NPL Report MOT 1

August 1996

History of Kilogram 18
And Other Important UK Reference Mass

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ABSTRACT

This report describes the history of and records the mass values assigned to the UK National Copy (No 18) of the International Prototype Kilogram and the other important mass standards which form the basis of the UK mass scale. Particular attention is paid to their mass stability, especially the effects of washing and cleaning Kg 18. Also included are details of their storage conditions and descriptions of the weighing equipment, weighing techniques and data analysis methods which have been used by the National Physical Laboratory (NPL) for the intercomparison and calibration of these standards in recent years. The evidence and the data upon which corrections have been applied to the mass value of Kg 18 to allow for mass regain after washing and cleaning are discussed, as are possible changes to its treatment in the future based on recent findings concerning Pt-Ir surfaces and their contamination.

ISSN 1361-4088

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TABLE OF CONTENTS

1INTRODUCTION

The UK National Copy of the International Prototype Kilogram, Copy No 18 (referred to here as Kg 18) forms the basis of the UK mass scale, both metric and imperial. The mass of Kg 18 is periodically determined by the International Bureau of Weights and Measures (BIPM) by comparing it with standards[1] which are in turn compared with the International Prototype Kilogram (see Figure 1).

Although it is now widely recognised that a material artefact, however carefully handled and stored, will not have a constant mass due to the physical and chemical changes which occur at its surface, it had been normal practice until relatively recently to assume that the mass of Kg 18 remained constant between calibrations at the BIPM. With the re-introduction in 1946 of cleaning of prototype kilograms before their standardisation at the BIPM, it soon became apparent that cleaning introduced significant changes in mass: examination of the post 1947 mass data on the UK reference standards which were calibrated by direct comparison with Kg 18 showed a general downward drift in their assigned mass values except when Kg 18 had been cleaned and re-standardised, when an abrupt increase in their values was seen; this indicated that the mass stability of Kg 18 after cleaning was worthy of detailed investigation. With the advent of modern mass comparators, which provide much improved performance and ease of use over their earlier counterparts, it is now possible to study closely the mass changes which occur due both to cleaning and to recontamination after cleaning. At the suggestion of the National Physical Laboratory (NPL), the BIPM carried out such a study on Kg 18 in 1985/6; the data obtained by the BIPM have subsequently been used by the NPL to apply a time-dependent correction to the mass value of Kg 18.

For historical completeness, this report summarizes the mass values which have been assigned to Kg 18 and all the other important UK kilograms since their manufacture and initial use up to the time of the Third Periodic Verification in the early 1990s; also included here are details of any cleaning and the methods of storing which have been used, where such information is available. As the material of construction, surface finish, age and general condition of each weight[1] will also potentially affect their mass stability, a detailed description is given of each of them together with information on their previous use. The

(1) Throughout this Report the term "weight" is used to represent an artefact, not a physical quantity.

mass balances and auxiliary equipment which have been used at the NPL to compare the important kilograms with Kg 18 are also described briefly, as these dictate the uncertainty of measurement associated with the mass comparison process. A brief account of the weighing schemes and data analysis methods used in recent years is also given.

To complete the picture, a brief outline is given of the important advances which have been made recently in understanding the physical and chemical mechanisms which cause mass changes in Pt-Ir artefacts, and how such changes might be minimised in the future.

2 DESCRIPTION AND HISTORY OF THE STANDARD WEIGHTS

2.1 KILOGRAM 18

The UK primary standard of mass is one of a group of forty weights made for the BIPM by Johnson Matthey and Co (London) in 1884[2]. The alloy of 90%Pt-10%Ir was the same as that which was used for the fabrication of the metre standards. The volume of each weight was measured at the BIPM[(2)] before it was polished, numbered and finally adjusted to 1 kg ± 1 mg. After extensive intercomparisons involving all forty kilograms and the International Prototype Kilogram[4], Copy No 18 (allocated by ballot) was received by the UK in 1889. About 1927, Kg 18 was transferred from the Standards Department of the Board of Trade (BoT) to the NPL, although formal responsibility for it was not vested in the NPL until 1947.

Before 1982, Kg 18 was stored in a cylindrical metal container, the cover being connected to the base by a screwed joint, which did not provide an air-tight seal. The weight rested on a pad of washed chamois-leather with restraining pads in the same material above and at three points on its cylindrical surface. From 1947 acid-free tissue paper was interposed between the pads and the Kilogram because stains had been observed on some other Pt-Ir kilograms after prolonged contact with chamois-leather. Since 1982 Kg 18 has been stored (and can be transported) in a new enclosure (see Figures 2(a) and 2(b)) consisting of a glass dome clamped onto a stainless steel base. A PTFE 0-ring provides a seal between dome and base but air movement is possible via an outlet carrying two fine filters (0.2 μm pore size cellulose

(2) ten determinations on each weight, using three different samples of distilled water; for details see Reference 3

tri-acetate membranes) in series. The weight rests on several layers of acid-free tissue paper on a pad of washed chamois leather. During transportation all movement is restrained by three side-arms and a top pad, all cushioned by washed chamois-leather and layers of acid-free tissue paper. The enclosure is kept in a safe in a ventilated semi-subterranean vault.

Kg 18 is in the form of a plain flat-ended cylinder, with height equal to diameter (39 mm) and having slightly chamfered edges. The surface condition is reasonable, showing a number of light irregular scratches only, not inconsistent with its limited use; there are no stains or visible films. The number 18 is marked on the cylindrical surface by slight depolishing. The BIPM calibration certificates give the volume at 0°C as 46.4149 cm^3 (density 21.5448 g cm^{-3}) and the coefficient of cubical expansion[3] between 0°C and t°C as $(25.869 + 0.00565t) \times 10^{-6}$ °C^{-1}. The expansion coefficient was originally derived from measurements made at the BIPM[5] of the linear expansion of Pt-Ir metre standards.

Table 1 indicates all the occasions on which Kg 18 has been cleaned[4]: there have been seven occasions altogether, five at the BIPM (including the initial cleaning after manufacture and adjustment) and two at the BoT/NPL. Apart from this, present practice at the NPL is simply to dust off all surfaces lightly immediately before placing on the balance, using a camel-hair brush. This technique is used on all the NPL kilogram weights discussed in this report.

2.2 KILOGRAMS A AND B

These are the newest of the NPL one-kilogram reference standards. They were made from a 90%Pt-10%Ir ingot produced by Johnson Matthey in 1979, compacted by extrusion into rod at the NPL, then diamond-turned in 1982 at the BIPM where the final weight adjustments and cleaning were carried out. They are stored at the NPL in the same safe as Kg 18, in enclosures of the same type. They have the same cylindrical form as Kg 18 but an obviously superior finish. The identifying letter is marked on the side by slight depolishing. The density of each weight was determined at the NPL at temperatures close to 20 °C, by hydrostatic

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(3) This is the most recent (1993) value, the coefficient of cubical expansion given prior to this was $(25.863 + 0.00562t) \times 10^{-6}$ °C^{-1}; it is assumed that the change is due to the adoption of the ITS90 temperature scale.

(4) The notes accompanying Table 1 highlight the basic differences in the cleaning techniques used from time-to-time.

weighing of the individual portions of the extruded rod after the initial skimming but before the diamond-turning and final adjustment of each weight. The coefficient of cubical expansion is assumed to be the same as for Kg 18, giving calculated volumes at 0°C of 46.4354 cm^3 for Kg A and 46.4399 cm^3 for Kg B. To date Kg A has not been cleaned since its first calibration at the BIPM; Kg B has been cleaned and washed again by the BIPM, in 1985.

2.3 KILOGRAM E

This weight is distinctive for several reasons; it is the oldest of the group described here, it is made of pure platinum so is softer than the Pt-Ir weights but, although it has no particular legal status, in practice it is considered the "next best" after Kg 18.

It was bought by W H Miller (Professor of Mineralogy at the University of Cambridge) from the maker, Mr Gambey (of Paris) on 16 September 1844 and named Kg E at that time. Miller[6] considered it to be "very accurately worked" and the metal to be "greatly superior" to that of the five new standard pounds he was measuring. After considerable initial use in Paris and Cambridge[5] it was deposited at the Royal Observatory (Greenwich), then transferred to the Standards Department of the Board of Trade after the constitution of that body in 1866. It was an "auxiliary standard" of the BoT until its official transfer to the NPL in November 1964, although it had been on long-term loan to the NPL from well before that date. Prior to 1982 it was stored in a velvet lined wooden box, but since then has been stored in the same way and under the same conditions as Kg 18, ie in a container of the type shown in Figure 2.

The surface of this plain cylindrical weight (which has no identifying mark) is in a rather poor condition for a reference standard, bearing many scratches due to much handling and use in the past and to its relative softness. However, with present-day care the mass seems very stable. Miller[7] determined the density of Kg E in 1844, by hydrostatic weighing at 15 °C and assuming a linear expansion coefficient of 9.00×10^{-6} $°C^{-1}$ to calculate the density and volume at 0°C (in present-day units: 21.13732 g cm^{-3} and 47.3096 cm^3 respectively). Since

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(5) In 1843, a committee was appointed to superintend "the construction of new Parliamentary standards of length and weight" to replace those destroyed in the burning of the Houses of Parliament in 1834; Miller was assigned the task of constructing the new standards of weight. As part of this work, Miller indirectly compared the new pound with the then standard kilogram (known as the "Kilogramme des Archives") using Kg E as the transfer standard.

about 1883 the volume at room temperature has been derived using 25.89 x 10^{-6} $°C^{-1}$ for the cubical expansion coefficient[8], compared with 27.00 x 10^{-6} $°C^{-1}$ used by Miller. The use of different expansion coefficients introduced a small systematic error(6) of 0.0017 cm^3 in the calculated volume at room temperature (equivalent to an error of about 2 μg on the buoyancy correction).

There is no record of this weight having been cleaned or washed (other than by Miller before measuring its density) but early records are insufficiently detailed to be absolutely certain. This probable absence of vigorous surface treatment together with its relatively long history, gives the weight particular interest.

2.4 KILOGRAM PI

This is actually a group of four weights (500 + 200A + 200B + 100)g, collectively referred to as Kg PI or ΣPI. They are from a set of 23 weights ranging from 500 g to 1 mg (known as "PI grams"). Apart from the weights of 10 mg and below, which are of aluminium wire, the set is in Pt-Ir. The set was made by Oertling in 1894 for the BoT, but was in use at the NPL for many years before being formally transferred to the NPL in November 1964. The weights are stored in a traditional wooden box with felt-lined cavities, which is kept in the safe with the other Pt-Ir weights.

The four weights comprising Kg PI are plain cylinders, the surfaces being in a fair condition only, due to their age and usage. A density value at 0 °C of 21.3544 g cm^{-3} has been used for many years(7), this being the mean of determinations at the BoT, but the exact source of this value and its uncertainty of measurement are not known. For the coefficient of cubical expansion a value of 25.70 x 10^{-6} $°C^{-1}$ has been assumed[9].

These weights have probably never been cleaned vigorously. In principle this standard suffers from two drawbacks relating to its mass stability: there is a larger surface-to-mass ratio than for a single kilogram weight, hence its mass will be more dependent on variations

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(6) This error was discovered during research for the preparation of this report, and corrective action has since been taken. The value given for the volume error includes the effect of changing from the water density values originally used in the volume determination to those in current use.

(7) the value used prior to the re-definition of the millilitre in 1964 was 21.355 g ml^{-1} at 0°C

in adsorbed surface contaminants; secondly, in the past it has been subjected to greater use than the other reference kilograms, resulting in a more worn surface. Despite this, it is considered a useful member of the group of Pt-Ir reference standard kilograms.

3 THE MASS COMPARISON PROCESS

3.1 THE BALANCES

Details of the balances used before 1914 are not given here. Apart from Kg 18, Kg E is the only weight for which values obtained prior to this date are being considered, and there are several other important factors, about which there is little information, which would also have contributed to the reliability of the mass values derived for Kg E during this early period (see Section 4.3).

Between 1914 and the development of the NPL 1 kg primary balance in the 1930s, the highest precision weighings of reference kilograms and pounds in the UK were made on "Balance No 17", supplied to the Standards Department, BoT, by Oertling. This balance was overhauled and transferred to the NPL in 1927, presumably at about the same time as Kg 18. It was a traditional, manually-operated, equal-arm, free-swinging balance, housed within a copper-clad case. Fitted with an optical lever system to measure the beam inclination, the precision attained by Balance No 17 was about ± 20 μg. It was superseded by the NPL-built balance which is described below.

Since 1933 the comparisons of kilograms at the top of the NPL mass hierarchy have been carried out on the balance shown in Figure 3, as were the pound-kilogram comparisons. This balance was designed and built at the NPL. Initial trials were conducted in 1933 and the balance was essentially completed by 1939, when war interrupted the final evaluation of the balance's performance; the final evaluation was eventually accomplished in 1947. The balance's design incorporated a number of features which, combined with the very careful attention given to all mechanical and physical details, especially its final adjustment, resulted in a performance which was significantly better than the best contemporary balances[10]. It is a two-pan, equal-arm, undamped mechanical type, with knife-edges defining the beam arm length. It was originally operated manually but was automated during the period 1981-1983, preliminary work being started in 1978. Full details of the design and adjustment of the

balance in its manual form are given in Reference 10, and a detailed description of it in its automated form can be found in Reference 11. The mechanical features of the balance which are of particular note are: the three-stage de-coupling of the pan suspension systems (see Figure 4); a "beam steady" device (see Figure 5) which maintains contact under reduced load between the knives and planes while interchanging weights; and the weight interchange mechanism, which actually interchanges two pan-plates on which the weights rest, thus minimizing wear on the weights. The balance was (and remains) mounted on an anti-vibration pedestal in a vault situated near the centre of a large semi-subterranean basement. The natural distribution of temperature within the vault is quite uniform and steady, the surrounding walls being about 60 cm thick. The robust balance cover (which can be seen in Figure 8), made of a 1.3 cm thick gunmetal casting, further improved the thermal stability and uniformity of the balance. After the initial loading of the pans, operation of the balance (including application of the sensitivity weights) has always been carried out by remote control, by means of long shafts passing through a partition to an adjoining room, thus minimizing thermal disturbance from the operator. Similarly, monitoring the beam inclination has always been achieved remotely using an optical lever system.

