.1. The results of the measurements, taking these adjustments into account, are given in Sections 4.2 and 4.3.

4.1 ADJUSTMENTS TO MEASUREMENTS

Assignment of a Mass Value to Kilogram 18

The BIPM certificate for Kilogram 18 gives a mass value on 22 October 1991 which corresponds to the weight having just been cleaned. Work carried out at BIPM [5] led NPL [6] to produce a mathematical model for the mass change in Kilogram 18 as it becomes contaminated in air. The mass gain (W^*) t days after cleaning is given by:-

$$W^* = 0.356097\ t^{0.511768} \qquad 4.1.1$$

The initial comparisons of the platinum-iridium and platinum standards were carried out during the period 13 October 1993 to 26 November 1993. On 13 October t is equal to 721 days giving a mass gain of 10.3 μg while at the end of the work t is equal to 766 days giving a mass gain of 10.7 μg. An average of these two figures leads to a mass gain of 10.5 μg being added to the calibrated value of Kilogram 18 at the time of the work. The mass value of Kilogram 18 was quoted as being 1 kg + 53 μg after cleaning so the value at October 1993 is taken to be 1 kg + 63.5 μg.

Centre of Gravity Correction

Where there is a difference in the height of the centre of gravity of a mass being calibrated from that being used as a standard, a correction must be applied to compensate for the difference in gravitational force acting on each of the weights. The formula for this corrected mass (m′) in terms of the measured mass (m) is:-

$$m' = m\gamma \qquad 4.1.2$$

where

$$\gamma = 1 + \frac{1}{g}\frac{\partial g}{\partial Z}(Z_{ref} - Z_{test}) \qquad 4.1.3$$

where

Z_j is the height of the centre of gravity of weight j above its base, in metres
g is acceleration due to gravity, m s^{-2}
γ is the gravitational correction

The gravitational gradient ($\partial g/\partial Z$) was measured in 1993 at a site approximately 20 metres from the location of the Mettler HK1000MC balance operating under ambient conditions. This site is about 5 metres from the vacuum HK1000MC. These measurements, carried out by the University of Edinburgh Department of Geology and Geophysics, found the gradient to be $(2\,948 \pm 28)\times10^{-9}\ s^{-2}$ [8].

The centre of gravity used for each of the stainless steel weights under discussion here is based on simple measurements of its dimensions. That of each of the platinum or platinum-iridium weights is based on the measured density and the assumption that they have a diameter equal to their height. The difference in height between different weight sets is given in millimetres in Table 4.1.1 with the corresponding mass correction being shown in Table 4.1.2.

TABLE 4.1.1: HEIGHT DIFFERENCES BETWEEN WEIGHTS (mm)

Weight	Pt-Ir/Pt	PI Grams	NPLW36	OC
PI Grams	-6.3			
NPLW36	10.5	16.8		
OC	9.0	27.2	-1.5	
NPLW55/56	16.7	23.0	6.2	7.7

TABLE 4.1.2: GRAVITATIONAL CORRECTIONS BETWEEN WEIGHTS (μg)

Weight	Pt-Ir/Pt	PI Grams	NPLW36	OC
PI Grams	-1.9			
NPLW36	3.1	5		
OC	2.7	4.6	-0.4	
NPLW55/56	4.9	6.8	1.8	2.2

4.1.3 Volume Corrections due to Temperature

The temperature was monitored during each measurement run that has been carried out as part of this exercise. The average temperature during a single run has then been used, in conjunction with the appropriate coefficient of cubic expansion, to correct the volume of the weights being compared. Typically the range of temperatures during a single run on the Precision Balance is of the order 10 mK while that when using the Mettler HK1000MC, operating under ambient conditions, is 40 mK.

4.1.4 Air Buoyancy Corrections

The air density was monitored throughout each weighing in order to apply air buoyancy corrections to the raw balance readings. Air density is calculated from temperature, pressure, humidity and carbon dioxide concentration using the empirical formula recommended by CIPM [7]. The instrumentation used for monitoring these parameters on each of the balances used is given in Section 3. The air density is multiplied by the difference between the volumes of the weights under comparison to give the air buoyancy correction.