Manual operation of the balance was slow and demanding on observer time and concentration (a full comparison between two kilogram weights required a minimum of 16 hours of observation, spread over two days with two observers). Automation of the balance allowed weighings to be made at any time with no operator present. Apart from the main beam arrest control, which remained manually-operated, the operation of the balance, including the sensitivity weight controls, was automated by motorizing the mechanical controls and coupling the motors to a controlling microcomputer. The original manual optical lever system attained the necessary high resolution using a scale situated 7 m from the balance; automation involved replacing this distant scale with a photodiode array mounted on top of the balance cover, the focal length of the original mirror being effectively shortened by the addition of a lens. This new optical system is shown in Figures 6(a) and 6(b)[8]. The introduction of sensors for air temperature, pressure and humidity which could be read automatically by a controlling microcomputer completed the automation. Hence the microcomputer controlled the following mechanical and data-gathering operations:

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(8) Figure 6(b) also shows an additional two mirrors and a lens. These (with a separate light source) were required until automation was completed, to give the operator an indication of the beam's position and hence facilitate smooth application of the "steady" mechanism.

(1) receiving initial data input and commands from the operator

(2) release and application of the pan stops

(3) release and application of the beam steady

(4) raising, interchanging and lowering the pan plates carrying the weights

(5) application and removal of the sensitivity weights

(6) monitoring and recording the position of the beam (turning-points of the swings)

(7) monitoring and recording the temperature, pressure and humidity within the balance enclosure

(8) determining the time of all operations and observations

(9) part-processing the data

(10) transmitting data, results and messages to a monitor screen and for subsequent data storage and processing by the mainframe computer.

The complete system, shown schematically in Figure 7, was installed in the outer rooms previously occupied by the operator. The innermost room still houses the balance, the middle room contains[9] the motorized controls, while the remaining control, measuring and recording equipment is in the outer room. Figure 8 gives a general view of the balance and the motorized controls from the middle room.

The instrumentation introduced for automation generates appreciable heat, particularly in the outer room. Prior to 1981 unfiltered air was drawn via an aperture into the inner (balance) room by a fan in the outer room door. Since 1981 there has been a powered flow of filtered air into the balance room, extracted by the fan in the outer room. The air flow helps to remove the heat, moisture and CO_2 caused by the operator whilst setting-up for a run and the heat generated by the controlling equipment during a measurement run.

The balance originally[10] attained an accuracy of about ± 1 μg but its performance appears to have deteriorated slightly in recent years. This might be due to wear of the knives and planes, which would have been accelerated by the increased use of the balance following automation. However, records show that there were a number of mechanical problems and changes during the 1960s, including the replacement of the central agate plane by one of synthetic sapphire in 1961, and a seizure of the weight exchange mechanism which resulted

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(9) Until recently, the instruments for measuring air pressure and CO_2 content were also housed in the middle room.

in several repairs and adjustments being carried out on the balance in 1965. Other factors which may contribute to its apparent deterioration include certain changes in the operating procedure; for example, prior to automation the balance was exercised before use by carrying out a short series of weighings to "stabilize the beam", whereas post-automation this was reduced to a simple interchange of the pans; the thermal stabilization time has been shortened: after automation the weights were normally loaded onto the balance in the morning and the balance run overnight, whereas manual weighings used to commence the following day. Before automation and the introduction of the evaluation of all the data by computer programme, the balance readings were inspected as the calculations were executed, and there is evidence that "out-of-line" results were rejected; this practice could have led to a more optimistic assessment of the balance's performance compared with post-automation results.

3.2 AIR DENSITY DETERMINATION

To determine air buoyancy corrections, the air density during weighings was calculated from measured values of temperature, pressure and humidity; more recently, CO_2 content has also been measured. Presumably in the very early days (ie from 1883) when the standards were the responsibility of the BoT, the formulae on which the air density calculations were based were those given in Reference 8 (pp 5-11). Just before the standard weights were transferred from the BoT in 1925 for use at the NPL, an internal NPL paper[12] was produced containing formulae and tables for air density; this paper was the basis for the information which was given in the then current edition of a book of reference data[13], which subsequently continued to reflect the data on which the NPL Mass Section based its air density calculations. In recent years, the formula recommended by the BIPM[14][15] has been used.

The methods described below for measuring the relevant parameters relate to the use of the NPL-built balance, ie to the post-1933 data. Values of the three main parameters of temperature, pressure and humidity were recorded regularly during the weighing procedure, although the frequency of measurement was restricted prior to automation. Since early 1983 the CO_2 content has also been measured, but only when comparing Pt-Ir and stainless steel kilograms, ie when the volume difference of the weights was large; for the data given here, it was assumed to be 400 ppm.

Temperature was measured originally by two mercury-in-glass thermometers sited inside the balance cover[10]. Initially this involved the observer entering the inner balance room, so measurements had to be restricted to before and after a weighing run to minimize thermal disturbance; later a telescope was used to facilitate reading from the middle room, enabling readings to be taken during a weighing run. This arrangement was in turn replaced by a 25 ohm 4-terminal platinum resistance thermometer, mounted vertically inside the balance case with the sensing region in approximately the same horizontal plane as the kilograms on the balance pans, the resistance bridge being housed in the outer room and now being read automatically.

Pressure was measured originally by a calibrated Fortin barometer, but this was replaced sometime prior to automation by a precision aneroid barometer (PAB) connected by polythene tubing to the balance case; again this facilitated readings being taken during a weighing run. Since automation the PAB has been replaced by a quartz bourdon tube barometer with electromagnetic nulling, having a resolution of 1 Pa; to correct for zero drift of the automatic barometer, a particularly well-calibrated PAB has been used to determine, in situ, the small correction to the reading.

Humidity was originally measured by two hair hygrometers inside the balance cover, calibrated frequently against an Assmann wet and dry bulb hygrometer; although they could be read from the middle room, hence during a weighing run, tapping before reading was not possible. Since automation the sensor of a humidity meter has been mounted inside the balance case, the meter itself being housed outside the balance room. This humidity meter was compared regularly against a dew point hygrometer reading to 0.1 °C.

Additional details on the instrumentation used during the period 1984 to early 1991, can be found in Reference 11.

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(10) A broken thermometer is perhaps the most likely cause of the mercury contamination found inside the balance case in the recent studies by Cumpson and Seah[16], when investigating the possible sources of contamination of Pt-Ir by mercury. Four mercury-in-glass thermometers were used in Balance No 17 for pre-1933 measurements.

3.3 WEIGHING METHOD AND PROCESSING OF BALANCE DATA

General method

The method discussed below relates to the NPL-built balance. Although the method differed in detail pre- and post-automation, the principles of operation were the same. In the post-automation work, the weighing procedure was controlled and monitored by the computer software and remained unchanged. During the period before automation there were no such controlling constraints on the procedure, which varied from time-to-time in certain details. The description in Section 3.3.2 refers to the post-automation weighing procedure[11]; variations in the detail of the pre-automation procedure are highlighted later in Section 3.3.3.

The NPL balance is a mass comparator: the two weights being compared are poised very closely (normally to within about 10 μg) using makeweights[12] and the residual mass difference measured. The residual mass difference is obtained from the change of rest-point when the weights are interchanged on the beam and the balance sensitivity, having applied the appropriate air buoyancy corrections. To determine and correct for unavoidable drift of the rest-points, a repeated double weighing procedure was used, each such procedure being referred to as a "weighing run". As the interchange of the weights on the beam is achieved by interchanging the pan-plates which carry the weights, the mass difference obtained includes that of the pans; to eliminate the mass of the pan-plates, the contents of the pans have to be transposed and the weighing run repeated with the weights in the new configuration.

Post-automation

The post-automation procedure for each weighing run was as follows. After loading and poising the balance, the beam arrest was released and the balance left to stabilize, with the beam steady applied, for a minimum of 8 to 10 hours. Before weighings started, the

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(11) It should be noted that the post-automation weighing procedure described here has since been slightly modified, following the introduction of a new controlling computer and software in 1993. These changes are described in Reference 17.

(12) Above 10 mg the makeweights are of Pt-Ir; below 10 mg they are of Al, with the exception of four weights which are of a cupro-nickel alloy (known as "Eureka") of density 8.9 g cm^{-3}. Prior to 1936, makeweights were not available to facilitate adjustment to better than 50 μg.

controlling program began with a preliminary interchange (lift, rotate, lower) of the pans plus their contents, to exercise the balance. For each comparison (ie rest-point determination) the beam steady was released, the first two turning-points ignored and the next seven (from which the rest-point was calculated) were recorded. The beam was steadied, the pans plus their contents were interchanged and the next rest-point determined. These interchanges and comparisons were repeated until thirteen rest-points had been determined, ie seven rest-points with weight A on the left and weight B on the right alternating with six rest-points with A on the right and B on the left. From these two sets of rest-points best-fit curves were calculated; the offset between the two curves, after correcting for buoyancy at each comparison, gave a drift-corrected measure of the mass difference between the pans plus their contents. Immediately after the thirteenth comparison, while the beam was still swinging freely, the two sensitivity weights (one at each end of the beam) were in turn applied then removed three times, recording the turning-points and calculating the rest-points as before. From the additional twelve rest-points obtained three curves were calculated, corresponding to "off" and "on" for each sensitivity weight. The difference between the curves gave a drift-corrected measure of the right and left sensitivities. The temperature, pressure and humidity within the balance case were automatically measured and recorded regularly throughout the weighing. The procedure described thus far constituted a weighing run. Without disturbing the contents of the pans (ie with the weights still in the same configuration, referred to as configuration X), the weighing run was repeated. After transposing the contents of the pans (ie with the weights in configuration Y) two further weighing runs were carried out. Thus a full comparison of two weights consisted of four 13-comparison double weighings.

Each of the four sets of data yielded a drift-corrected measure of the mass difference between the pans plus contents which can be expressed in the form:

$$(m_A + w_A + p_1) - (m_B + w_B + p_2) = R(X)/2S + b_i \quad (i = 1 \text{ to } 13) \qquad (1)$$

where m_A and m_B are the masses of weights A and B, w_A and w_B are the masses of makeweights W_A and W_B, p_1 and p_2 are the masses of the pans, S is the mean sensitivity, b_i is the nett buoyancy correction for the ith comparison due to the volume difference between

the pans' contents[13], and $R(X)$ is the difference between the two best fit curves through the two sets of rest points for configuration X.

Re-arranging (1) gives

$$(m_A - m_B) + (p_1 - p_2) = R(X)/2S + b_i - (w_A - w_B) = m(X) \quad (2)$$

A mean of the two results with the weights in configuration X, $m(\bar{X})$, is obtained; hence

$$(m_A - m_B) + (p_1 - p_2) = m(\bar{X}) \quad (3)$$

Similarly, when the contents of the pans are transposed (giving configuration Y), equation (2) becomes

$$(m_B - m_A) + (p_1 - p_2) = R(Y)/2S - b_i + (w_A - w_B) = m(Y) \quad (4)$$

and equation (3) becomes

$$(m_B - m_A) + (p_1 - p_2) = m(\bar{Y}) \quad (5)$$

Subtracting (5) from (3) eliminates the masses of the pans:

$$m_A - m_B = (m(\bar{X}) - m(\bar{Y}))/2 \quad (6)$$

Thus equation (6) yields the measured mass difference for the comparison of weights A and B.

After automation, some of the data were handled by the controlling microcomputer (to assist the operator in poising the balance, etc) and all data were finally processed on a mainframe

(13) As the pans themselves are closely equal in mass and volume, the difference between their buoyancy corrections is small and will vary by less than 1 μg for any likely variation in air density during a weighing run. As their mass difference $(p_1 - p_2)$ is eliminated by the procedure used, the virtually constant nett buoyancy correction for the pans can be ignored.

computer. The software[14] was originally run in Algol-60 on an ICL 2972 but was converted to Fortran-77 by May 1989 before transferring to a replacement mainframe (Digital VAX 6230). After August 1989 only the Fortran version, run on the VAX 6230, was used to process data. Conversion of the software and the change of mainframe computer was tested by processing the data from twenty-seven mass comparisons on both computing systems. Results showed very occasional small changes in the mass difference of less than 0.8 μg, the most likely cause being slight differences in the mainframe computers' library routines used for curve-fitting.

3.3.3 Pre-automation

As already remarked, the weighing procedure pre-automation varied from time to time in certain details and differed in certain respects to the more rigorously controlled post-automation procedure. The stabilization time between loading and using the balance was longer than post-automation, usually about 15 hours, but the measurement of air density parameters was much less frequent and more difficult, although this was improved latterly, and measurements were almost certainly less accurate. Only two weighing runs were carried out for each comparison, one in each of the X and Y configurations. The main differences in the weighing run itself were in the number of observations taken and in the method of calculation of the results. The number of turning-points used to determine a rest-point varied from five to seven, the calculation of the rest-point being based on a weighted mean. The number of interchanges carried out (hence rest-points determined) varied between nine and fifteen; often the first two were not used (being regarded as preliminary exercising of the balance "to bring the beam into a stable condition"[10]) and linear interpolation was used to calculate the difference between the two sets of rest-points, rather than the offset between the two best fit curves. The balance readings were inspected as the calculations were executed, and there is evidence that "out-of-line" results were rejected. Not only was assessment of the data limited by the lack of suitable software to fully analyze the data statistically, but the lack of a second set of comparison data precluded an inspection of the repeatability of the measurement of the mass difference from day to day.

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(14) A description of the main operations carried out by the software, codename "Runbal", can be found in Appendix 1 of Reference 11. The software was originally written in 1981 [18]; a detailed description of the data analysis carried out by the software as at May 1990 is given in Reference 19.

3.4 WEIGHING SCHEMES AND THE EVALUATION OF THEIR RESULTS

The initial stages (ie at the kilogram level) of the UK mass calibration chain are shown in Figure 1. The first two stages are carried out by the BIPM and provide calibration data which relate the mass value of Kg 18 indirectly via a group of Working Standards (WS) to that of the International Prototype Kilogram (K). The subsequent stages are carried out by the NPL, and the first of these involves comparing Kg 18 with the four other major kilograms described above in Section 2. When a group of kilogram reference standards are intercompared it has been normal NPL practice to adopt a weighing scheme where each weight was compared with each of the others in the group, following the full weighing sequence described above in Section 3.3 for the comparison of each pair of weights; for example, when calibrating Kgs A, B and E with reference to Kg 18, six comparisons were carried out. This is referred to as a comparison "square". Details of all the weighing schemes involving Kg 18 carried out during the period 1979 to 1990 are given in Appendix 2 of Reference 11.

When a complete comparison square has been carried out, evaluation and fitting of the data is relatively simple, and can be done by manual calculation. However, this method yields only very limited statistical information. In more recent times, much more rigorous statistical analysis of the data has been provided by the development of the program "Massrun"[18]. As with the "Runbal" program, the "Massrun" software was originally written in Algol-60 and run on the ICL 2972 mainframe; it was converted to Fortran-77 and transferred to the VAX 6230 mainframe by mid-1989. Both the simple, manual method of evaluation and the program "Massrun" are described in detail in Reference 11.

4 MASS VALUES AND STABILITY OF THE STANDARD KILOGRAMS

4.1 GENERAL RELIABILITY OF DATA

The confidence that can be placed in the UK mass scale depends primarily on the uncertainties associated with the mass values of the standards involved and those uncertainties introduced by the weighing process. The former depends not only on the uncertainty in the mass value assigned to the weight at the time of its calibration, but also on its mass stability between calibrations.

The balance used to compare Kgs E, A, B and PI with Kg 18 in recent years was capable of doing so to within $\pm$ 1 μg or so; whereas before 1933 the balance used had an associated uncertainty of $\pm$ 20 μg, and much earlier (ie before 1914) it must be assumed that the uncertainty of the comparisons was somewhat greater than this. Consideration of the stability of the standards will therefore be restricted generally to the post-war period, as not only was the new NPL balance fully operational but any cleaning or other treatment to which the standards were subjected is well documented; since 1982, Kgs 18 and E have also been stored under improved conditions. The apparent stability of Kgs E, A, B and PI will also depend to some extent upon the validity and accuracy of the assumptions made about the stability of Kg 18. In turn, the data on Kg 18 will depend on the stability and treatment of the BIPM working standards (WS) and ultimately on that of the International Prototype, K.

4.2 MASS OF KILOGRAM 18

4.2.1 Measured Mass Values

The mass of Kg 18 has been measured on 12 occasions by the BIPM and twice by the NPL using standards borrowed from the BIPM for the purpose. The measured values obtained for the mass of Kg 18 are collected in Table 1, together with the basis of measurement (ie which standards were used[15]). The uncertainty of measurement given by the BIPM has varied from time to time; this is discussed further in Section 4.6.

For almost the first sixty years of its existence (ie until about 1950) Kg 18 was assumed to maintain a constant value between standardisations at the BIPM. The differences observed were probably considered to have little significance and to be within the uncertainties associated with the procedures used for the dissemination of Kg 18, thus the mass value used for Kg 18 for the calibration of the other NPL kilograms was always that given in the latest BIPM certificate. However, following wartime studies at the BIPM[20] on the cleaning of prototype kilograms, the practice of cleaning before a standardisation was re-introduced by the BIPM in 1946. It soon became apparent that cleaning gave rise to measurable mass changes, as illustrated by the mass losses recorded for Kg 18 during the standardisations of 1948 and 1978 (see Table 2); subsequently the profile of the mass regain which followed the

(15) More information on the BIPM standards can be found in Reference 1; see also Note (e) of Table 4 concerning Kg 44.

cleaning of Kg 18 was demonstrated in papers by P H Bigg[21] and A Williams[22]. As a result of these observations and at the suggestion of the NPL, the effects of cleaning Kg 18 and its mass regain after cleaning were studied by the BIPM over a 14-month period during 1985-6. In the study, Kg 18 was subjected to three successive cleaning operations, the mass change for each being - 12 μg, - 9 μg and + 2 μg, respectively (only the nett result of - 19 μg is given in Tables 1 and 2). After the last cleaning, the mass regain was measured using the BIPM's NBS-2 balance[16]. The four weights involved were left undisturbed on the balance pans, to provide an uninterrupted series of measurements; this ensured that the changes which were measured were not influenced by any handling of the weights, thus giving a more realistic indication of the effects of re-contamination. The data obtained[23][24] is given in Table 3 and plotted in Figure 9. For all but two values the estimated uncertainty of measurement was between ± 0.5 μg and ± 0.8 μg (for the February and April 1986 values it was ± 1.1 μg to ± 1.3 μg).

Mass regain after cleaning

Inspection of the data from the BIPM study showed that the rate-of-change of mass with time was very rapid immediately after cleaning, potentially slowing down longer-term, and a need to inspect the historical data on Kg 18 in more detail was indicated. As well as listing all the measured mass values, Table 1 gives all the dates and methods of cleaning, where known, of Kg 18; altogether it has been cleaned seven times. The BIPM studies on methods of cleaning during the 1940s resulted in the development of a technique combining solvent cleaning with steam washing[25]. This cleaning procedure has been used by the BIPM since 1946, the only variation being changes in the solvent used: the original use of redistilled petrol being replaced by benzene, which (due to its likely carcinogenic properties) was in turn replaced by a mixture of equal parts of ethanol and ether[17]. A full description of the present-day cleaning procedure is given in Reference 26; Figures 10(a) and 10(b) show the two stages of the procedure: (a) initially rubbing with chamois leather moistened with a 50:50 mixture of ethanol and ether, followed by (b) washing in a jet of steam. Table 2 relates the measured mass changes to cleaning, and to the period which had elapsed since the previous cleaning; each weighing has been numbered to identify the source of each calculated mass

(16) see Appendix 1 of Reference 1 for details of the balance

(17) Benzene was still being used at the time of the three cleanings of Kg 18 carried out as part of the mass regain study of 1985-6.

change.

The values obtained for the average rate of gain of mass over the longer term will depend on the ability of the cleaning method to restore the surface of the weight to a comparable condition on each occasion, as well as on the storage conditions and use of the weight between weighings. Those figures printed in bold in Table 2 are those which are considered to be the more representative of the true situation. These show that the average rate of gain of mass has been generally consistent and was about 2.65 μg/year for periods of between 7 and 25 years (Table 2). Note that the last entry (no 13, of 1991) represents the mass value obtained (by the BIPM) by correcting the measurement data to correspond to the date of cleaning of Kg 18, unlike the earlier post-cleaning values; therefore this value does not include the rapid regain in mass which occurs immediately after cleaning. Using a more typical post-cleaning value (average of entries 7, 9 and 11) of (1 kg + 58.3 μg) with the before-cleaning value of (1 kg + 75 μg) gives a change rate of 2.8 μg per year for the 6 year period. Apart from the earliest, and possibly least accurate, value of + 0.7 μg/year, the only other out-of-line figure (+ 3.8 μg/year) was for a period spanning the time when the BIPM cleaned all its standards, which is suspected to have introduced a discontinuity.

4.2.3 Assigned Values

The confirmation of the mass regain after cleaning which the 1985/6 measurements provided led to the NPL introducing an important change. When calibrating the other NPL weights, instead of using the BIPM-certified post-cleaning value[18], mass values were assigned by the NPL by extrapolating the BIPM data on Kg 18 beyond the final (May 1986) value of (1 kg + 63.1 μg). The values which were assigned to Kg 18 and the basis upon which the corrections were made are discussed below.

(a) October to November 1986: Kg 18 = 1 kg + 64 μg

This was based on the last value reported by the BIPM (1 kg + 63.1 μg), adjusted for a rate of increase in mass of 0.22 μg/month (approx 2.65 μg/year) for a period of 5 months. This rate of increase was based on the gain in mass of 17 μg measured by the BIPM between April 1978 and November 1984 on Kg 18, the previous washing being 79 months earlier (the rate of 5 μg/year indicated by the 1985/6 BIPM study being considered too high); the rate of

(18) Under normal circumstances this would have been the March 1985 value of 1 kg + 57 μg.

increase was assumed to be linear.

(b) January to March 1988: Kg 18 = 1 kg + 65 μg

Linear extrapolation using a rate of increase in mass of 0.22 μg/month (as above) to February 1988 (21 months) gave Kg 18 = 1 kg + 68 μg; this was rejected because it gave values for Kgs A, B, E and PI which were all considered to be rather different from their expected values. Instead, a correction based on a rate of 1 μg/year, which had been found by the BIPM[1][27] to be more appropriate to later in the post-cleaning period, was applied to the 15 months since the previous value was assigned in November 1986.

(c) January to February 1990: Kg 18 = 1 kg + 67 μg

The 1 μg/year rate was again applied to the two years following February 1988.

The extrapolated values for Kg 18 were then used to calculate the values assigned to Kgs E, A, B and PI on the above three occasions; their mass values are given in Tables 4, 5 and 6.

Discussion of Other Possible Extrapolations of Mass Value

At this point (1990) it was decided that the BIPM 1985/1986 mass regain data should be re-examined, and the data were fitted to a single-term power function of time; note that the 8th data point was regarded as an outlier, and omitted. This data fit yielded the following expression

$$\text{Mass Kg 18} = 1\ \text{kg} + [55 + 0.356\,097 \times t^{0.511678}]\ \mu\text{g} \qquad (7)$$

where t is the time in days after cleaning. The curve illustrating this fit is shown in Figure 11 and the extrapolated values it gave for Kg 18 at the times of interest are given in Table 7. Note that the values used contemporaneously for Kg 18 were not those listed in Table 7, but were those given above in Section 4.2.3.

Subsequently (in 1991) Kg 18 was weighed, cleaned, then weighed again by the BIPM as part of the Third Verification of National Prototype Kilograms. It is of interest to note that the mass value obtained prior to cleaning (Table 2, entry no 12) agrees well (within 2 μg) with that predicted by equation 7.

To provide more realistic assessments of the stability of the other kilograms, the principle of using an adjusted value for Kg 18 as the basis can be extended back to earlier weighings. Table 7 therefore also includes assigned values for Kg 18 on the basis that its mass on cleaning in 1978 would have been initially restored to (1 kg + 55 μg) and that its mass regain would have been as given by equation 7. Note that again the prediction over a 6-year period lay within 2 μg of the BIPM measured value (November 1984).

4.3 MASS OF KILOGRAM E

It is of historical interest to list, in Table 4, all officially recorded mass values for Kg E from 1845, although prior to about 1933 the uncertainties were considerably greater than at present. All these values are plotted in Figures 12(a) and the more recent, hence the more reliable, values in Figure 12(b). The first entry in Table 4 refers to the "Kilogramme des Archives", which was the original standard of the kilogram[19]. The values for Kg E show a steady loss during the period from 1845 to 1883 (455 μg in 38 years) but the next two values (for the years 1891 and 1908) are distinctly out of line and widely discordant (1288 μg difference). There appears to be no reliable explanation for this discontinuity, although it has been suggested[29] that between 1891 and 1908 the Standards Department of BoT may have been experimenting with weighings in vacuum, as a result of which Kg E may have been subjected to prolonged exposure to vacuum before re-exposure to air, causing the loss observed in 1908 and the subsequent regains in the period up to about 1930 (some 800 μg in 25 years).

In examining the stability of Kg E due attention must be made to the mass values adopted for Kg 18. For the more recent measurements, a truer indication of stability should be obtained using adjusted values for Kg 18 which allow for its mass variations with and subsequent to cleaning. Table 8 gives the mass values for Kg E using the values for Kg 18 taken from Table 7; these values cover the period since both kilograms have been stored under well-controlled conditions. Note that the values used contemporaneously for Kg E were those listed in Table 4; those listed in Table 8 are given here only for consideration of

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(19) The Kilogramme des Archives was made in Paris in 1799 and adjusted to be as close as possible in mass to that of a cubic decimetre of water. The present International Prototype Kilogram was selected by the Comité International des Poids et Mesures (CIPM) in 1883 from a group of three, after being compared in 1880 with the Kilogramme des Archives and being found to have a mass which was "indistinguishable from that of the Kilogramme des Archives"[28]; the CIPM's decision was formally ratified by the Conference Général des Poids et Mesures at its first meeting in 1889.

Kg E's true stability.

4.4 MASS OF KILOGRAMS A AND B

The mass values of Kgs A and B are given in Table 5. These kilograms are relatively new and may well require several years to stabilise (see Section 5). Comparatively few values are available for them as yet, and Kg B was cleaned again in 1985. A detailed discussion on their stability has been therefore been deferred, although in the longer term, because of their superior finish, they should be more stable than the other NPL kilograms.

4.5 MASS OF KILOGRAM PI

Mass values for Kg PI from 1922 onwards are given in Table 6 and plotted in Figure 13. The values up to 1970 are rather scattered but show an overall loss of about 100 μg in the 48 years. There appears to be a discontinuity between 1970 and 1980 (53 μg difference), followed by more stable values in the most recent decade (8 μg span). As with Kg E, values for Kg PI have been recalculated for the period since 1980 using values assigned to Kg 18 on the basis of equation 7; these recalculated values are given in Table 8, and show remarkable stability (span 3 μg in 8 years) given the poorer storage conditions for this standard and its larger surface-to-mass ratio.

4.6 UNCERTAINTIES OF MEASUREMENT

The uncertainties of measurement of mass have undoubtedly been reduced over the decades, and we now have a much better awareness and understanding of the many sources of uncertainty that there are. The total uncertainty of measurement of mass at any stage of the mass calibration chain can be considered as arising from two sources: the standard weight and the intercomparison process

The estimated uncertainty of measurement associated with the determination of the mass of Kg 18 by the BIPM has varied: the original calibration certificate (1889) gave ± 2 μg; subsequent certificates gave no statement of uncertainty until those of 1978 and 1986, which gave a total uncertainty (at the 1σ level) of ± 8 μg. This was composed of type A components (± 1 μg) arising from the BIPM weighing process, plus type B (± 8 μg) associated with their

working standards. For the latest (1991) calibration, the total uncertainty has been reduced to ± 2.3 μg. However, we are now aware that an additional uncertainty arises from the progressive change in mass of Kg 18 following cleaning and calibration. Prior to the recent work on mass regain after cleaning, no allowance was made for these changes either in terms of a correction or an additional source of uncertainty. Although this change has been corrected for since 1986, there is still an appreciable (if smaller) uncertainty arising from this change.

The uncertainties arising from the comparison process have improved considerably over the decades: it is not possible to estimate the uncertainties of measurement which prevailed pre 1914; the balance used post-1914 had an associated uncertainty of measurement of ± 20 μg, at best, whereas the performance of the new NPL-built balance reduced the uncertainty due to the balance alone to ± 1 μg, when it was brought into use in the 1930s. The improved environmental conditions which accompanied the introduction of the NPL balance would also have reduced the uncertainties associated with the corrections for air buoyancy effects; the uncertainty of the measurement of the relevant parameters, hence of the air density, were further reduced with the automation of the balance in the 1980s.

The uncertainties of measurement of the recent NPL weighings at the kilogram level are examined in detail in Reference 11, and a typical summary, which applies to an intercomparison carried out in February 1988, is given here in Tables 9(a), (b) and (c).