4.2 MEASUREMENT SCHEME FOR THE PRECIOUS METAL WEIGHTS

All five of the precious metal kilograms were compared directly against each other on the NPL Precision Balance. These results were then analysed using both the square technique [3] and the NPL least squares analysis package 'MASSRUN', the basis of which is described by Hunt [9]. Mass values were assigned to the secondary kilograms from the value of Kilogram 18 calculated in Section 4.1. These values are shown below in Table 4.2.1 together with their values in 1988.

TABLE 4.2.1: VALUES OF NPL Pt & Pt-Ir STANDARDS

(Based on kg 18= 1 kg + 63.5 μg)

Weight	October 1993 Deviation from 1 kg (μg)	1993 Estimated Uncertainty (k=1) (μg)	1988 Value Deviation from 1 kg (μg)	1988 Estimated Uncertainty (k=1) (μg)	Change (μg)
E	-2 125.1	5.4	-2 127.0	8.8	+1.9
PI	-44 023.4	5.4	-44 028.0	8.8	+4.6
A	88.8	5.4	76.0	8.8	+12.8
B	190.4	5.4	179.0	8.8	+11.4

Note: The 1988 value for Kilogram E has been amended to correct an error in the coefficient of thermal expansion used until 1991 (see section 2.1.2)

The mass value obtained for Kilogram E is only 1.9 μg greater than its value in 1988, well within the uncertainty of the assigned value, which provides confidence in the mass gain model that has been used for Kilogram 18 in this exercise.

The changes in the mass values of Kilograms A and B are consistent with the increase in their mass since they were first acquired by NPL. The table in Appendix 1 gives the values for all of the weights listed above, except Kilogram PI, during the period 1978 to 1993.

Approximately every six months after this initial assignment of values to NPL's precious metal kilograms, Kilograms 18 and E have been compared to allow the mass gain model of Kilogram 18 to be further tested. In April and September 1994 this task was carried out using the NPL Precision Balance but from April 1995 onwards it has been carried out using the Mettler HK1000MC operating under ambient conditions. When the HK1000MC has been used Kilograms A and B have also been included in the measurement process. The results obtained during this exercise, based on Kilogram E having a stable value of 1 kg - 2 125.1 μg, are shown in Table 4.2.2, with the mass changes being illustrated graphically in Figure 4.2.1.

TABLE 4.2.2: VALUES OF NPL PRECIOUS METAL KILOGRAMS 1993-6

BASED ON E = 1 kg -2125.1 μg (all are departure from 1 kg in μg)

Weight	18			A	B
Date	Measured	Predicted	Difference		
October 1993		63.5	0.0	88.8*	190.4*
April 1994	69.9*	64.9	5.0		
September 1994	66.1*	65.6	0.5		
April 1995	69.4	67.0	2.4	89.0	194.5
November 1995	75.4	68.0	7.4	87.5	195.7
March 1996	76.5	68.6	7.9	92.8	198.7