5 IMPROVEMENTS IN THE FUTURE

This report summarises the mass values of the reference kilograms upon which the UK mass scale has been based for the last 100 years or so. The accurate monitoring of the mass stability of Kg 18 in recent years has shown that if the measurement of mass is to be achieved to the microgram level in reality, then the mass changes, which it is widely agreed are due to surface effects, must be minimised and corrections for mass change with time applied where possible. In order to do this, it is necessary to understand the physical and chemical changes which are occurring at the surface of the material due to contamination. The recent work of Cumpson and Seah has already shown that the major potential sources of contamination are hydrocarbons[30] and mercury[31]. Cumpson and Seah also developed and presented theoretical models for the growth of contamination which are shown to agree with the

available measured mass data on Kg 18, confirming that contamination grows as the square root of time[20]. Prediction of mass change corrections by extrapolation over a long period is obviously only satisfactory if the storage conditions (hence contamination potential) are consistent; the longer the period the more unreliable such predictions will be. Restoration of the mass of a Pt-Ir standard by removal of the contamination is the obvious alternative. The procedure currently used[26] involves rubbing the surface manually, and although excellent results have been achieved at the BIPM, other national standards laboratories have not had good results when trying to replicate the method. Therefore there is a requirement for the development of an automated method of cleaning which will reproducibly remove the identified contaminants and return the surface to a well-defined state. Several methods have already been proposed, for example UV/ozone cleaning[30], but results of tests to establish the efficacy of these methods when used on Pt-Ir kilograms are still awaited.

ACKNOWLEDGEMENTS

The authors would like to thank D R Armitage for his help and encouragement in the preparation of this report

(20) This also supports the earlier adoption of equation 7 to predict the short-term increases in the mass of Kg 18: the difference between extrapolated values using equation 7 and that given by Cumpson and Seah is less than 1 μg over 9 years.

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TABLE 1: SUMMARY OF MEASURED MASS VALUES OF Kg 18

Date	Observer	Basis	Mass* /μg	Comments (and see notes below)
1889	BIPM	International Prototype	70	After initial cleaning[a]
Jan 1924	BIPM	Kg 7, Kg C	51	After cleaning[b] at BoT, Jan 1923
Oct 1933	BIPM	Kg 7	58	No cleaning
Dec 1933	NPL	Kg 9 (from BIPM)	50	"Short test" only, no cleaning
Sep 1946/ Jul 1947	NPL	Kg 44 (from BIPM) Kg E, Kg PI (NPL)	106	No cleaning
1948	BIPM	Kg 9, Kg 31[c]	141	Before cleaning
Nov 1948	BIPM	Kg 9, Kg 31	71	After cleaning[d] at BIPM
Jan 1961	BIPM	Kg 9, Kg 25, Kg 31	59	After cleaning[e] at NPL, Sept 1960
1978	BIPM	Kg 9, Kg 25, Kg 31, Kg 63	105	Before cleaning
Apr 1978	BIPM	As above	59	After cleaning[f] at BIPM
Nov 1984	BIPM	Kg 9, Kg 31	76	Before cleaning
Mar 1985	BIPM	Kg 9, Kg 31	57	After cleaning[g] at BIPM. See also Table 3.
Jun 1991	BIPM	Kg 9, Kg 31, via Kg 8(41), Kg 32	75	Before cleaning
Oct 1991[j]	BIPM	As above	53	After cleaning[h] at BIPM. Extrapolated value: see note (j).

* Deviation from 1 kg.

Notes:

After manufacture, all the new kilograms were cleaned with alternate jets of steam and ethanol vapour.

A liquid mixture of ethanol/ether/ammonia was "applied" (no details given).

(c) Before the 1948 weighings at BIPM, the BIPM standards (including the International Prototype) were cleaned.

Rubbed with chamois leather soaked in benzene then with chamois leather soaked in ethanol, followed by washing with jets of steam. Exact date unknown.

(e) Steam cleaning only, using process similar to BIPM.

(f) As (d). Exact date unknown.

(g) As (d). Whole cleaning and weighing operation performed 3 times, ending 19 February 1985.

(h) cleaning procedure applied twice between the before and after values given; benzene now replaced by a 50:50 mixture of ethanol and ether. A full description of the cleaning process used on this occasion at the BIPM is given in Reference 26.

(j) These measurements were actually made during the period Nov-Dec 1991. The value given was obtained by BIPM by extrapolating back to the date of cleaning, on the basis of a rate-of-change of 0.0368 μg per day.

TABLE 2: MASS CHANGES RELATED TO THE CLEANING OF Kg 18

No	Date Cleaned	Date[a] Weighed	Mass* /μg	Weighings on which change based	Change /μg	Period /years	Change Rate /μg per year
	1889						
1		1889	70				
	Jan 1923						
2		Jan 1924	51				
3		Oct 1933	58	2 and 3	7	9.5	0.7
4		. . . [b]Jul 1947	106	2 and 4	55	23.5	2.3
5		1948	141	2 and 5	90	24	3.8
	1948						
6		Nov 1948	71	**5 and 6**	**70**	**25.5**	**2.7**
	[c]Sep 1960						
7		Jan 1961	59				
8		1978	105				
	1978						
9		Apr 1978	59	**8 and 9**	**46**	**17.5**	**2.6**
10		Nov 1984	76				
	Feb 1985						
11		[d]Mar 1985	57	**10 and 11**	**19**	**7**	**2.7**
12		Jun 1991	75				
	Oct 1991						
13		[e]Oct 1991	53	12 and 13	22	6	3.7

* Deviation from 1 kg

(a) In some cases (especially earlier years) only the BIPM certificate date is available.

(b) Value obtained by NPL. All other values obtained by BIPM.

(c) Cleaned by NPL; no solvent rubbing, steam-jet cleaning only.

(d) see also Table 3.

(e) Measurements made Nov-Dec; BIPM extrapolated back to date of cleaning, so the value will not include the rapid changes seen after cleaning as in earlier data.

TABLE 3: BIPM STUDY OF MASS REGAIN OF Kg 18

Date	Mass* /μg
As measured by BIPM:	
19 Feb 1985	(3rd cleaning and washing)
14-19 Mar 1985	56.9 ± 0.8
13-14 May 1985	58.1 ± 0.6
24-26 Jun 1985	59.8 ± 0.6
10-11 Sep 1985	60.2 ± 0.7
17-25 Oct 1985	61.3 ± 0.5
25-26 Nov 1985	60.8 ± 0.4
11-12 Dec 1985	62.1 ± 0.4
18-19 Feb 1986	†59.5 ± 1.3
7-8 Apr 1986	62.4 ± 1.1
5-6 May 1986	63.1 ± 0.5
Values subsequently assigned by NPL by extrapolation‡ of the BIPM results:	
Oct-Nov 1986	64
Jan-Mar 1988	65
Jan-Feb 1990	67
Re-measurement by BIPM (Third Verification, before cleaning) Jun 1991	75

* Deviation from 1 kg.

† omitted from data fit; BIPM reported unfavourable atmospheric conditions.

‡ using bases described in Section 4.2.3 (a), (b) and (c).

TABLE 4: MASS VALUES OF Kg E

Date	Observer	Basis	Mass* /μg	Comments (and see notes below)
1845	Miller	Kg des Archives	- 1563	After initial cleaning (a)
1875	Chaney	Unknown	- 1844	
1879	Chaney & Marek at BOT	Unknown	- 1923	
1883	Marek at BIPM	Unknown	- 2018	
1891	Chaney	Kg 18	- 1678	
1908		Kg 18	- 2966	Unexplained discontinuity (b)
1914		Kg PI	- 2350	Started using "balance no.17" (c)
1919		Kg PI	- 2259	
Jan 1923		Kg 18 = 1 kg + 51 μg	- 2241	Before pound/kg comparisons
Feb 1923		As above	- 2222	After pound/kg comparisons
Mar 1927	NPL	As above	- 2180	
Jul 1933	NPL	Kg 18 = 1 kg + 58 μg	- 2150	Started using new NPL balance (d)
Nov 1933	NPL	As above	- 2152	
Nov 1938	NPL	Kg E + Kg PI = 2 kg - 46156 μg	- 2156	Sum of E and PI used as basis
May 1940	NPL	As above	- 2142	
Mar 1949	NPL	Kg 18 = 1 kg + 71 μg Kg 44 = 1 kg +270 μg	- 2118	See note (e)
Sep 1957	NPL	Kg 18 = 1 kg + 71 μg	- 2118	
Sep 1960	NPL	As above	- 2124	Before Kg 18 cleaned at NPL
Sep 1960	NPL	Kg 18 = 1 kg + 59 μg	- 2119	After Kg 18 cleaned at NPL then weighed at BIPM

* Deviation from 1 kg

Cont

TABLE 4 (Cont): MASS VALUES OF Kg E

Date	Observer	Basis	Mass* /μg	Comments (and see notes below)
Mar 1961	NPL	As above	- 2135	
Dec 1961	NPL	As above	- 2151	
Apr 1965	NPL	Kg 18 = 1 kg + 59 μg	- 2162	
Jun 1970	NPL	As above	- 2156	
Jun 1980	NPL	Kg 18 = 1 kg + 59 μg	- 2136	Kg 18 cleaned and weighed at BIPM in 1978 (f)
May 1984	NPL	Kg A = 1 kg + 68 μg Kg B = 1 kg + 176 μg	- 2119	Aug 1982 BIPM values for Kgs A and B
Sep 1984	NPL	Kg 18 = 1 kg + 59 μg	- 2147	
Nov 1986	NPL	Kg 18 = 1 kg + 64 μg	- 2131	Note adjustments to Kg 18 value for last 3 entries (g)
Mar 1988	NPL	Kg 18 = 1 kg + 65 μg	- 2128	
Feb 1990	NPL	Kg 18 = 1 kg + 67 μg	- 2129	

* Deviation from 1 kg.

Notes:

(a) Washed in alcohol Sept 1844

(b) This large discontinuity has never been explained adequately, but see Section 4.3.

(c) See Section 3.1

(d) The new NPL balance (described in Section 3.1) was not in its final form in 1933, lacking the "steady" mechanism for example. Kg 18 was weighed at BIPM between the July and Nov 1933 NPL weighings, but as it was not cleaned the new value was used for both weighings.

(e) Kg 44 (the Australian National copy) had been weighed at BIPM in Sept/Oct 1946 and was made available to NPL for the 1949 weighings.

(f) A constant value of 1 kg + 59 μg was assumed for Kg 18 from the Sept 1960 cleaning to the June 1970 weighing. However, before cleaning Kg 18 at BIPM in 1978 a value of 1 kg + 105 μg was obtained.

(g) Values for Kg 18 extrapolated from March 1985 value of 1 kg + 57 μg. See discussion in Section 4.2.3.

TABLE 5: MASS VALUES OF Kg A AND Kg B

Date	Observer	Basis	Mass* /μg		Comments (and see note below)
			Kg A	Kg B	
Aug 1982	BIPM	Kg 9, Kg 31	68	176	
Nov 1984	BIPM	Kg 9, Kg 31	-	175	Before cleaning
Mar 1985	BIPM	Kg 9, Kg 31	-	167	After cleaning at BIPM (a)
Nov 1986	NPL	Kg 18 = 1 kg + 64 μg	66	172	Note extrapolated values used for Kg 18; see discussion Section 4.2.3
Mar 1988	NPL	Kg 18 = 1 kg + 65 μg	76	179	
Feb 1990	NPL	Kg 18 = 1 kg + 67 μg	-	179	

* Deviation from 1 kg.

Note:

(a) Rubbed with chamois leather soaked in benzene then with chamois leather soaked in ethanol, following by washing with jets of steam. Whole operation performed three times.

TABLE 6: MASS VALUES OF Kg PI

Date	Basis	Mass* /μg	Comments
Dec 1922	Kg 18 = 1 kg + 51 μg	- 43967	
Mar 1923	As above	- 43916	
Mar 1927	As above	- 44019 and - 44026	
Jun 1927	Kg E = 1 kg - 2180 μg	- 43994	March 1927 standardisation of Kg E
Dec 1930	Kg E + Kg PI = 2 kg - 46179 μg	- 44030	
Jun 1932	Kg E = 1 kg - 2151 μg	- 44013	
Jul 1933	Kg 18 = 1 kg + 58 μg	- 44005	Started using new balance at NPL. See note (d) Table 4
Nov 1933	As above	- 44005	
Oct 1938	Kg E + Kg PI = 2 kg - 46156 μg	- 44000	
Nov 1938	As above	- 44000	
May 1940	As above	- 44014	
Mar 1949	Kg 18 = 1 kg + 71 μg Kg 44 = 1 kg + 270 μg	- 44039	See note (e) Table 4
Sep 1957	Kg 18 = 1 kg + 71 μg	- 44043	
Sep 1960	As above	- 44048	Before Kg 18 cleaned at NPL
Sep 1960	Kg 18 = 1 kg + 59 μg	- 44049	After Kg 18 cleaned at NPL then weighed at BIPM
Mar 1961	As above	- 44051	
Dec 1961	As above	- 44067	
Apr 1965	As above	- 44075	
Jun 1970	As above	- 44073	
Jun 1980	Kg 18 = 1 kg + 59 μg	- 44020	Kg 18 cleaned and weighed at BIPM in 1978. See note (f) Table 4
May 1984	Kg A = 1 kg + 68 μg Kg B = 1 kg + 176 μg	- 44021	August 1982 BIPM values for Kgs A and B
Nov 1986	Kg 18 = 1 kg + 64 μg	- 44028	Note adjustments to Kg 18 value for last 2 entries. See note (g) Table 4.
Mar 1988	Kg 18 = 1 kg + 65 μg	- 44027	

* Deviation from 1 kg

TABLE 7: MASS VALUES ASSIGNED TO KG 18 USING EQUATION 7

Date cleaned by BIPM	Date used	Time elapsed (days)	Correction /μg	Mass* of Kg 18	
				Assigned	Measured
Apr 78	Jun 80	790	(55) + 10.8	66	
	Sep 84	2342	(55) + 18.9	74	
	Nov 84	2400	(55) + 19.1	74	76
19 Feb 85	end Oct 86	628	(55) + 9.6	65	
	mid Feb 88	1095	(55) + 12.8	68	
	end Jan 90	1810	(55) + 16.5	72	
	(Jun 91)	2293	(55) + 18.6	74	75

* Deviation from 1 kg

TABLE 8: MASS VALUES ASSIGNED TO KGS E AND PI USING CORRECTED VALUES OF KG 18 BASED ON EQUATION 7

Date	Mass* Kg 18	Mass* Kg E	Mass* PI
Jun 80	66	- 2129	- 44027
Sep 84	74	- 2132	
Nov 86	65	- 2130	- 44027
Mar 88	68	- 2125	- 44024
Feb 90	72	- 2124	

* Deviation from 1 kg

Following NPL practice, the uncertainties given in the Tables below are presented at the 2σ level

TABLE 9(a): SUMMARY OF UNCERTAINTIES IN DETERMINING MASS AT THE 1 KG LEVEL WITH NPL BALANCE: FOR COMPARISON CARRIED OUT FEB 1988

Source of uncertainty	Uncertainty/± μg		
	Type A	Type B	TOTAL
Kg 18			
BIPM - certified value[a]		16	
NPL adjustment[b]		3	
Kgs A, B, E, PI			
Comparisons (data fit)	5.0		
Sensitivity of balance		2.5	
Buoyancy correction[c]		3.0	
TOTALS	5.0	16.7	17.5

Notes: (a) since 1991, reduced from 8 μg to 2.3 μg at the 1 σ level
(b) for February 1988 (this uncertainty increases with time)
(c) see Tables 9(b) and 9(c) for details

TABLE 9(b): UNCERTAINTY IN DETERMINATION OF AIR DENSITY

Source of uncertainty	Uncertainty	$U(\rho_A)/\pm$ μg cm^{-3}
Temperature	± 0.01 °C	0.044
Pressure	± 0.1 mbar	0.119
Humidity	± 2%	0.209
CO_2 content	± 25 ppm	0.012
BIPM equation	± 12 x 10^{-5}	0.144
TOTAL		0.284

TABLE 9(c): TYPICAL VOLUME DIFFERENCES

Weighing	Δv/cm^3	U(Δv)/± cm^3	U(BC)/± μg
A = B	0.0045	0.0014	1.68
18 = B	0.025	0.0016	1.92
18 = E	0.895	0.0029	3.49
E = PI	0.483	0.0035	4.20

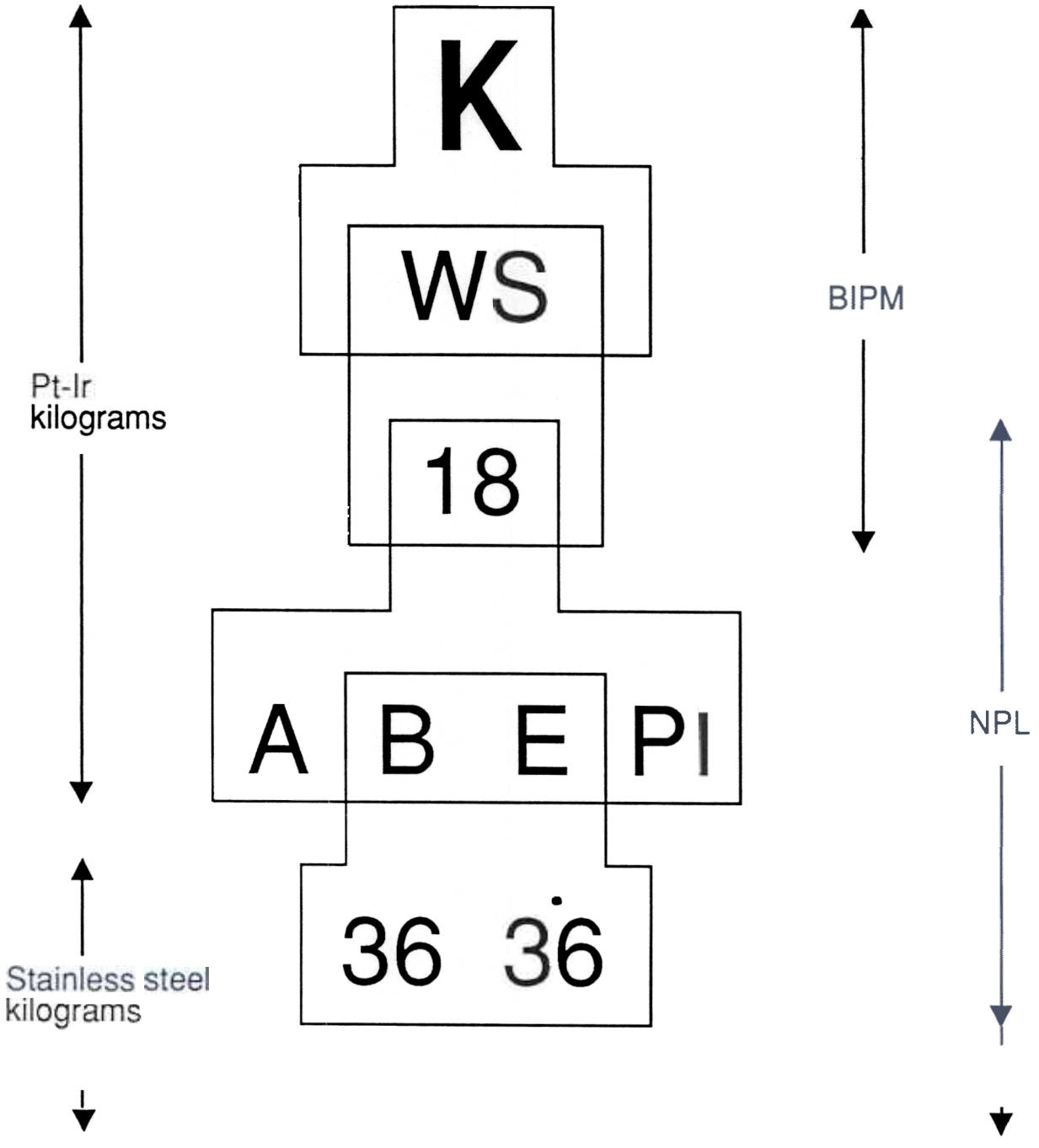


Figure Mass traceability chain at kg level

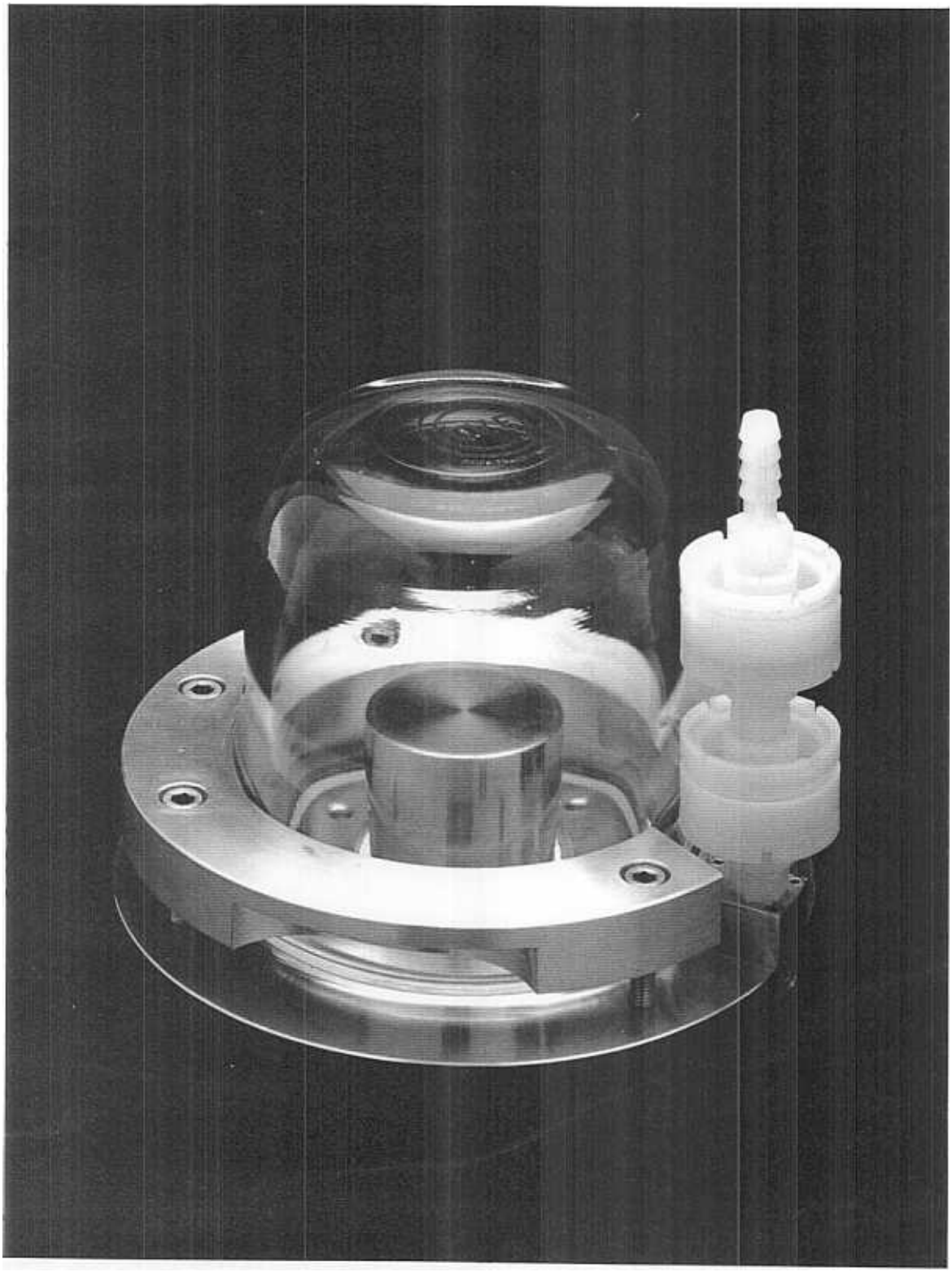


Figure 2(a): Storage and transportation case for the NPL platinum-iridium kilograms

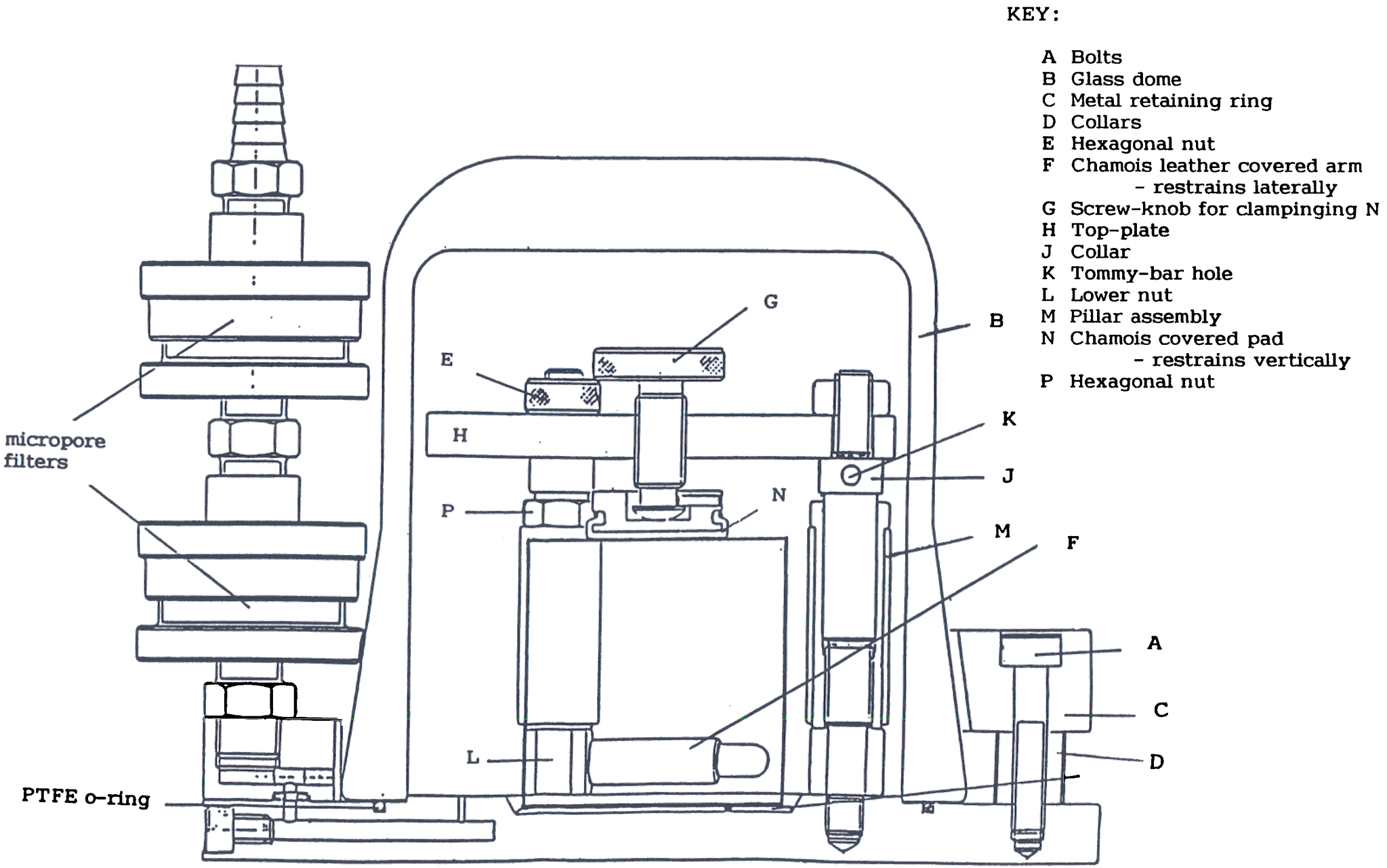


Figure 2(b) Storage and transportation case for the NPL platinum-iridium kilograms