* Weighing carried out on the NPL Precision Balance

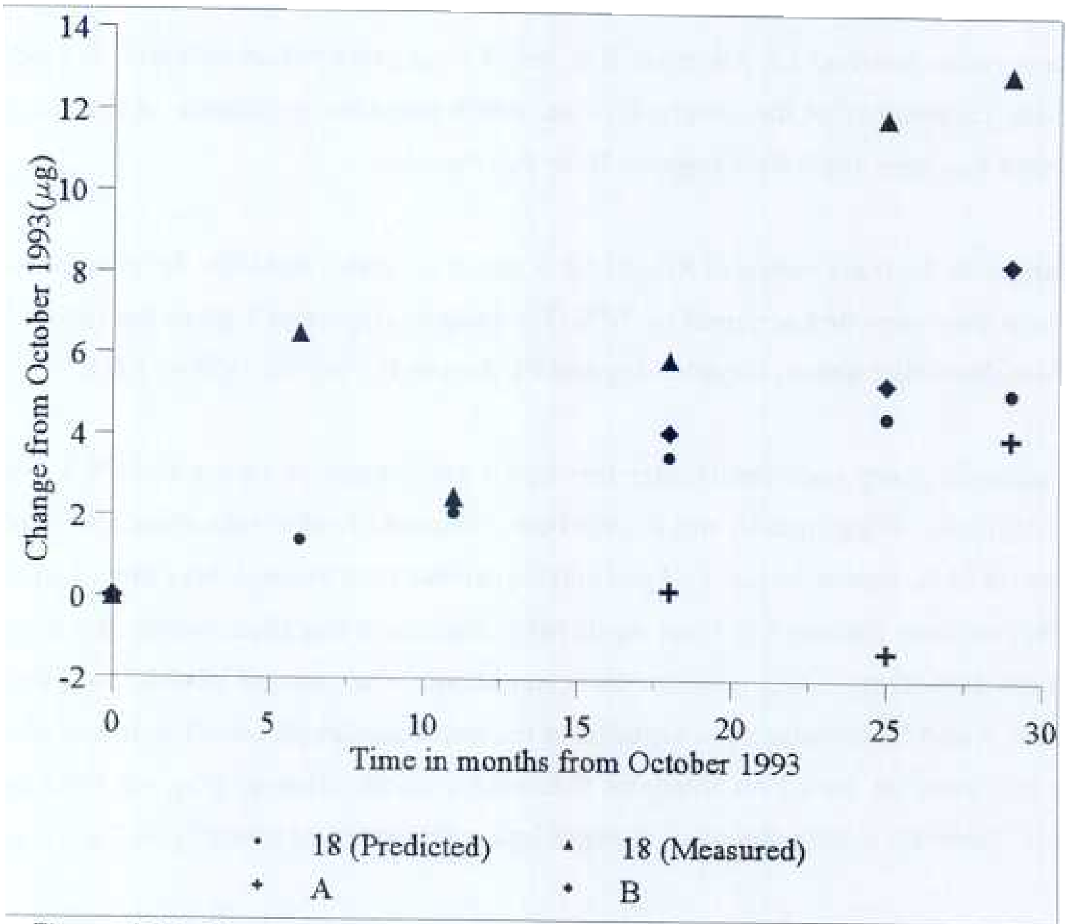

Figure 4.2.1: Change in Mass Values of Pt-Ir Kilograms Since October 1993 Relative to Kilogram E

It may be observed from the data that, if Kilogram E is assumed to be stable, Kilogram 18 is gaining mass more rapidly than the model predicts. There are four possible explanations for this:-

(i) The value of Kilogram E changed by 5 μg between April and November 1995. This is unlikely as the values of Kilograms A and B remained stable relative to that of Kilogram E during this period.

(ii) The model for the mass gain of Kilogram 18 only applies for a limited time after cleaning. At first glance this is a possibility as the data on which the mass gain model is based were gathered over a relatively short period (441 days). However, the model certainly agreed with experimental values when Kilogram 18 was compared with Kilogram E in October 1993, 766 days after cleaning, and it is unlikely that the rate of mass gain would start to increase after that time without external influences. The good agreement between the predicted and the pre-cleaning value before the Third Verification also supports the mass gain model over this time-scale [6].

The use of different balances for the measurements introduces systematic offsets. The results obtained using the Mettler HK1000MC balance in April 1995 agree very well with those from the Precision Balance in October 1993 and April 1994. Other weighings have also been carried out over the last five years to ensure that consistent results are obtained from all the kilogram balances in use in the Mass Section of NPL. This indicates that there is no reason to suspect this as a source of error.

The value of Kilogram 18 changed by approximately 5 μg between April and November 1995. During this period the observed values of Kilogram 18 changed by +6.0 μg relative to Kilogram E, +7.5 μg compared with Kilogram A and +4.8 μg relative to Kilogram B. However, the model predicts a change in value of +1.0 μg.