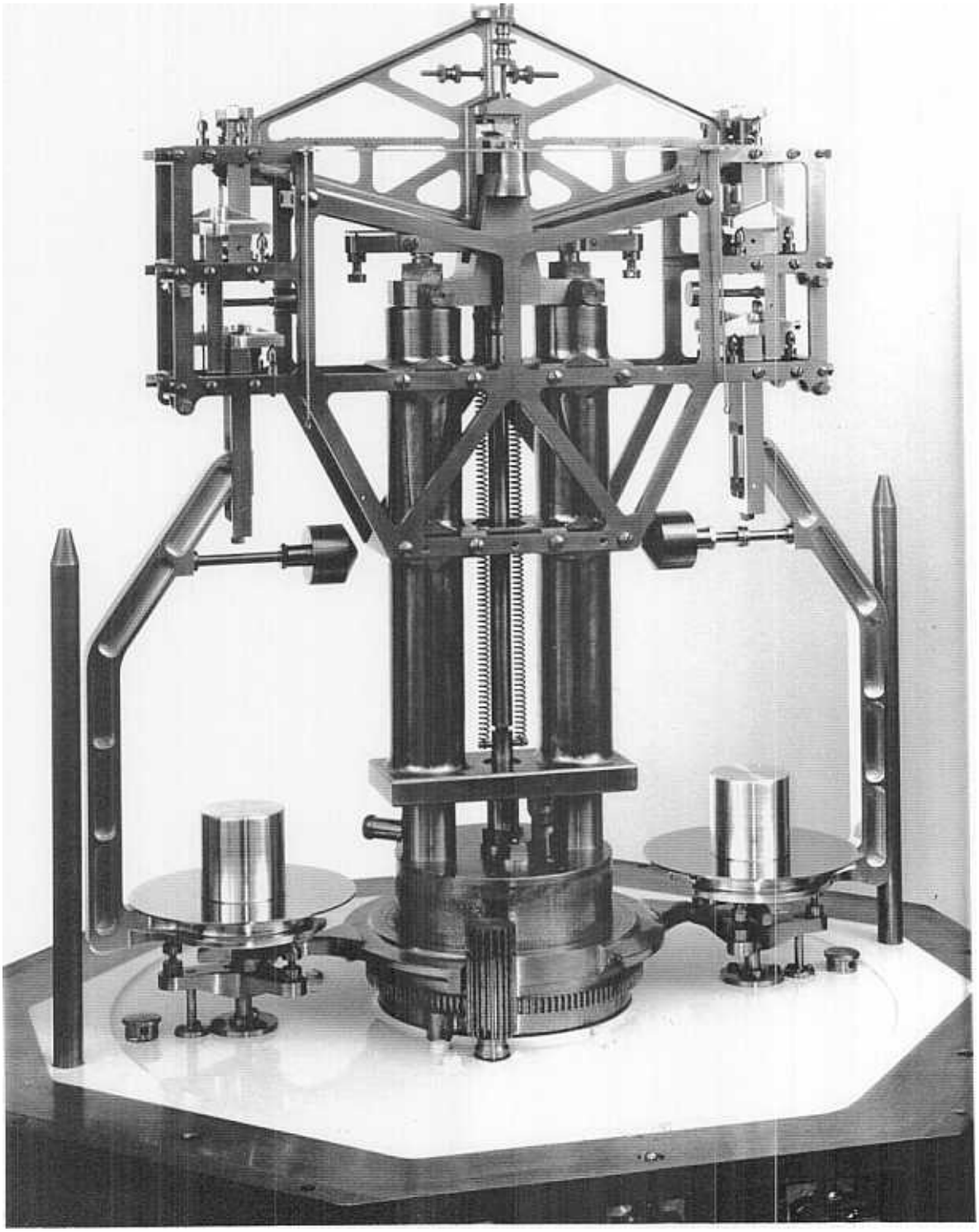


Figure The NPL-built kg primary balance

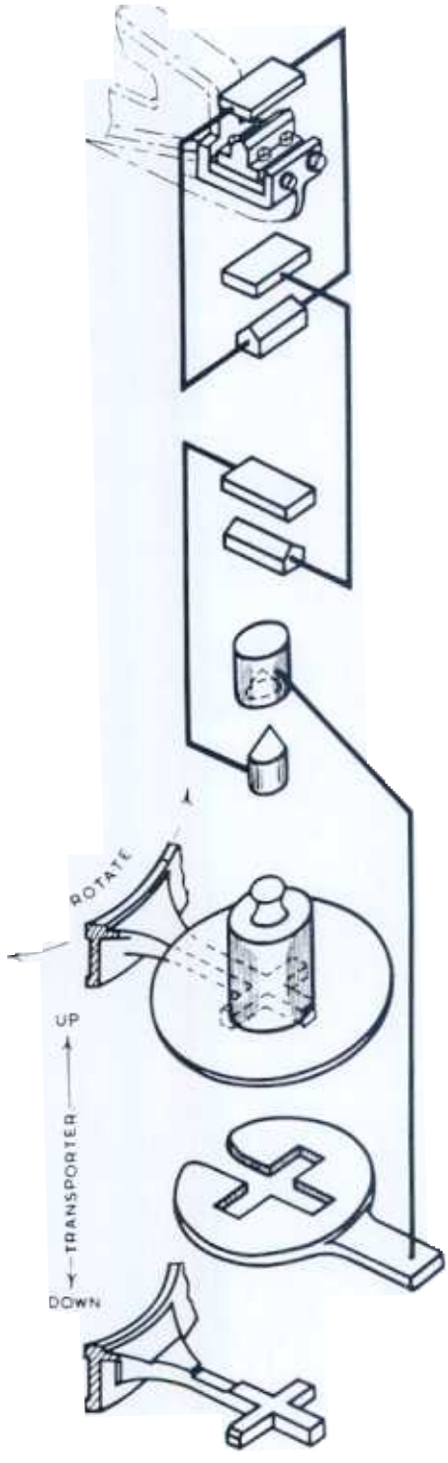
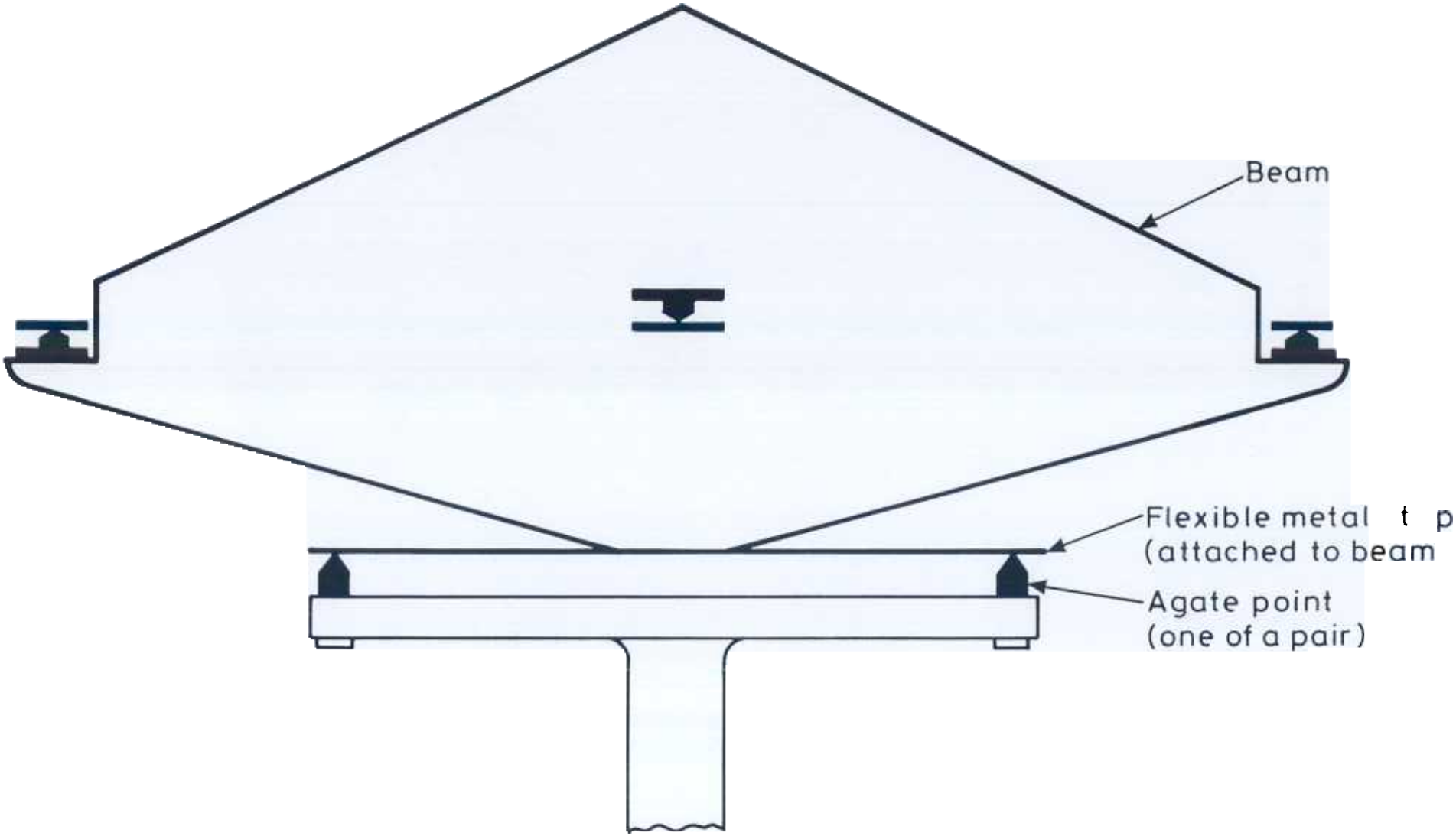


Figure 4: Three stage de-coupling suspension and weight interchange system



Devic for eady he beam he NPL pri ry bala

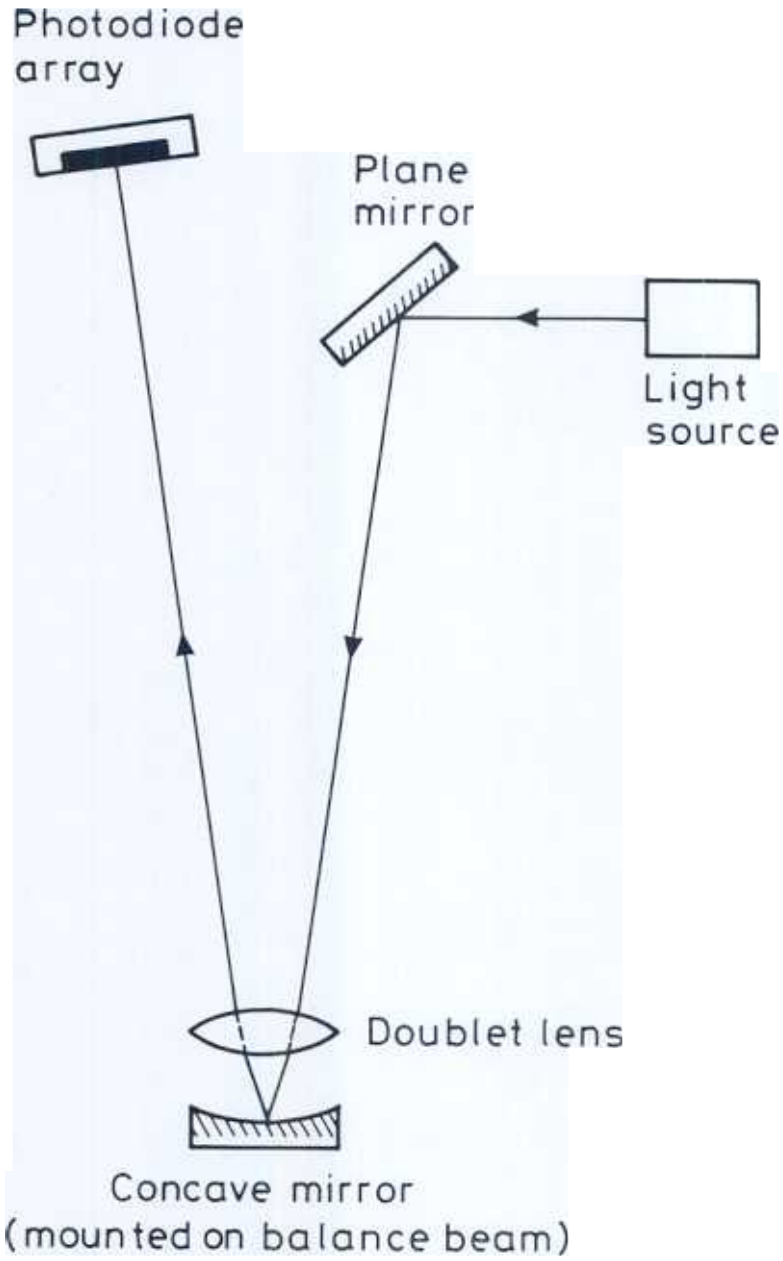


Figure 6(a): Optical lever system used to monitor the inclination of the balance beam

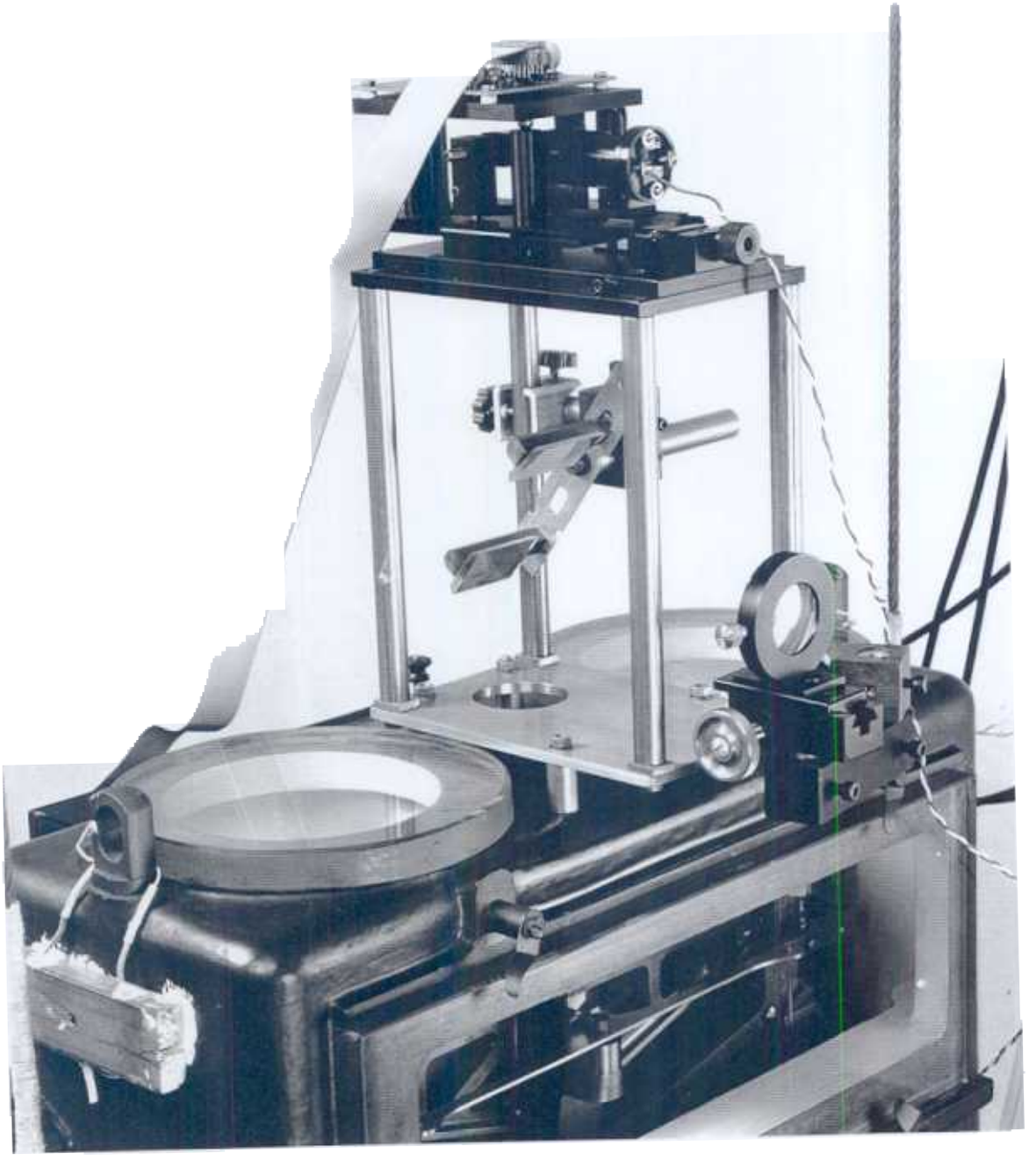


Figure 6(b): Optical lever system mounted above the balance beam

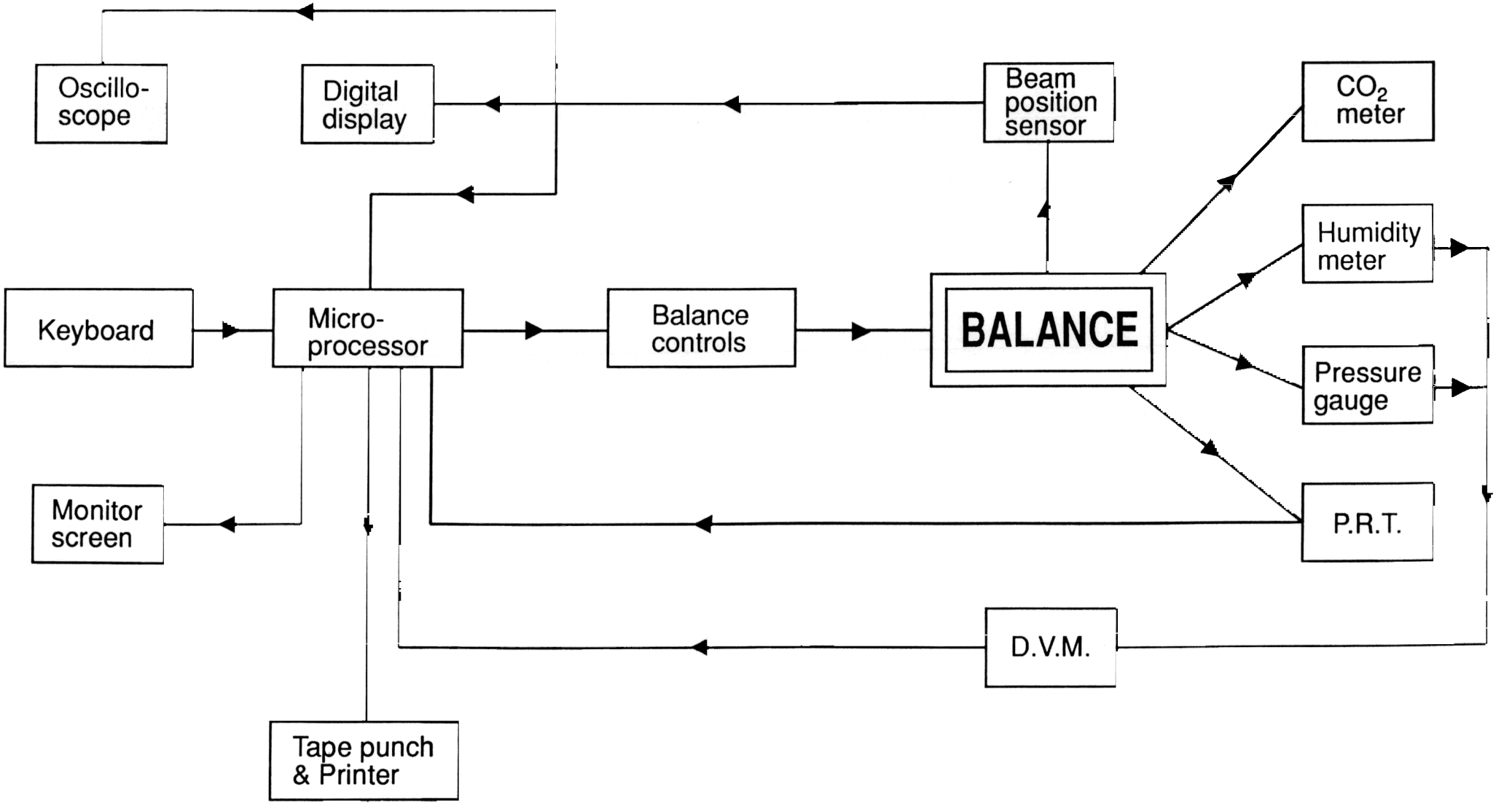


Figure 7 Control, measuring and recording system for the automated balance - note that the punch tape and printer has now been replaced by disk storage

Figure 8: General view of the balance with motorized remote controls

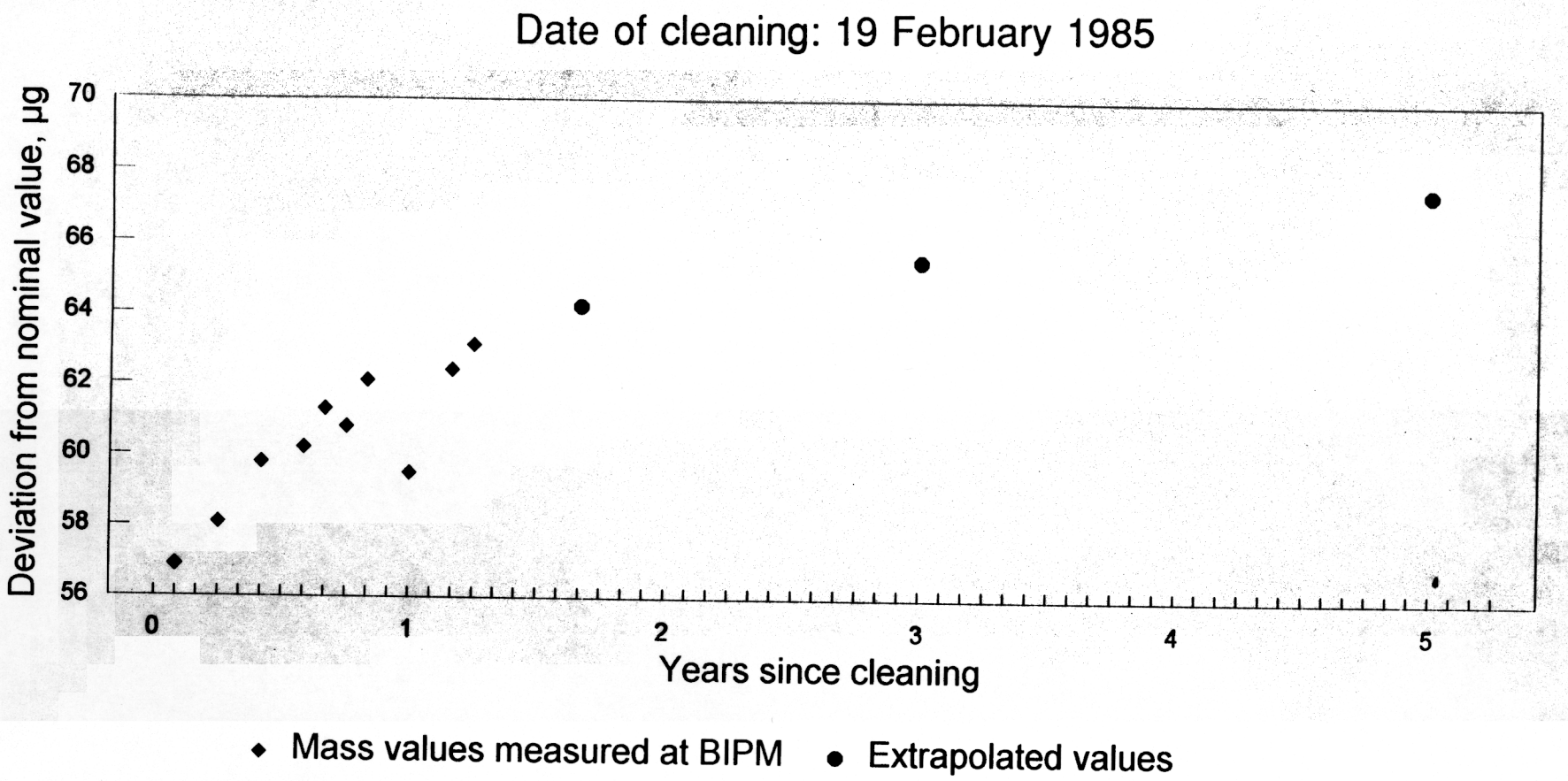
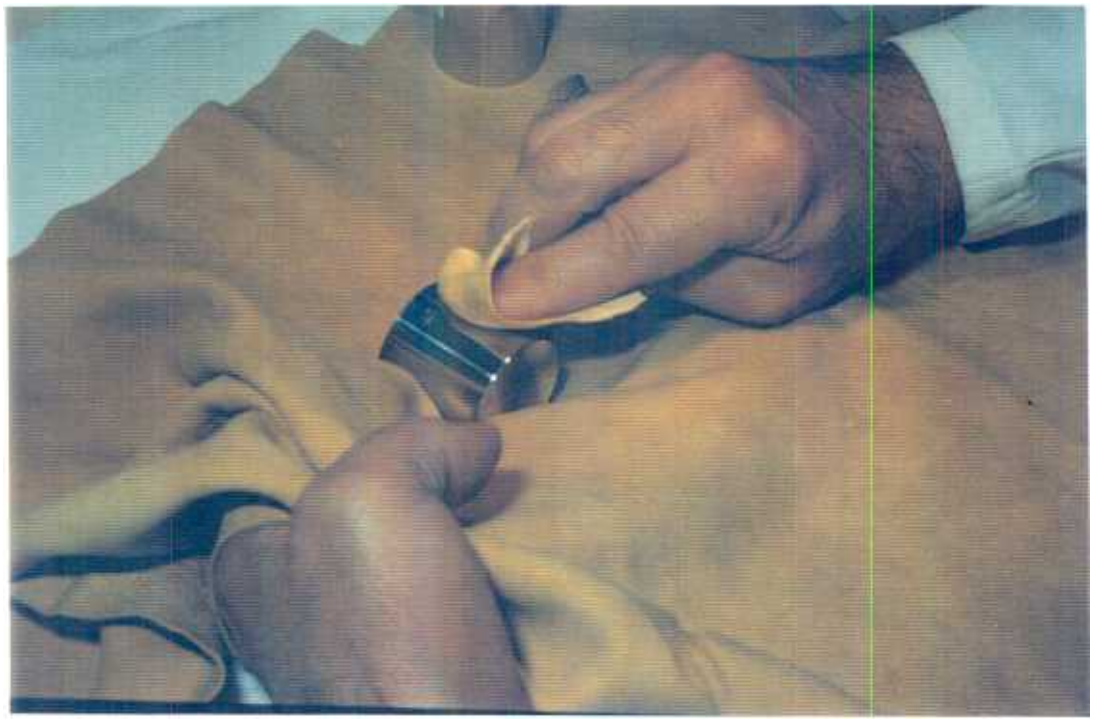
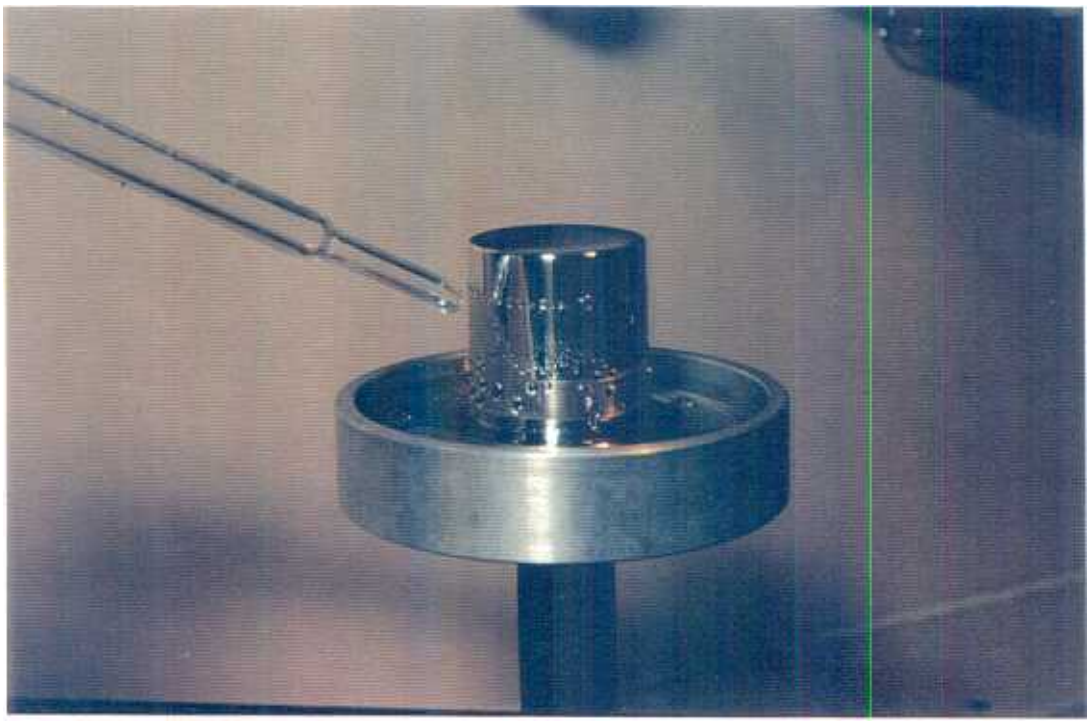


Figure 9: Mass regain of Kg 18 after cleaning in 1985, plus the values assigned to Kg 18 by extrapolation (see Section 4.2.3)



(a): by means of chamois leather moistened with a mixture of equal parts of ether and ethanol