It must be concluded that the most likely cause of the anomaly in the results monitoring Kilogram 18's mass value is that the weight gained approximately 5 μg between April and November 1995. It is not clear how this could have happened, but further monitoring should establish whether the value of Kilogram 18 is once more following the predicted mass gain model.

MEASUREMENT SCHEME FOR THE STAINLESS STEEL KILOGRAMS

Set NPLW 36 and Set OC

Kilograms A and B were used as standards in the assignment of values to the stainless steel kilograms. The initial measurements were carried out in March 1994 on the Mettler HK1000MC (vacuum) balance. These measurements involved the comparison of kilograms A, B, 36, 36D, OCDD and OCTD with each other.

These weights have also been re-calibrated several times since then, mainly using the Mettler HK1000MC operating under ambient conditions. Table 4.3.1 shows the results obtained for Set 36, OCDD and OCTD.

The results indicate that the values obtained for set NPLW 36 have been quite consistent on both the ambient and vacuum HK1000MC since March 1995. There is a slight anomaly in the mass difference between 36 and 36D during July 1995, but this is immediately after 36D suffered minor damage. However, this appears to have been a short term change to the mass of 36D, the present difference is similar to that before the damage occurred. This implies that, while the damage looks significant, it has not affected the mass value of the weight.

The values obtained for set OC are not as consistent as those for set 36. Apart from the values shown here, there have also been inconsistencies in their values when used in the monitoring of other weights during this period. Historically set OC has been relatively unstable, probably due its relatively poor surface finish compared with NPL's other primary kilogram standards. Although they have been calibrated in 1996, it is not anticipated that they will be used for any further research work.

TABLE 4.3.1: VALUES OBTAINED FOR WEIGHT SETS NPLW 36 and OC (1994-6)

(all are departure from 1 kg in μg)

Date	36	36D	OCDD	OCTD	Basis
March 1994	2504†	1321†	1279†	315†	A=1 kg + 88.8
					B=1 kg + 190.4
Mar 1995	2530	1344			A=1 kg + 88.8
					B=1 kg + 190.4
April 1995			1293	316	A=1 kg + 89.0
					B=1 kg + 194.5
Jun 1995	2522	1335			A=1 kg + 89.0
					B=1 kg + 194.5
Jul 1995	2520†	1354†			A=1 kg + 89.0
					B=1 kg + 194.5
Aug 1995			1347		E=1 kg - 2 125.1
May 1996	2519	1327			A=1 kg + 92.8
					B=1 kg + 198.7
June 1996			1340	362	55dd=1 kg + 691
					55td=1 kg + 516

†Based on weighings carried out on the vacuum balance

4.3.2 Sets NPLW 55 and 56

These weights entered the NPL hierarchy of weight sets for the first time during this exercise. They have been compared with Kilograms A, B and E, on the Mettler HK1000MC. The mass values obtained obtained for set NPLW55 are shown in Table 4.3.2.

TABLE 4.3.2: VALUES OBTAINED FOR SET NPLW55 (1995-6)

(all are departure from 1 kg in μg)

Date	55	55d	55dd	55td	Basis
Aug 1995	496	510	694	527	A=1 kg + 89.0
					B=1 kg + 194.5
May 1996	494	521	691	516	A=1 kg + 92.8
					B=1 kg + 198.7

Similar measurements have been carried out on set NPLW 56, the results of which are shown in Table 4.3.3.

TABLE 4.3.3: VALUES OBTAINED FOR SET NPLW56 (1995-6)

(all are departure from 1 kg in μg)

Date	56	56d	56dd	56td	Basis
Mar 1995			-1064	-710	A=1 kg + 88.5
					B=1 kg + 190.2
Jun - Jul 1995	-661	-1044	-1063	-714	A=1 kg + 89.0
					B=1 kg + 194.5
Nov 1995		-1043			E=1 kg - 2125.1
Feb 1996	-673	-1055	-1062	-718	B=1 kg + 195.7
Apr 1996	-658	-1039	-1051	-706	A=1 kg + 92.8
					B=1 kg + 198.7
Spread(μg)	15	16	13	12	
Max change between successive measurements (μg)	15	16	11	12	

From the above table it can be seen that the mass values of set NPLW 56 were quite stable during the period of this exercise.