(b): using a jet of steam

Figure 10: Cleaning a prototype kilogram

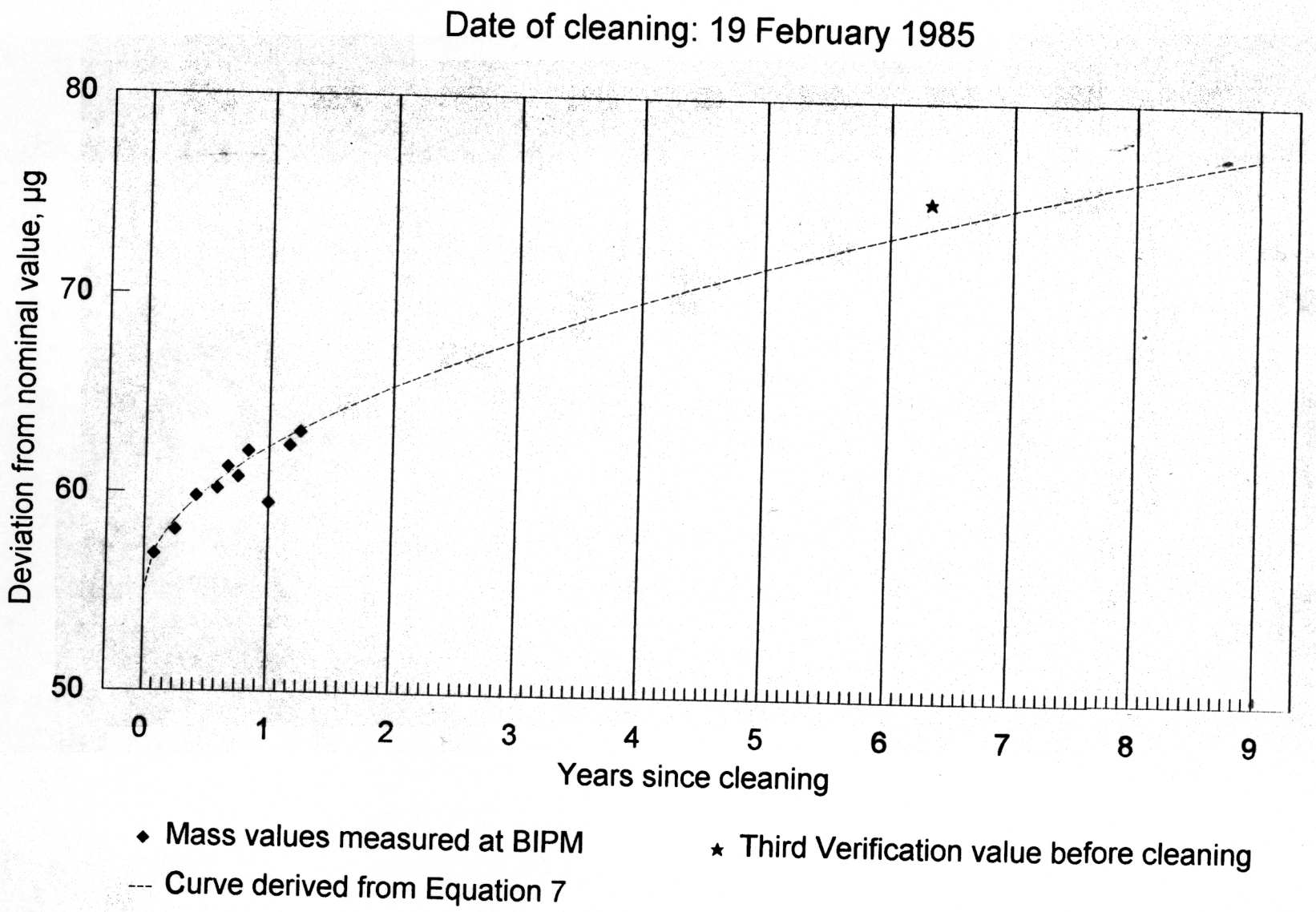


Figure 11: Fit of Kg 18 mass data after cleaning in 1985 based on equation 7

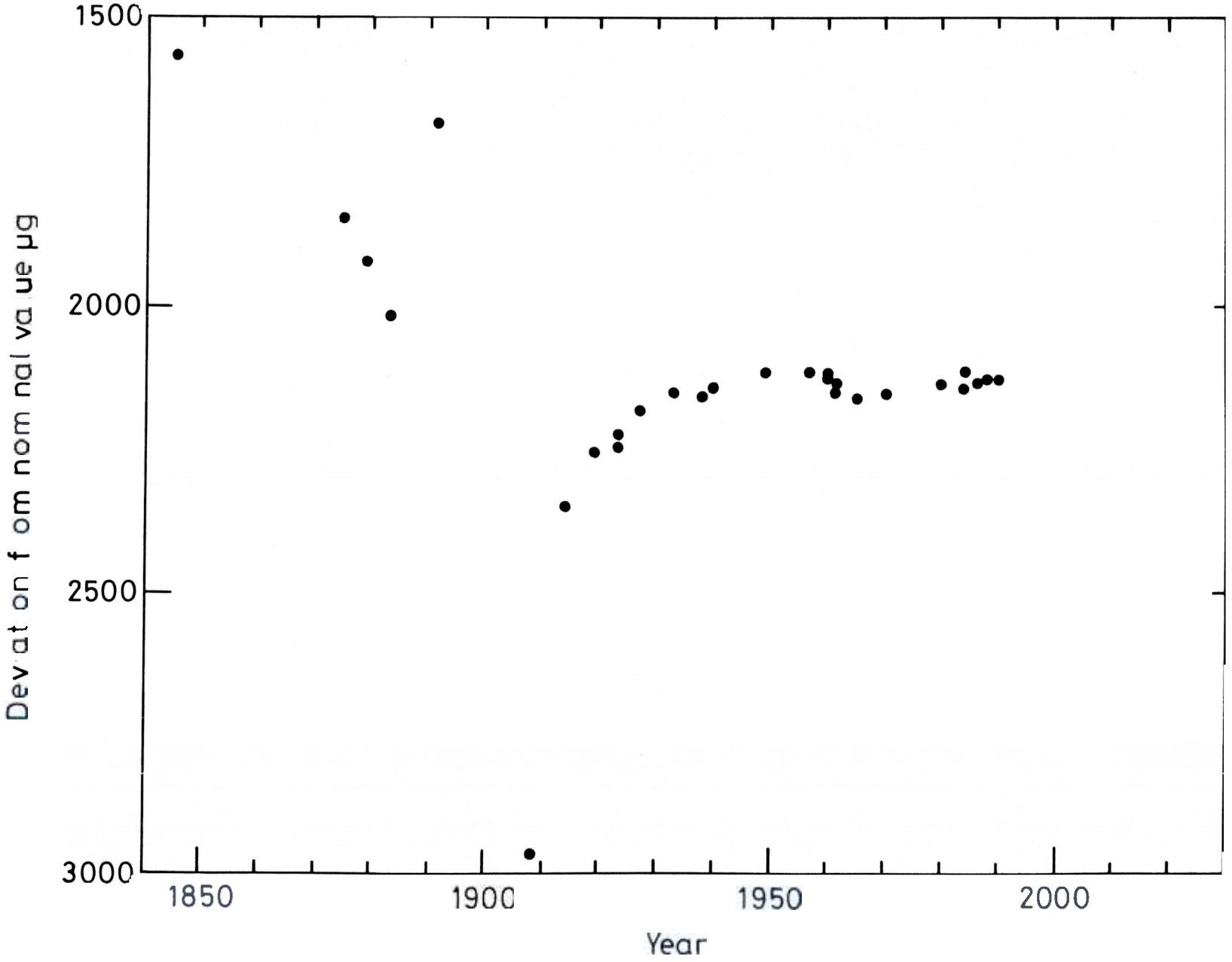


Figure 12(a): Mass values Kg E

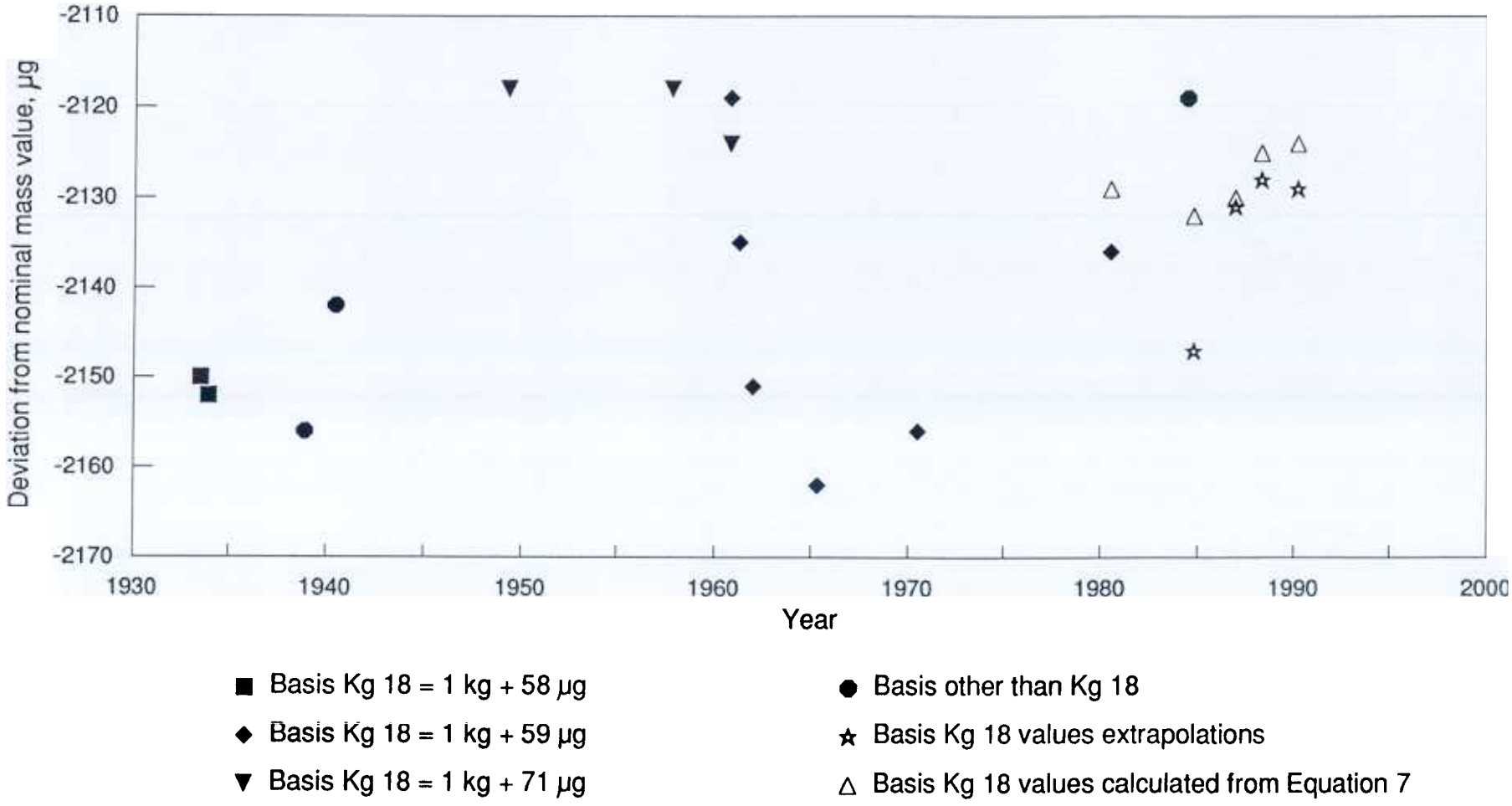


Figure 12(b): Mass values of Kg E after 1933

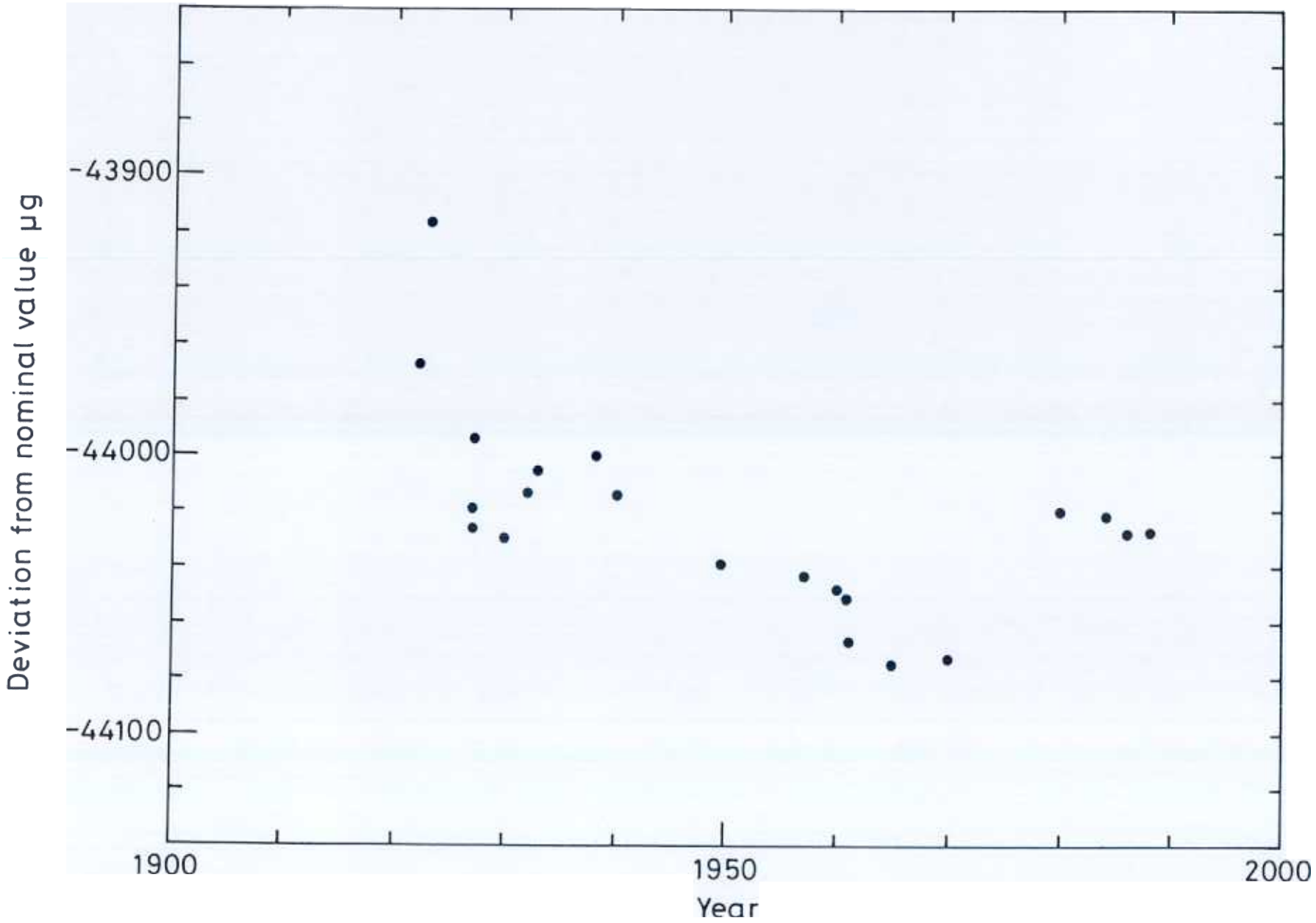


Figure 13: Mass values of Kg PI