The double and triple dot weights were also compared with set NPLW 36 in July 1995, just prior to 36D being damaged. The mass values of the two sets were found to agree with each other to better than 1 μg which gives additional confidence in the repeatability of the measurements.

5 UNCERTAINTY BUDGET

An uncertainty has been assigned to each of the weights described here with the calculations being carried out in accordance with the ISO publication 'Guide to the Expression of Uncertainty in Measurement' [10]. All figures quoted here are at the coverage factor of k=1 in accordance with the ISO document.

5.1 TYPE B UNCERTAINTIES

Uncertainty on Kilogram 18

The uncertainty quoted on the BIPM certificate for Kilogram 18 is 2.3 μg. An additional contribution to the uncertainty in the mass value of Kilogram 18 arises due to the uncertainty in the mass gain model. This was calculated from the parameters shown in Table 5.1.1.

TABLE 5.1.1: UNCERTAINTY IN THE VALUE OF KILOGRAM 18

Parameter	Uncertainty (μg)
Uncertainty from 1991 BIPM Certificate	2.3
Uncertainty of weighings used to produce model (worst case)	1.4
Standard deviation of difference between model and experimental values (1985-6)	0.1
Total	**2.7**

This uncertainty is supported by the fact that Kilogram E, which is believed to be stable, was found to have a value within 1.9 μg of that obtained in 1988.

Uncertainty on other Precious Metal Standards

The assigned mass value of Kilogram 18, and its uncertainty, were used in the initial allocation of values and uncertainties to the precious metal kilograms. However, during all the subsequent measurements, because it is a more stable weight, the mass value and associated uncertainty of Kilogram E were used in the assignment of values and uncertainties to Kilograms A and B.

Volume Uncertainty

Virtually all of the weights used in this exercise have had their densities determined hydrostatically. As with all measurements, that of density has an uncertainty associated with it. The density uncertainty leads to a corresponding uncertainty in volume, which produces a contribution to the air buoyancy correction uncertainty. This air buoyancy uncertainty is calculated by multiplying the uncertainty in the volume of the weight by the typical air density at NPL, 1.2 kg m^{-3}.

Make-weight Uncertainty

Whenever stainless steel kilograms have been compared with platinum or platinum-iridium standards, masses of up to 100 mg have been used to poise the two loads within 5 mg of each other. The uncertainty in the mass value of such weights is typically just below 0.5 μg.

Make-weights were also used during the initial measurements on the Precision Balance in order to poise the loads to better than 20 μg. The uncertainty on these weights is typically also 0.5 μg.

In general, when the HK1000MC was used two make-weights were used for each measurement. Their uncertainties have been added arithmetically, owing to the correlation between their values to give an uncertainty of 1 μg.

5.2 TYPE A UNCERTAINTIES

Balance Performance

A measure of the short term repeatability of a balance is indicated by the standard deviation that is obtained from repeated comparisons of the same pair of weights. In the case of the Precision Balance two weights are swapped thirteen times during a single measurement run. The standard deviation of the change in rest point, corrected for air buoyancy effects, is calculated by the least squares algorithm used in producing a mass difference. The standard deviation of a measurement run on the Precision Balance, when two masses of similar density are being compared, is typically 2 μg.

The corresponding standard deviation from a set of measurements on the Mettler HK1000MC is approximately 1 μg. However, if the balance is being used to compare a stainless steel kilogram with a platinum-iridium one this figure typically rises to 2 μg.

Weighing Scheme

The uncertainty due to the weighing scheme may be obtained from the least squares analysis of the results of all the weighings. It will take into account such factors as weights being placed on the balance in a slightly different manner and any slight changes due to the handling of weights.

Air Density Measurement

All of the parameters which are measured in order to calculate the air density have an associated uncertainty, with an additional contribution coming from the empirical equation used in the calculation. These contributions are added in quadrature to produce an overall uncertainty for the air density which is multiplied by the volume difference between the standard and the weight being assigned a value to give a corresponding mass uncertainty.

The uncertainties (at a coverage factor of k=1) associated with each piece of equipment used in such measurements are indicated in Sections 3.1.5, 3.2.2 and 3.3.2.

In addition to the measured parameters the empirical equation used for the calculation contributes a further 0.000 12 kg m^{-3} [11].

The carbon dioxide concentration was not measured during any of the measurements described here. However, it is reasonable to believe that the concentration is within 50 parts per million of the 400 parts per million that was assumed throughout.

5.3 OTHER POTENTIAL UNCERTAINTY SOURCES

The following represent potential sources of error whose contributions were considered but not included owing to their small magnitude.

Thermal Expansion Coefficient

From the density determinations of the weights it is estimated that the uncertainty in this figure is 1.5×10^{-6} °C^{-1}. For each 1 °C that the temperature deviates from 20 °C the error in volume due to this parameter is 0.00019 cm^3. Treating this in the same manner as the volume uncertainty gives a mass uncertainty of 0.2 μg °C^{-1}.

Gravitational Gradient

The uncertainty in this parameter is approximately one part in one hundred. Such an error corresponds to a mass uncertainty of approximately 0.05 μg for the comparison of NPL's tallest stainless steel kilograms with a platinum iridium one. When considered alongside a total uncertainty of about 13 μg this is clearly insignificant.

Centre of Gravity Height

The uncertainty in the height of the centre of gravity of the knobbed stainless steel weights is less than 2 mm. A 2 mm error in the height would lead to a systematic error of 0.5 μg error in mass which in not significant in the context of the stainless steel kilogram uncertainty budget.

6 SUMMARY

Measurements have been made on NPL's best one kilogram weights over a thirty month period, with consistent results being obtained throughout. The results illustrate that high precision mass standards may be measured with a good reproducibility over such a period using three different mass comparators.

The uncertainties obtained here for the precious metal kilograms are much lower than those obtained previously, 10.8 μg for Kilogram A or B compared with the previous value of 17.5 μg (coverage factor k=2). This is mainly due to the lower uncertainty in the mass value of Kilogram 18. BIPM assigned an uncertainty of 8 μg (k=1) to the certified value of Kilogram 18 in 1985 but reduced this to 2.3 μg (k=1) in 1991.

The uncertainty of measurement for the mass values of NPL's best stainless steel kilograms is estimated to be 28 μg, which compares favourably with the previous value of 33 μg (both figures relate to k=2). Once more a significant part of this improvement is due to the reduced uncertainty in the value of Kilogram 18.

It would prove difficult to reduce the uncertainty in the mass value of the stainless steel kilograms significantly below that achieved here without a much improved method of measuring air density. Work is in progress at NPL, and other national measurement institutes around the world, to develop such a method. If this work is successful, smaller uncertainties in the mass values of the stainless steel kilograms may be obtained in future re-verification exercises.

ACKNOWLEDGEMENTS

The authors are indebted to their colleagues in the Mass and Density Standards Section of the Centre for Mechanical and Optical Technology, NPL, for their support and practical contributions to this work.

This work is made possible by funding from the Department of Trade and Industry's National Measurement Programme for Mass.

7 REFERENCES

[1] Girard, G. Le nettoyage-lavage des prototypes du kilogramme au BIPM. BIPM, 1990

[2] Lewis, S.L. and Havard, D.C. History of Kilogram 18 and Other Important UK Reference Mass Standards. NPL Report MOT 1, 1996

[3] Havard, D.C. and Lewis S.L. Initial Stages in Disseminating the UK Mass Scale: From the National Prototype Kilogram to the Stainless Steel Reference Kilograms. NPL Report MOM 98, 1995

[4] Poynting, J.H. Proceedings of the Royal Society, **28**, 2, 1878

[5] Procès Verbaux du CIPM, pp56-8, 1986

[6] Armitage, D.R. and Havard, D.C. Initial Stages in the Dissemination of the Mass Scale in the UK, Proceedings of Mass and its Measurement, Modena, Italy, September 1993

[7] Davis, R.S. Metrologia, **27**, pp 139-144, 1990

[8] Charles, K. And Hipkin, R.G. Relative Gravity Observations Made at the National Physical Laboratory, Teddington, University of Edinburgh Department of Geology and Geophysics, 1993

[9] Hunt, R.A. The Assignment of Values to a Set of Weights, NPL Report MOM 50, 1981

[10] International Organisation for Standardization, Geneva, Switzerland, Guide to the Expression of Uncertainty in Measurement, First Edition, 1993

[11] Giacomo, P. Metrologia, **18** pp 33-40, 1982

APPENDIX 1: HISTORICAL MASS VALUES OF NPL'S PRECIOUS METAL KILOGRAMS

TABLE A1.1: HISTORICAL VALUES OF NPL'S PRECIOUS METAL KILOGRAMS
(All numbers are in μg and represent departure from 1 kg)

Date	Laboratory	18	E	A	B
May 1978	BIPM	105 pre lavage			
		59 post lavage			
June 1980	NPL		-2136		
Aug 1982	BIPM			68	176
May 1984	NPL		-2119		
Sep 1984	NPL		-2147		
Apr 1985	BIPM				175 Pre lavage
					167 Post lavage
Nov 1984	BIPM	76 pre lavage			
Mar 1985	BIPM	57 post lavage			
Nov 1986	NPL		-2131	66	172
Mar 1988	NPL		-2128	76	179
Jun 1991	BIPM	75 pre lavage			
Oct 1991	BIPM	53 post lavage			
Oct 1993	NPL	63.5	-2125.1	88.8	190.4

Note: The 1988 value for Kilogram E has been amended to correct an error in the coefficient of thermal expansion used until 1991 (see section 2.1.2)

APPENDIX 2: EXAMPLES OF UNCERTAINTY BUDGETS

A2.1 BUDGET FOR Pt-Ir KILOGRAM A

Type A:			Mass Uncertainty (μg)
Balance			2.0
Weighing scheme			3.5
Air Density Parameters	Uncertainty	Air Density Uncertainty (kg m^{-3})	
Temperature	0.01 °C	0.000 043	0.0009
Pressure	0.05 mbar	0.000 059	0.0012
Dew-point	0.25 °C	0.000 069	0.0015
CO_2 concentration	50 ppm	0.000 025	0.0006
Equation		0.000 12	0.0025
Total Type A			**4.1**
Type B:			
Standard (kg 18)			2.7
Standard Volume	0.001 cm^3		1.2
Kilogram A Volume	0.001 cm^3		1.2
Make-weights			1.0
Total Type B			**3.4**

Overall Uncertainty for Kilogram A (k=1) **5.4 μg**

A2.2 UNCERTAINTY BUDGET FOR A WEIGHT FROM NPLW SET 56

			Mass Uncertainty (μg)
Type A:			
Balance			2.0
Weighing scheme			
Air Density Parameters	Uncertainty	Air Density Uncertainty (kg m^{-3})	
Temperature	0.01 °C	0.000 043	3.4
Pressure	0.05 mbar	0.000 059	4.6
Dew-point	0.25 °C	0.000 069	5.4
CO_2 concentration	50 ppm	0.000 025	1.9
Equation		0.000 12	
Total Type A			
Type B:			
Standard (kg A)			
Standard Volume	0.001 cm^3		
NPLW 56 Volume	0.001 cm^3		1.2
Make-weights			
Total Type B			

Overall Uncertainty for a kilogram from set NPLW 56 (k=1) **13.9 μg**